ELECTRODICS AND ELECTROBIOLOGY

VOLTAMMETRIC STUDIES ON GLASSY CARBON ELECTRODES-III.
A COMPARATIVE STUDY OF ELECTRON-TRANSFER KINETICS OF Ti^{4+}/Ti^{3+} REDOX COMPLEXES ON GLASSY CARBON AND MERCURY ELECTRODES

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Voltammetric behaviour of Ti^{4+}/Ti^{3+} redox system in H_2SO_4 and the effect of addition of usual complex forming ions viz. Cl^-, acetate, EDTA, oxalate, thiocyanate, phosphate, citrate and tartrate — into this medium are studied on Glassy Carbon (GC) electrodes and the results are compared with the behaviour reported on Hg in the literature. The kinetics of the complex formation step has a major influence on voltammetric behaviour (acetate, oxalate and thiocyanate). The charge transfer rate is generally slower on GC when compared to Hg (tartrate). The reactant as well as product is weakly absorbed on GC in EDTA medium. Larger anions such as citrate and tartrate show blocking effects on stationary GC electrode when compared to dropping mercury electrode. From the analytical view point oxalate and thiocyanate are recommended for quantitative estimations in acid medium and citric acid/trisodium citrate medium gives well defined results in neutral and alkaline medium.

INTRODUCTION

A well defined polarographic wave for Ti^{4+} ions was reported as early as 1932 [1]. Since then, extensive studies on the Ti^{4+}/Ti^{3+} redox couple have been carried out from analytical [2-4], electrodekinetic [5], thermodynamic [6,7] and electrosynthetic [8-17] points of view. In spite of such extensive studies, only some quantitative information on this redox system are available [6,7]. Even the standard electrode potential E° of this redox system in non-complexing media is still a subject of study in 1980 [18]. The poor and at times even contradictory reports on this redox system are mainly due to the fact that both Ti^{4+} and Ti^{3+} ions may undergo hydrolysis even at very low pH values according to the equations (1) and (2).

$$Ti^{4+} + OH^- \rightleftharpoons Ti(OH)^{3+} + OH^- \rightleftharpoons Ti(OH)^{2+}_2 + OH^- \rightleftharpoons Ti(OH)^+_3 .(1)$$

$$Ti^{3+} + OH^- \rightleftharpoons Ti(OH)^{2+} + OH^- \rightleftharpoons Ti(OH)^+_2 + OH^- \rightleftharpoons Ti(OH)_3... (2)$$

In addition, hydration/dehydration equilibria are also involved.

$$Ti(OH)^{2+}_2 \rightleftharpoons TiO^{2+} + H_2O \qquad ...(3)$$

Some recent studies [19] suggest that even in very stable complexing media some irreversible hydrolysis takes place slowly. A comprehensive review on these aspects is available [6].

In spite of the above situation regarding uncomplexed species, recent studies [20] have attempted to evaluate both equilibrium constant K and kinetic rate constant K_c of complex formation reactions such as,

$$Ti^{4+} + HSO^-_4 \rightleftharpoons Ti(HSO_4)^{3+} \qquad ...(4)$$

However, all these work are confined to Hg electrode. Studies on solid electrodes are very limited [17, 21, 22].

Recently we have initiated some research work in this laboratory to establish the influence of electrode materials on electrochemical

processes with special reference to Glassy Carbon (GC) electrodes. The nature of GC surface structure and transformation [22] and its influence on the well known ferricyanide/ferrocyanide redox system [23] formed the first two parts of this series. In the present work we have studied the influence of different complexing agents on the electrochemical behaviour of Ti^{4+}/Ti^{3+} redox system. Since polarographic data on various complexes are available (see under discussion) we have compared our results on GC with the literature data on Hg. Although $HClO_4$ would have been a better base electrolyte to study the influence of other complexing anions (because of its uncomplex forming nature), availability of more polarographic data in H_2SO_4 and our own synthetic interest in this medium [9-17] have prompted us to select this as the base electrolyte medium.

EXPERIMENTAL

5mm diameter Glassy Carbon electrode (GC 30-A. Tokai, Japan) inserted and fixed into a glass tube using epoxy was used as a working electrode in a typical H type cell containing Pt counter electrode. The working GC electrode was polished to mirror finish using finer emeries of upto 4/0 (John Okay, U.K.) washed thoroughly with water and finally with trichloroethylene. The electrode was then inserted into the electrochemical cell and electrochemically activated by potentiodynamic cycling between-0.5V and 1.3V for 15 minutes at slow-sweep rates (less than 100 mV/sec). This procedure was arrived at from the earlier work in this series [23] and gave reproducible results (- $\pm$ 5mV in potential and - $\pm$ 3% accuracy in peak current values). All other details regarding cells and instruments have been reported earlier [22-24].

Practically all the polarographic studies reported so far, use the $TiCl_4$ stock solutions directly. To the knowledge of the authors, A.R. grade of this solution is not available commercially. Moreover the Cl^- ions have been shown to have specific influence on GC electrode processes [22-24]. Hence chloride free Ti^{4+} solutions would be desirable. Although freshly precipitated $Ti(OH)_4$ may be redissolved in strong acid [18-20] very strong Ti^{4+} solutions (0.1M for example) could not be prepared by this method especially

in medium of lower acidity. Hence in the present work Ti^{4+} solutions were prepared from GR TiO_2 power and H_2SO_4 through the formation of intermediate titanyl sulphate powder $(TiOSO_4)$ according to the method described earlier [24, 25]. Ti^{4+} solutions of required strength could be prepared by this method and the solutions were also stable at least for a few weeks [25] except in a few complexing media (See under Results). All the other chemicals used were of GR grade and water was distilled thrice before use.

RESULTS

Cyclic voltammograms were recorded for 3-15 mM Ti^{4+} solutions in H_2SO_4 and in presence of additional complexing agents in the sweep rate range of 5-320 mV/sec. Some typical voltammograms are presented in Fig 1-9. The peak current constant $(i_p/ACV^{1/2}$ where i_p is the peak current, A is the electrode area, C is the concentration of electroactive species and V is the sweep rate), peak potential $(E_{p,c}, E_{p,a})$ and peak potential separation $(\triangle E_p)$ values are presented in Table I. Specific characteristics of individual complexes will be described below.

of H_2SO_4, if Ti^{4+} ion concentrations exceed 100 mM, a reduction wave appears at less negative potentials $(E_{1/2} = -0.50V$ vs SCE) (Fig.1 c). Corresponding to this cathodic wave, an anodic peak appears on the subsequent anodic sweep. The anodic peak current increases with increase in the cathodic potential limit (Fig.2). The anodic peak current also increases with time if the electrode is kept at cathodic potentials (< -0.600 mV) for specified time intervals before anodic cycling.

Since in 2.0M H_2SO_4 medium when Ti^{4+} concentration was less than 15 mM no redox waves for Ti^{4+}/Ti^{3+} system were noticed, the influence of different complexing ligands in producing redox waves for Ti^{4+}/Ti^{3+} system could be analysed in this concentration range. Addition of even substantial quantities of Cl^- ion does not produce any redox wave (Figs. 1 b and d).

Addition of acetate anions results in a voltammogram of Ti^{4+} species which contains two poorly defined waves (Figs. 3 a and b).

Table 1: Redox peak potentials and cathodic peak current constants of Ti^{4+}/Ti^{3+} redox system in different media

No.	Medium	Ti^{4+} concentration (mM)	$\dfrac{i_p}{ACV^{1/2}}$ [a]	$E_{p, red}$ (V vs SCE)	$E_{p, ex}$ (V vs SCE)	E_p (Volt)
1.	0.5M H_2SO_4	8.5	—	—	—	—
2.	2.0M H_2SO_4	124.7	453.7	—0.650	+0.470	1.120
3.	4.0M CH_3COOH + 0.04 M H_2SO_4	6.63	—	—0.740	—	—
4.	0.1M Na_2SO_4 + 0.02 M EDTA disodium salt	8.50	881.0	—0.240	—0.170	0.070
5.	2.0M H_2SO_4 + 0.6M $Na_2C_2O_4$	8.50	431.5	—0.360	+0.060	0.420
6.	2.0M H_2SO_4 + 0.6M KCNS	8.50	533.4	—0.200	—0.090	0.110
7.	2.0M H_3PO_4	11.09	277.1	—0.500	+0.020	0.520
8.	0.5M H_2SO_4 + 0.8M citric acid	8.50	371.6	—1.000	+0.400	1.400
9.	0.5M H_2SO_4 + 0.4M trisodium citrate	8.50	376.4	—1.200	—0.230	0.970
10.	0.5M H_2SO_4 + 0.6M trisodium citrate	8.50	374.0	—1.300	—	—
11.	2.0M H_2SO_4 + 1.0M sodium tartrate	12.50	383.1	—0.950	+0.400	1.350

a - i_p in μA, A in cm^2, C in mM and V in volts per sec.

At lower concentrations of Ti^{4+} ions ($<$10mM) the cyclic voltammograms with and without these ions are quite identical in 2M H_2SO_4. No distinct cathodic peak due to reduction of Ti^{4+} is noted (Figs. 1a and b). However, in the same concentration

No anodic wave is noticed. The wave heights are smaller when compared to cathodic peak currents noticed in other media under identical Ti^{4+} concentration and sweep rate V. The relative heights of the two waves depend on the acid strength (Figs. 3 b and c) and
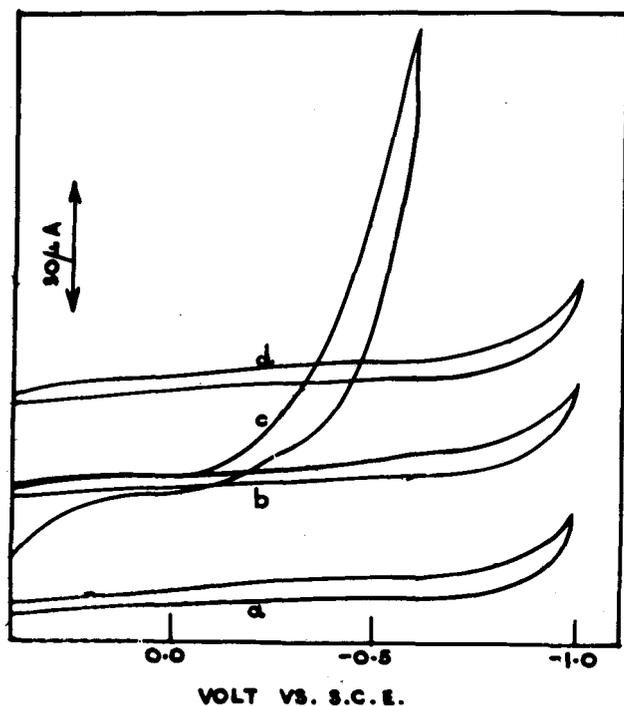
Fig.1: Redox behaviour of Ti^{4+}/Ti^{3+} couple in presence of sulphate/chloride anions. Sweep rate 10 mV/sec(a) 0.5M H_2SO_4 (b) a + 8.5mM Ti^{4+}(c) a + 124.7mM Ti^{4+}(d) 1.0M HCl + 8.5mM Ti^{4+}

at higher acidities they merge into a single wave (Fig. 3 d).

Addition of EDTA disodium salts results in the sharp well defined and highly reversible cyclic voltammogram (Fig.4). The peak current constant obtained is the highest among the complexing agents employed in the present work. However, the complex seems to be quite unstable in H_2SO_4 medium. For example, a 5 mM Ti^{4+} solution was found to hydrolyse within one hour, after the mixing of EDTA with Ti^{4+} solutions. However Ti^{4+} solutions of lower concentrations ($<$ 1mM) are quite stable and also show simple reversible diffusion controlled behaviour.

The effect of addition of oxalate anions on the redox waves are presented in Fig.5. On increasing the concentration of oxalate anions the cathodic wave shifts to less negative potentials and the anodic waves shifts to less positive potentials (Fig. 5 b-e). The reversibility improves at higher concentrations of oxalate anions. $i_p/V^{1/2}$ values decrease with increase in sweep rates at lower concentrations of oxalate anions. At higher concentrations ($>$0.6 M) $i_p/V^{1/2}$ becomes constant. This indicates that the cathodic process changes from a kinetically controlled process at low oxalate concentrations to a diffusion controlled one at higher concentrations. The voltammetric characteristics reported in Table I for this system corresponds to the diffusion controlled region mentioned above.
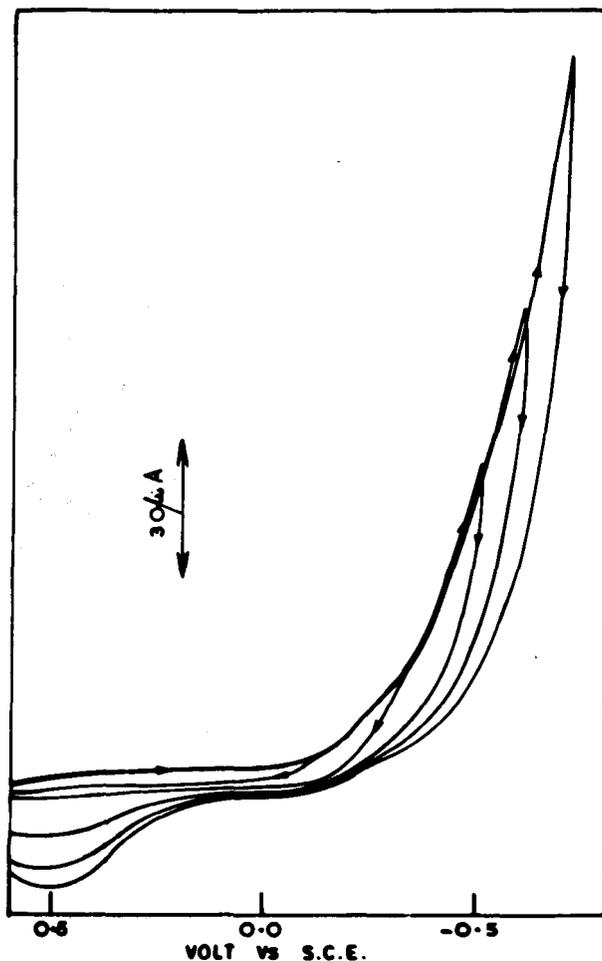

Fig. 2: Effect of cathodic sweep limit on the redox behaviour of Ti^{4+}/Ti^{3+} couple in sulphate medium. Sweep rate 10mV/sec. Solution 2.0M H_2SO_4 + 124.7 M Ti^{4+}

The effect of CNS^- ion is quite similar to the oxalate anion (Fig.6) Increased thiocyanate concentrations increase the reversibility of the system. With $\geqslant$ 0.8M thiocyanate concentration, the redox wave becomes completely diffusion controlled (constant $i_pV^{1/2}$ value). A distinct feature, however, is that the anodic peak potential does not change with increasing concentration of CNS^- in contrast with the behaviour of oxalate anions (compare anodic waves of Figs. 5 & 6).

Addition of phosphate anions to any H_2SO_4 solution containing Ti^{4+} ions result in immediate precipitation of the titanium compound. Hence the general procedure adopted in this work could not be used to obtain the cyclic voltammograms for this system. Fig. 7 shows the cyclic voltammograms of $TiCl_4$ (formed by air oxidation of LR $TiCl_3$ solution) in 2M phosphoric acid. A quasi-reversible redox behaviour is noticed. The cathodic wave is found to be diffusion controlled.
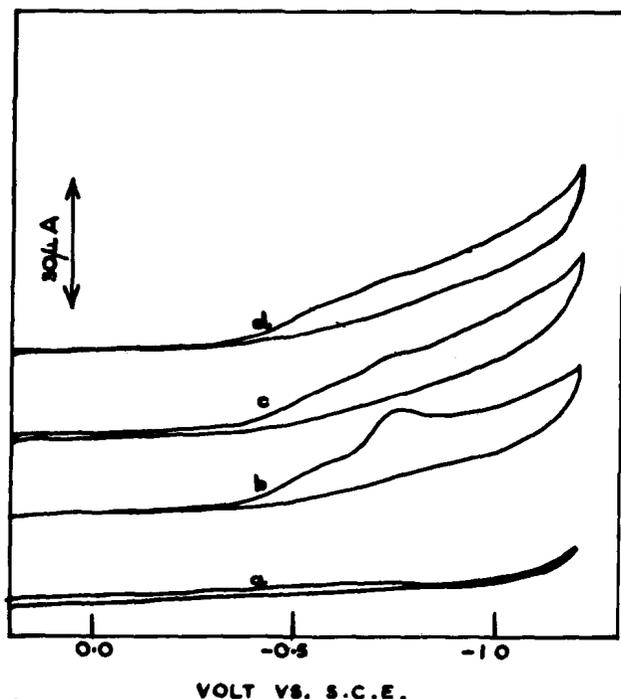
Fig. 3: Redox behaviour of Ti⁴⁺/Ti³⁺ couple in presence of acetate anions. (a) 4.0M CH₃COOH + 40mM H₂SO₄ (b) a + 6.63 mM Ti⁴⁺ (c) b + 40 mM H₂SO₄ (d) C + 40 mM H₂SO₄

As stated earlier Ti⁴⁺ salts easily hydrolyse even at low pH. But very good stability of these salts are noted in citrate medium over a wide pH range. The Ti⁴⁺ salt solutions in 2M H₂SO₄ in presence of citrate do not show hydrolysis even at pH of 10. Typical voltammograms with increased pH are presented in Fig. 8. The cathodic peak shifts to more cathodic potentials with increase in pH. Another significant feature is the behaviour of the anodic peak with change in pH. With increase in pH the anodic peak at ≈ 0.40V completely disappears and a new wave appears around −0.23V (Figs. 8 b and c), and with further increase in pH the anodic wave at ≈ −0.23V also disappears even though the cathodic wave is still present (Fig. 8d).

In tartrate medium also the Ti⁴⁺ salts are quite stable over a wide pH range, and give well defined voltammograms on GC electrode (Fig. 9). However the peak potentials do not shift substantially with pH as in the case of citrate complexes.

DISCUSSION

The sulphate complex

Two waves for the reduction of Ti⁴⁺ ions in 2N H₂SO₄ at potentials below -0.400V (vs NHE) had been noticed [26] which was at
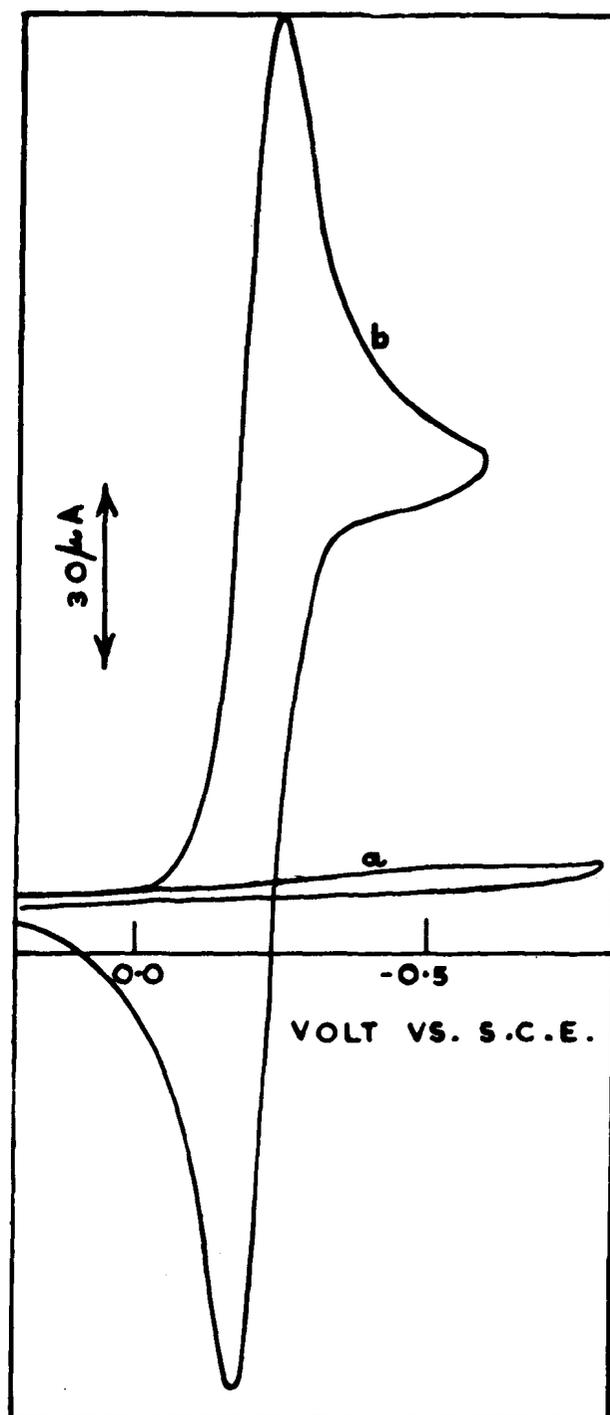

Fig. 4: Redox behaviour of Ti⁴⁺/Ti³⁺ couple in presence of ED-TA disodium salt. Sweep rate 10mV/sec.
(a) 0.1M Na₂SO₄ + 20mM EDTA sodium salt
(b) a + 0.5mM Ti⁴⁺

tributed to the reduction of Ti⁴⁺ ions and Ti³⁺ ions respectively. The reasoning is based on an earlier assignment of -0.369V (vs NHE)
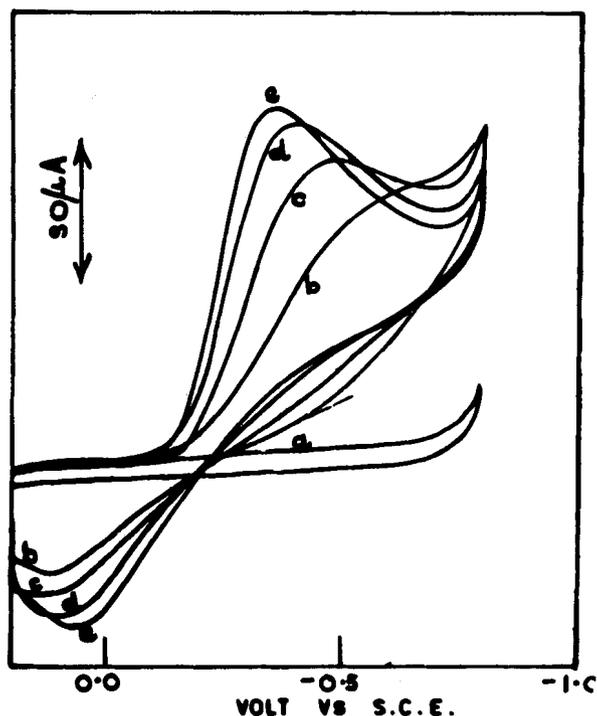
Fig. 5: Redox behaviour of Ti^{4+}/Ti^{3+} couple in presence of oxalate anions. Sweep rate 10mV/sec
(a) 2.0M H$_2$SO$_4$ + 0.1M Na$_2$C$_2$O$_4$ (b) a + 8.5mM Ti^{4+} (c) b + 0.1M Na$_2$C$_2$O$_4$ (d) C + 0.2M Na$_2$C$_2$O$_4$ (e) d + 0.2M Na$_2$C$_2$O$_4$

as the redox potential of Ti^{3+}/Ti^{2+} species [27]. This assignment however has been proved to be incorrect [28] even though this value has entered into many Tables of standard electrode potentials [3]. However in later works [29, 30] only a single wave at considerably more cathodic potentials ($\simeq$ -0.900 V) has been observed, when the sulphate concentration is around 1.0M as in [26]. The apparent discrepency between these works may be easily understood by considering the equilibria represented in eq.4. The uncomplexed species is responsible for the more cathodic wave. The sulphate complex gives the wave at less negative potential. Equilibrium (4) may be shifted to the right by either increasing the Ti^{4+} concentration (where Ti^{4+} concentration is $>$100 mM) or by increasing the sulphate ion concentration (as by Habashy who observed a new wave at less negative potentials in 1 mM Ti^{4+} solutions when 10M H$_2$SO$_4$or NaHSO$_4$ are employed). On GC electrodes the supporting electroylte reduction starts at the potentials which are less negative than the reduction potential of uncomplexed Ti^{4+} ions. Hence no separate wave could be noticed for uncomplexed Ti^{4+} (low Ti^{4+} and low H$_2$SO$_4$ concentrations) species. However when higher Ti^{4+} concentrations are employed the sulphate complex is formed (as expected from eq. 4) and hence gives the peak. The oxidation wave observed following cathodic peak is thus due to the oxidation of Ti^{3+} complex formed during the cathodic sweep. Ti^{4+} [31] and Ti^{3+} ions [32] have been shown to form stable sulphate complexes which lends support to this point of view.
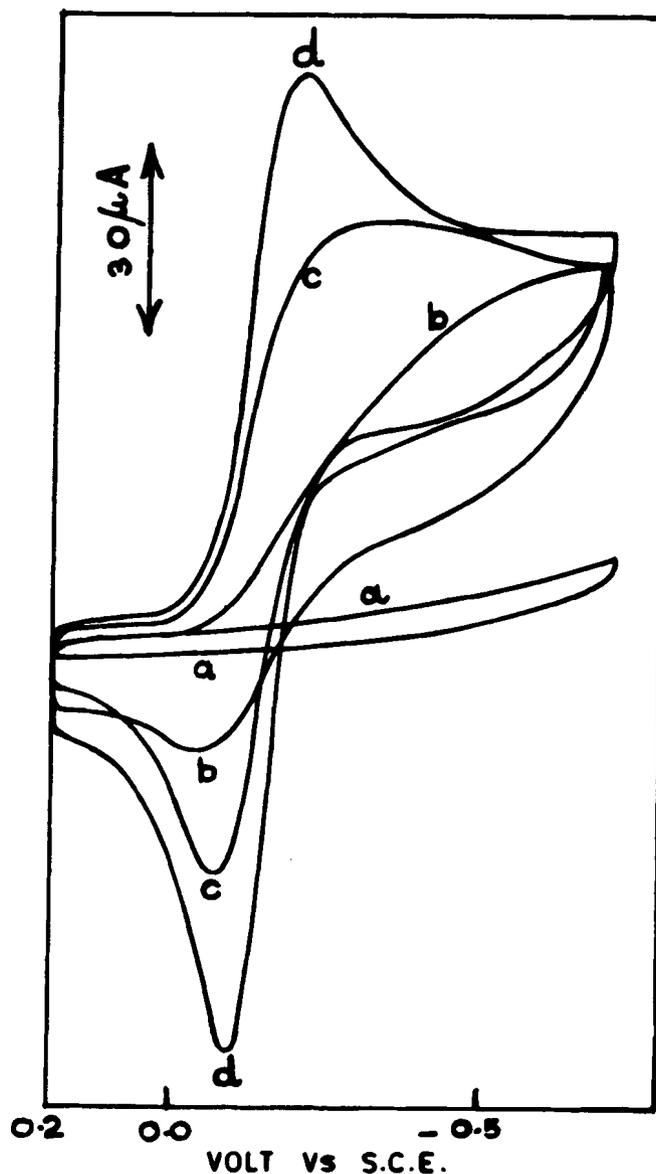

Fig. 6:Redox behaviour of Ti^{4+}/Ti^{3+} couple in presence of thiocyanate anions. Sweep rate 10 mV/sec.
(a) 2.0M H$_2$SO$_4$ + 8.5mM Ti^{4+} (b) a + 0.2M KCNS (c) b + 0.2M KCNS (d) c + 0.4M KCNS

Complex formation between Ti^{4+} and HSO$^-_4$ species has also been confirmed by some recent polarographic works [20, 33]. Similar behaviour is noticed on copper electrodes also [17].

Effect of chloride

The chloride complexes of Ti^{4+} [31] as well as Ti^{3+} [32] are shown to be weaker than the corresponding sulphate complexes. Hence the titanium ions are expected to be either free or in the form of sulphate complexes in the medium containing Cl$^-$ and SO$_4^{2-}$.
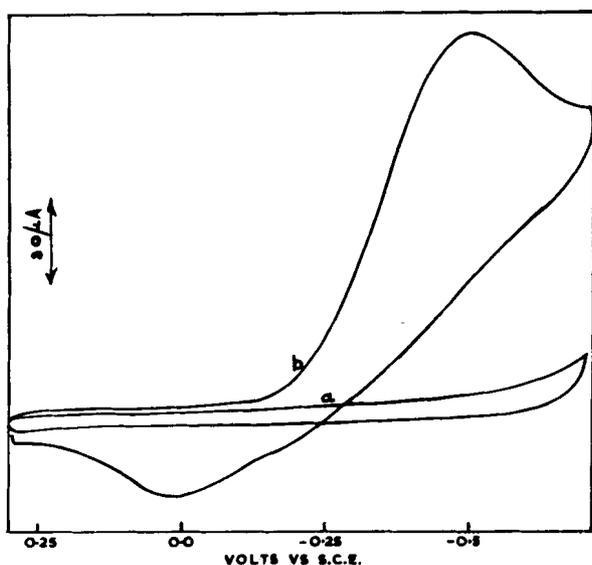
Fig. 7:Redox behaviour of Ti^{4+}/Ti^{3+} couple in phosphoric acid medium. Sweep rate 10 mV/sec.
(a) 2.0M o-phosphoric acid (b) a + 11.09mM Ti^{4+}

In the polarography also no cathodic wave is noted at potentials less negative than -0.9V [2,3]. On the basis of these data no cathodic wave due to the chloride complexes are expected on GC electrode. The present experiments also confirm this. No wave was observed even when large excess of Cl- ions was added (Fig. 1).

Effect of acetate

Although two reduction waves for Ti^{4+} ions are noticed, the wave characteristics are not well defined and hence no detailed study was possible (Fig. 3). Pecsok has reported similar ill-defined reduction waves on Hg electrode [34]. These waves are probably due to adsorbed Ti^{4+} - acetate complex or due to a bulk Ti^{4+} - acetate complex species formed in solution by a slow chemical reaction.

Effect of EDTA

Of all the Ti^{4+} complexes investigated in the present work, the EDTA complex shows the highest reversibility (smallest peak separation) (Table - I). The EDTA complex forms quite easily in this medium. The peak current constant value observed for this complex is quite high when compared to all other Ti^{4+} complexes. In general, the peak current for the one electron reversible process would be slightly higher than the irreversible process [35], the diffusion coefficient for the Ti^{4+} EDTA complex may also be greater. But even these two factors may not account for such a high value of peak current constants for this complex when compared to all complexes (Fig.4, Table-I). This high value could be due to the contributions from weak adsorption of reactants and products (i_a) in addition to that from the diffusion current (i_p) [36].

As stated earlier Ti^{4+} hydrolyses in EDTA medium even at mM

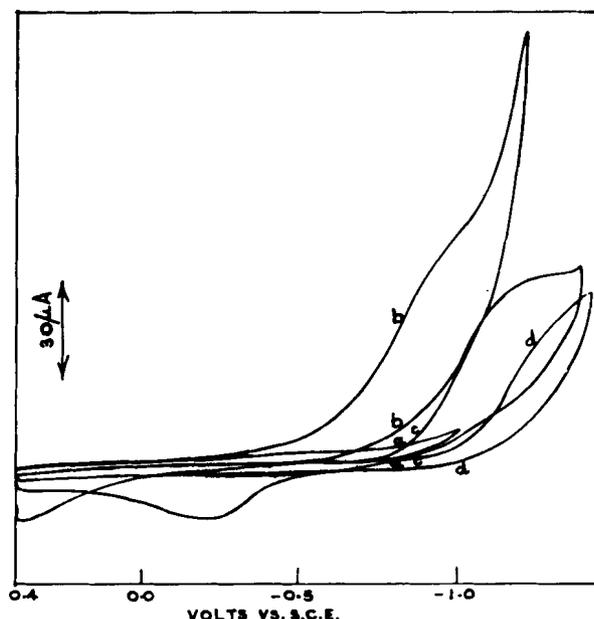Fig. 8:Redox behaviour of Ti^{4+}/Ti^{3+} couple in presence of citrate anions. Sweep rate 10mV/sec.
(a) 0.5M H_2SO_4+8.5mM Ti^{4+} (b) a + 0.8M citric acid (c) a + 0.4M trisodium citrate (d) a + 0.6M trisodium citrate
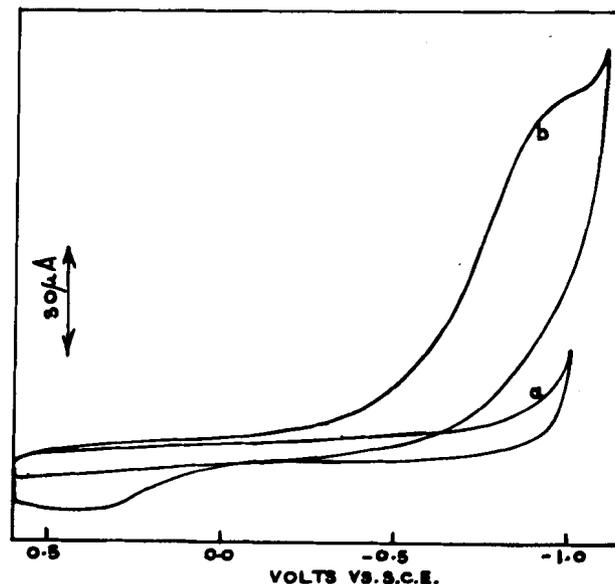

Fig. 9:Redox behaviour of Ti^{4+}/Ti^{3+} couple in presence of tartrate anions. Sweep rate 10mV/sec.
(a) 2.0M H_2SO_4 + 1.0M sodium tartrate, (b) a + 12.5mM Ti^{4+}

concentrations. Hence the effect of concentration on the peak current could not be considered in detail. It must be noted that in the earlier polarographic studies of Ti^{4+} EDTA complexes [37 - 39], concentrations less than 1 mM Ti^{4+} solutions were employed. At such low concentrations of Ti^{4+} EDTA complexes,

well defined diffusion controlled voltammograms are also noticed on GC electrodes. However the background currents are now not at all negligible when compared to the Ti^{4+} complex reduction current.

Effect of oxalate

Reversible polarographic wave for Ti^{4+} oxalate complex was established as early as 1939 [40]. The earliest report on homogenous redox catalysis was also carried out in oxalic acid medium [41]. The effect of pH on this complex has been studied in some detail [42 - 44]. Cyclic voltammetric study on Hg also has been reported [45]. All these studies have been carried out with Ti^{4+} in 0.2M oxalic acid medium. No H$_2$SO$_4$ was added.

As is clearly seen from Fig. 5, addition of low concentrations of oxalate anions to a solution containing Ti^{4+} salt in H$_2$SO$_4$ results in a kinetic rather than diffusion controlled cyclic voltammogram. This may be due to the chemical ligand exchange reaction of the type,

$$Ti^{4+}_{nH_2} + HC_2O_4 \rightleftarrows |Ti(HC_2O_4)|^{3+}_{(n-1)H_2O} + H_2O \quad ...(5)$$
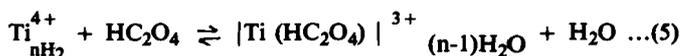
The rate of formation of the oxalate complex depends on the medium. At higher oxalate concentrations the complex formation would be complete and then the electron-transfer process would become diffusion controlled. This is responsible for the improved reversibility noticed at higher C$_2$O$_4^{2-}$ ion concentrations (Fig. 5). Increased oxalate ion concentration also stabilises the Ti^{3+} oxalate complex resulting in its oxidation at lesss anodic potentials (Fig. 5) Formation of oxalate complexes of Ti^{4+} and Ti^{3+} species in HClO$_4$ medium have also been established using polarographic technique [46].

Effect of thiocyanate

The effect of thiocyanate on the electrochemical behaviour of Ti^{4+} ions in sulphuric acid is quite similar to that of oxalate complex. The chemical reaction controlling the rate at lower CNS- concentration may be given by (6) quite similar to (5).

$$Ti^{4+}_{nH_2} + CNS^- \rightleftarrows Ti(CNS)^{3+}_{(n-1)H_2O} + H_2O \quad ...(6)$$
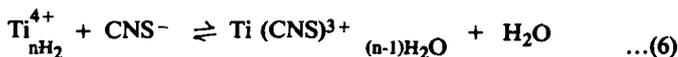
Stable Ti^{3+} thiocyanate complex seems to be formed even when CNS- concentration is very low and this may be responsible for the fact that its oxidation peak potential does not depend on CNS- concentration (Fig. 6). Polarographic data on the formation and stability of these complexes in HClO$_4$ medium [47-50] are available.

Effect of phosphate

As reported in the earlier section the phosphate complex seems to be one of the least stable ones in aqueous solution. Polarographic reports are also very scarce [51]. A cyclic voltammetric study on HMDE is however available [45]. Under identical conditions, the phosphate complex shows a slower charge transfer rate on GC when compared to Hg (Compare ref. 45 and Fig. 7).

Effect of citrate

In citrate medium, Ti^{4+} ions have been shown to give reversible polarographic waves [52]. Reproducible well defined waves are obtained upto a pH value of 11.5 [53]. The E$_{1/2}$-pH diagram shows three slopes suggesting the existence of three different complexes at these pH regions [53]. In HClO$_4$ acid medium both the equilibrium and kinetic rate constants of the Ti^{4+}-citrate complex formation have been evaluated [54, 55]. The complex formation in H$_2$SO$_4$ medium has also been established [33, 56] using polarographic technique.

On GC electrode in H$_2$SO$_4$ medium, no reduction wave is noted at potentials near -0.40V as on Hg electrode [33, 56]. However a reduction wave closer to the background wave (-1.000 V) is noticed (Fig. 8b). With increased citrate concentration and pH, the cathodic wave shifts to more cathodic potentials (Fig.8c and d). Since the change of anodic peak potential (E$_{pa}$) is not regular with pH and the appearance of E$_{pa}$ at -0.230 V occurs only when E$_{pa}$ at +0.400V completely disappears, it may be concluded that the anodic waves are due to two distinct Ti^{3+} citrate complexes rather than due to a single Ti^{3+} - citrate species connnected by pH equilibria. In strong alkaline medium, the Ti^{3+} species become inactive (no anodic wave in Fig. 8d)

Effect of tartrate

In tartrate medium also the Ti^{4+} ions give well defined polarographic waves [52, 53]. Impedance and Faradaic rectification [57, 58] techniques have been used to evaluate the relatively fast electron transfer rate on Hg electrode. However on GC, even in extreme acidic conditions and excess tartrate, the rate seems to be very much slower as indicated by a large peak separation of 1.300 V (Fig. 9). This is in accordance with the general trend of a slower rate constant of GC when compared to metal electrodes [23]. From the exchange current density value reported in ref. 57, the heterogeneous rate constant k$^\circ_h$ may be calculated using eq. (7).

$$i_\circ = nFA \ k^\circ_h \ c_x^\alpha \ C_R^{(1-\alpha)} \quad ...(7)$$

If α is assumed to be 0.5, k$^\circ_h$ value for this reaction on Hg is found to be 9 x 10^{-3} cm/sec. From the ΔE$_p$ value on GC electrode using Nicholson's method [59] k$^\circ_h$ is found to be $\leq$ 10^{-6} cm/sec. Such a wide difference in k$^\circ_h$ between Hg and GC electrode is highly surprising. In addition to the general trend of lower k$^\circ_h$ on GC electrode mentioned above, greater blocking effect of adsorbed tartrate ions on electron transfer on GC is probably involved. More detailed studies including capacitance measurements in tartrate medium on GC electrode may provide further insight into this process.

CONCLUSION

The present study indicates that the medium has a great influence on the electrochemical behaviour of Ti^{4+}/Ti^{3+} redox couple. In sulphate media, increasing Ti^{4+} or SO$^{2-}_4$ concentration results in the formation of a sulphate complex that is more easily reducible. In

H_2SO_4 medium, formation of other complexes may itself become a rate determining process as in the case of oxalate and thiocyanate complexes. Adsorption of the electroactive species may also play an important role as in the case of EDTA complex of Ti^{4+}. Adsorption of electroinactive large anions such as tartrate may block the electron transfer resulting in slower kinetics. Some Ti^{4+} complexes (citrate and tartrate) which show well defined waves on Hg at $E_{1/2}$ less negative than - 0.800 V are not clearly noticed on Glassy Carbon, probably because of general trend of slow electron transfer rate on GC electrode in addition to blocking effect [23]. Quantitative comparisons are made wherever the media employed are the same. As pointed out earlier, establishing the precise structural formalae of Ti^{4+}/Ti^{3+} complexes is the most difficult and unsettled problem in this area although substantial qualitative evidences exist [53, 60]. Because of this limitation, many information on Ti^{4+}/Ti^{3+} redox complexes still remain qualitative.

From the analytical point of view, the present study indicates that very strong H_2SO_4 or $NaHSO_4$ concentrations (>10 M in SO_4^{2-}) are required for the quantitative estimation of Ti^{4+} in these media. Quantitative voltammetric estimations may however be achieved in H_2SO_4 containing oxalic acid (>0.6M) or KCNS (>0.8M) medium. For estimating Ti^{4+} in alkaline media, citric acid/trisodium citrate medium may be used. For the estimation of very low concentrations, EDTA medium may be used. In such cases background corrections must always be carried out.

From the electrosynthetic viewpoint [8-16] the present study at least offers an explanation for the use of strong H_2SO_4 medium for the indirect electroreduction [9-16] as well as indirect amination [8]. The easily reducible Ti^{4+} - sulphate complex species are formed only in such media.

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