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A Polarographic Study of the Titanium–Ethylenediaminetetraacetate Complexes[1,2a]

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RECEIVED JUNE 29, 1953

Titanium(III) and (IV) in solutions of ethylenediaminetetraacetic acid yield well-formed, reversible polarographic waves. Below *p*H 2, the half-wave potential is independent of *p*H. Above *p*H 2.5 the dependence is linear and indicates that two hydrogen ions are involved in the electrode reaction. As the *p*H is increased the waves become more irreversible, the diffusion currents are diminished, and the solutions become colloidal. The diffusion current of the wave is a direct measure of the concentration of the complex in the presence of either an excess of titanium or of the complex former. Measurements of *p*H, total titanium, total complexing agent and diffusion currents indicate that, below *p*H 2, the TiY complex (H_4Y = ethylenediaminetetraacetic acid) is reduced to the TiY^- complex. The TiY complex is in equilibrium with the TiO^{++} ion. Above *p*H 2.5, the $TiOY^{=}$ complex is the predominant species and is likewise reduced to the TiY^- ion. As the *p*H is increased above 3, the TiO^{++} becomes increasingly hydrolyzed to colloidal titanium dioxide. In spite of the complications arising from numerous titanium species, in moderate concentrations of ethylenediaminetetraacetate, *p*H 2 to 5, the titanium waves are reproducible and analytically useful.

The natural abundance of titanium and the increasing use of this light metal in high temperature alloys has encouraged further studies of its chemical properties and a search for improved methods for its determination. Since a major difficulty in working with titanium is to keep it in solution, further information concerning its complex ions is very desirable.

The polarography of titanium(III) and (IV) in ethylenediaminetetraacetic acid has been briefly studied by Blumer and Kolthoff.[3] They conclude that between *p*H 1 and 2.5 the electrode reaction is probably

$$TiY^- = TiY + e^-$$

and calculated an approximate value of the dissociation constant for TiY of 2×10^{-18}. (For convenience, the formula H_4Y is used for ethylenediaminetetraacetic acid and "Versene" refers to its anions.) They also stated that above *p*H 2.5 the half-wave potential of the complex was dependent upon both *p*H and Versene concentration, and that the waves were irreversible. The possibility of the existence of hydroxy complexes and polynuclear complexes was suggested. The waves of titanium in tartaric acid,[4-6] citric acid,[5,6] and oxalic acid[7] solutions have also been studied.

This paper summarizes the results of a systematic study of the polarography of titanium(III) and (IV) in solutions of ethylenediaminetetraacetic acid and its salts.

Experimental

All polarograms were taken using a calibrated Sargent Model XXI Polarograph and an H-cell with an external saturated calomel electrode. A grounded water-bath, maintained at 25.0 ± 0.1°, was employed. No damping was used, and the internal resistance of the cell (about 200 ohms) was considered negligible. The capillary used has an *m* value of 1.925 mg./sec., and a drop time of 4.55 sec. at 0.0 v. *vs.* S.C.E. and 4.99 sec. at −0.4 v. *vs.* S.C.E. Residual currents were sometimes measured, but in most cases corrections were made for them by extrapolation. Purified nitrogen was used to remove oxygen from the solutions to be tested. Since no maxima were observed, suppressors were not added. *p*H measurements were made with a Beckman model H-2 *p*H meter.

Titanium solutions were prepared from distilled titanium tetrachloride in either 3 *M* hydrochloric acid or 3 *M* sulfuric acid. Some sulfuric acid solutions and all perchloric acid solutions were made from J. T. Baker C.P. titanium dioxide which had been fused with potassium pyrosulfate, dissolved in concentrated acid, and recrystallized (as hydrous oxide) three times at *p*H 2. Titanium(III) solutions were prepared in sulfuric and hydrochloric acids from the titanium(IV) solutions by reduction with zinc amalgam, or by electrolysis using a mercury cathode. These solutions were prepared fresh daily and stored under carbon dioxide. Since titanium(III) reduces the perchlorate ion, it was impossible to prepare titanous solutions in perchloric acid. Stock solutions were analyzed either gravimetrically by precipitation of titanium dioxide, or by passage through a Jones reductor into an excess of ferric sulfate solution followed by titration of the ferrous ion with ceric sulfate.

Solutions of Versene were made from Bersworth Chemical Company reagent grade disodium salt of ethylenediaminetetraacetic acid, dihydrate. They were standardized when necessary with calcite. Supporting electrolytes were prepared from reagent grade chemicals.

Results and Discussion

Titanium(III) and (IV) in Versene below *p*H 8 give well-formed waves with horizontal plateaus. Graphs of log $i/(i_d - i)$ *versus* $E_{d.e.}$ gave inverse slopes of 0.0572 for 0.9 m*M* titanium(IV) perchlorate in 1 m*M* Versene, 0.1 *M* acetic acid, 0.2 *M* perchloric acid, *p*H 0.78; 0.0580 for 0.7 m*M* titanium(IV) perchlorate in 5 m*M* Versene, 0.1 *M* acetate buffer, 0.2 *M* sodium perchlorate, *p*H 5.10; and 0.0605 for 0.3 m*M* titanium(III) chloride in 0.1 *M* Versene, *p*H 4.87; corresponding to the theoretical value 0.059 for a reversible one-electron reduction. All waves were nearly reversible (values of $E_{3/4} - E_{1/4}$ between 0.055 and 0.063) except above *p*H 7 and below *p*H 0.5. Titanium(III) solutions give waves with half-wave potentials 5 to 15 millivolts more positive than those for titanium(IV) under the same conditions.

Theoretical equations for the half-wave potential should apply.[8] The Ilkovic equation is obeyed regarding proportionality of i_d and $\sqrt{h}$, at mercury column heights of 43 to 73 cm., to within 2.2% below *p*H 2 and to within 3.0% at higher *p*H, and therefore the current is diffusion rather than rate controlled.

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(1) Presented before the Analytical Division at the 124th National Meeting of the American Chemical Society, Chicago, Ill., September 1953.

(2) (a) Based upon a thesis submitted by E. F. Maverick to the faculty of the University of California, Los Angeles, in partial fulfillment of the requirements for the degree of Master of Science; (b) University Fellow, 1952–1953.

(3) M. Blumer and I. M. Kolthoff, *Experientia*, **8**, 138 (1952).

(4) V. Caglioti and G. Sartori, *Gazz. chim. ital.*, **66**, 741 (1936).

(5) R. Strubl, *Collection Czech. Chem. Commun.*, **10**, 475 (1938).

(6) M. Kalousek, *ibid.*, **11**, 592 (1939).

(7) R. L. Pecsok, THIS JOURNAL, **73**, 1304 (1951).

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 217 ff.

Effect of Time.—Solutions of titanium(IV) in Versene below *p*H 2 are very stable and their polarograms are unchanged 17 days after preparation. However, solutions of titanium(IV) in Versene at higher *p*H develop a yellow color after standing about 60 hours; at the same time their polarograms develop maxima and minima and become irreversible.

Solutions of titanium(III) in Versene are very easily oxidizable. Therefore Versene solutions of both titanium(III) and (IV) were polarographed immediately after preparation to obtain all the data used in this paper.

Effect of *p*H.—A plot of half-wave potential *versus* *p*H (Fig. 1) shows a nearly *p*H-independent range below *p*H 2.5 and a *p*H-dependent range between *p*H 3 and 8. The slope in the dependent range is −0.114 volt per *p*H unit when the titanium perchlorate–acetate buffer-5 mM Versene system is used, and −0.104 volt per *p*H unit with the titanium chloride-0.1 M Versene system. The corresponding slope for titanium(III) in 0.1 M Versene is −0.108 volt per *p*H unit. These data indicate that in the *p*H-dependent range two hydrogen ions are consumed per electron in the electrode reduction.

Effect of Versene Concentration.—Within experimental error, half-wave potentials above *p*H 3 are independent of Versene concentration, which was varied from 1 mM to 0.1 M using 1 mM and 0.35 mM titanium(IV) in 0.1 M acetate buffer. Below *p*H 3, because of the low solubility of ethylenediaminetetraacetic acid in acid solutions, the Versene concentration was varied only from 1 to 5 mM in 0.1 M perchloric acid and 0.1 M acetic acid, but this variation had no effect on the half-wave potential.

Effect of Titanium Concentration.—Above *p*H 3, in 0.1 M Versene, the diffusion current increases linearly with increasing titanium concentration, and the half-wave potential is independent of titanium concentration. It was difficult to prepare homogeneous solutions above 3 mM in titanium (IV) at *p*H 4, above 0.8 mM at *p*H 6, and above 0.5 mM at *p*H 8. Solutions of higher than the above titanium concentrations were cloudy, indicating the presence of colloidal titanium dioxide, and gave waves which were irreversible and of less than the calculated height. At *p*H 4.5 it was possible to prepare homogeneous solutions of titanium(III) up to about 1.1 mM in titanous ion; all waves were reversible and the diffusion current was directly proportional to concentration of titanium(III) in this range.

Effect of Supporting Electrolytes and Other Ions.—Zinc ion, when added to Versene solutions as zinc acetate, had no appreciable effect on the residual currents. However, when a zinc solution, made by dissolving the metal (used in preparing Jones reductors) in hydrochloric acid, was added to Versene solutions, residual currents were increased markedly and non-reproducibly. Titanium(III) solutions for quantitative work were therefore prepared by reduction with a mercury cathode.

To test the effect of sulfate ion a solution of 3 mM titanium(IV), 5 mM Versene and 0.3 M sulfuric acid was prepared. At *p*H 1.5, the diffusion current was found to be 5.55 microamperes. When sodium sulfate was added to make the solution about 1 M in sulfate ion, the diffusion current (wave at −0.22 volt) decreased to 3.27 microamperes and a wave appeared at about −1 volt, which was irreversible and resembled those obtained by Kalousek.[6] When, on the other hand, Versene was added in small increments to a solution containing 1 mM titanium(IV), 1 M sodium sulfate and 0.14 M sulfuric acid, the second wave was visible even at 5 mM Versene and only about 90% of the total titanium appeared in the Versene complex. It is believed that the second wave is due to a sulfate complex of titanium, and that, since chloride ion probably complexes titanium to an even greater extent, the presence of large amounts of chloride or sulfate ion should not be tolerated in the most exacting work.

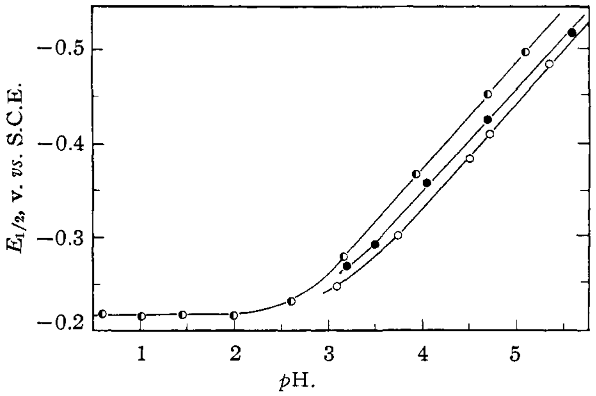

Fig. 1.—Half-wave potential *vs.* *p*H: ◐, 0.8 mM titanium(IV) perchlorate, 5.1 mM Versene, 0.1 M acetic acid, 0.2 M perchloric acid; ●, 0.3 mM titanium(IV) chloride, 0.1 M Versene; ○, 0.3 mM titanium(III) chloride, 0.1 M Versene.

Migration Studies.—To obtain more insight into the state of the titanium(IV) ion, or ions, in acid solutions, migration studies were conducted. A cell was constructed in which the cathode and anode compartments were filled with 3 M sulfuric acid or 9 M perchloric acid, and separated from each other by sintered glass walls. The compartments were then connected by a bridge containing 29 mM titanium(IV) in 3 M sulfuric acid in the first case, and 44 mM titanium(IV) in 9 M perchloric acid in the second case. The results may be summarized as follows.

Acid	Current, amp.	Duration of experiment, hr.	(Ti) in cathode, mM	(Ti) in anode, mM
Sulfuric or perchloric	None	17.5	1.1	0.95
Sulfuric	0.5	3	2.0	10.0
Perchloric	0.25	3	12.3	4.0
	0.5	1.5		

In both cases the titanium in the anode compartment was largely in the form of the yellow peroxy complex. It is apparent that in sulfuric acid titanium is predominantly present as an anion, or anions, and therefore is complexed by sulfate to a large extent. Titanium(IV) is evidently much less complexed by perchlorate than by sulfate, and in subsequent work it was assumed to exist largely as a positive ion in dilute perchlorate solutions.

Calculation of Dissociation Constants

It is evident from the data previously described that there are at least two Versene complexes of titanium(IV), one whose reduction is independent of hydrogen ion concentration and one whose reduction depends approximately on the square of the hydrogen ion concentration. In attempting to calculate dissociation constants for these complexes we have assumed their formulas to be TiY and $TiOY^{-2}$, respectively, and that of the titanium(III) complex to be TiY^-.

Since in the presence of excess Versene the height of the waves is directly proportional to the concentration of titanium, and in the presence of excess titanium the height is directly proportional to Versene concentration, the diffusion current of these waves is in any case a measure of the concentration of titanium–Versene complex. In subsequent data the concentration of complex has been calculated from the diffusion current given by a known amount of titanium in a very large excess of Versene.

The total concentration of Versene being known, the concentration of "free" Versene may be obtained by difference. The concentration of "uncomplexed" titanium is likewise represented by the difference between the total titanium and complexed titanium concentrations.

The literature is not clear concerning the true formula for the "uncomplexed" titanium(IV) ions or aggregates. The migration studies previously noted suggest that titanium(IV) is probably highly complexed in strong solutions of sulfate. In dilute aqueous solutions a hydrolyzed ion, such as TiO^{+2}, which many authors regard as the actual ion (or even an anion such as $Ti(OH)_6^{-2}$, as suggested by Rumpf[9]), seems likely. In aqueous solutions of *p*H greater than 2, it is probable that any "uncomplexed" titanium(IV) is present as colloidal titanium dioxide. Therefore we have calculated two dissociation constants for the TiY complex; one based on the assumption that Ti^{+4} represents the "uncomplexed" ion and the other based on the assumption that any Ti^{+4} formed is immediately hydrolyzed to TiO^{+2}. Two calculations have also been made for the $TiOY^{-2}$ dissociation, first assuming TiO^{+2} as the free ion, and secondly assuming rapid hydrolysis of TiO^{+2} to colloidal TiO_2. The results of such calculations give support to the more highly hydrolyzed species in each case.

The true dissociation constant of TiY is

$$K_1 = (Ti^{+4})(Y^{-4})/(TiY) \qquad (1)$$

Since at any point

$$\Sigma(Y) - (TiY) = (H_4Y) + (H_3Y^-) + (H_2Y^{-2}) + (HY^{-3}) + (Y^{-4}) \qquad (2)$$

where Σ(Y) represents total concentration of Versene in all forms; therefore

$$(Y^{-4}) = \frac{\Sigma(Y) - (TiY)}{\frac{(H^+)^4}{k_1k_2k_3k_4} + \frac{(H^+)^3}{k_2k_3k_4} + \frac{(H^+)^2}{k_3k_4} + \frac{(H^+)}{k_4} + 1} \qquad (3)$$

where k_1, k_2, k_3 and k_4 are Schwarzenbach's dissociation constants for H_4Y.[10] Substituting 3 in 1 we obtain

$$K_1 = \frac{(Ti^{+4})[\Sigma(Y) - (TiY)]}{(TiY)\left[\frac{(H^+)^4}{k_1k_2k_3k_4} + \frac{(H^+)^3}{k_2k_3k_4} + \frac{(H^+)^2}{k_3k_4} + \frac{(H^+)}{k_4} + 1\right]} \qquad (4)$$

Using equation 4, the determination of K_1 was attempted as follows. A solution was prepared which was 0.1 *M* in sodium nitrate and 1.380 m*M* in titanium(IV) sulfate. A standard solution of 5.124 m*M* Versene in 0.1 *M* sodium nitrate was added in measured amounts. Polarograms were taken after each addition, and the corresponding *p*H and diffusion current measured. Since a solution of 1.380 m*M* titanium(IV) sulfate, 5.124 m*M* Versene and 0.1 *M* sodium nitrate at *p*H 2.22 gave a diffusion current of 4.95 microamperes, (TiY) was calculated at each Versene concentration from the relationship

$$(TiY) = 1.380 \times i_d/4.95 \qquad (5)$$

As is shown in Table IA, K_1 calculated from these data is $4 \pm 3 \times 10^{-20}$.

If the "uncomplexed" titanium(IV) ion is TiO^{+2} rather than Ti^{+4}, then the dissociation of the TiY complex is represented by

$$TiY + H_2O = TiO^{+2} + Y^{-4} + 2H^+ \qquad (6)$$

which is the combination of a simple dissociation and a subsequent hydrolysis

$$Ti^{+4} + H_2O = TiO^{+2} + 2H^+ \qquad (7)$$

The apparent dissociation constant of the TiY complex, K_6, is therefore the product of K_1 and K_7.

The value of K_6 can be obtained from the data in Table IA, using the expression

$$K_6 = \frac{(TiO^{+2})[\Sigma(Y) - (TiY)](H^+)^2}{(TiY)\left[\frac{(H^+)^4}{k_1k_2k_3k_4} + \frac{(H^+)^3}{k_2k_3k_4} + \frac{(H^+)^2}{k_3k_4} + \frac{(H^+)}{K_4} + 1\right]} \qquad (8)$$

K_6 is the product of K_1 and the square of the hydrogen ion concentration, and is also shown in Table IA. The data yield a value for K_6, the product of the dissociation constant of TiY and the constant of hydrolysis of Ti^{+4} to TiO^{+2}, of $7 \pm 5 \times 10^{-23}$.

Both of the above interpretations yield reasonably constant values for the dissociation constant over a range of Versene and titanium concentrations. However, the combination of the TiO^{+2} ion and TiY complex involves a constant, K_6, which is much more sensitive to hydrogen ion concentration than K_1. In collecting the data for Table IA, the *p*H was held nearly constant. Further experiments were therefore suggested, in which the total Versene and titanium concentrations were held constant and the *p*H varied.

A solution was prepared which was 0.894 m*M* in titanium(IV) perchlorate, 1.025 m*M* in Versene, 0.1 *M* in acetate buffer and 0.18 *M* in perchloric acid. The *p*H of this solution was varied from 0.03 to 9.04, and the diffusion current at each *p*H recorded. Figure 2 is a plot of $i_d/Cm^{2/3}t^{1/6}$ *versus* *p*H taken from these data.

The diffusion current constants below *p*H 2.2 are quite reproducible at 1 and 5 m*M* Versene in a given

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[9] M. E. Rumpf, *Ann. chim.*, **8**, 456 (1937).

[10] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

TABLE I

CALCULATION OF DISSOCIATION CONSTANTS

A. For TiY at low *p*H, variable Versene concn.

*p*H	Σ(Y) × 10^4, *M*	Σ(Ti) × 10^3, *M*	(TiY) × 10^4, *M*	(Ti)[a] × 10^4, *M*	(Y^{-4}), *M*	K_1 × 10^{20}	K_6 × 10^{23}
1.34	1.00	1.351	0.83	12.7	2.59×10^{-21}	3.95	8.26
1.35	1.97	1.328	1.52	11.8	7.50×10^{-21}	5.90	11.8
1.37	3.80	1.278	2.79	9.99	2.00×10^{-20}	7.16	13.0
1.37	6.33	1.209	5.35	6.74	1.94×10^{-20}	2.44	4.44
1.44	9.24	1.131	7.38	3.93	6.82×10^{-20}	3,63	4.79
1.50	13.6	1.014	9.06	1.08	2.78×10^{-19}	3.31	3.31
1.53	17.1	0.921	8.78	0.43	6.54×10^{-19}	3.20	2.79

B. For TiY at low *p*H, variable *p*H

*p*H	Σ(Y) × 10^3, *M*	Σ(Ti) × 10^4, *M*	(TiY) × 10^4, *M*	(Ti)[a] × 10^4, *M*	(Y^{-4}), *M*	K_1	K_6 × 10^{23}
1.91	1.025	8.94	8.68	0.26	2.85×10^{-18}	8.53×10^{-20}	1.29
1.60	1.020	8.90	7.92	0.98	3.24×10^{-19}	4.02×10^{-20}	2.54
1.35	1.012	8.84	7.45	1.39	4.42×10^{-20}	8.24×10^{-21}	1.65
1.01	0.994	8.67	5.09	3.58	3.94×10^{-21}	2.70×10^{-21}	2.58
0.87	.982	8.57	3.52	5.05	1.44×10^{-21}	2.07×10^{-21}	3.76
.62	.973	8.48	2.56	5.92	1.69×10^{-22}	3.90×10^{-22}	2.24
.41	.955	8.32	1.53	6.79	2.74×10^{-23}	1.23×10^{-22}	1.85
.03	.914	7.96	0.44	7.52	9.13×10^{-25}	1.56×10^{-23}	1.36

C. For $TiOY^{-2}$ at *p*H greater than 2

*p*H	Σ(Y) × 10^3, *M*	Σ(Ti) × 10^4, *M*	(TiY) × 10^4, *M*	(Ti)[a] × 10^4, *M*	(Y^{-4}), *M*	K_{10}	K_{12} × 10^{21}
2.20	1.020	8.90	7.68	1.22	4.12×10^{-17}	6.55×10^{-18}	0.26
2.91	1.013	8.84	7.60	1.24	3.50×10^{-15}	5.22×10^{-16}	0.79
3.62	1.003	8.75	7.28	1.47	1.58×10^{-13}	3.20×10^{-14}	1.89
4.13	0.986	8.60	6.96	1.64	1.88×10^{-12}	4.44×10^{-13}	2.44
5.20	.930	8.10	4.93	3.17	3.80×10^{-10}	2.44×10^{-10}	9.71
6.06	.913	7.95	3.98	3.97	1.44×10^{-8}	1.44×10^{-8}	10.9

[a] Concentration of "uncomplexed" titanium.

supporting electrolyte, although they vary considerably between electrolytes (nitrate, sulfate, perchlorate, acetate, etc.). The diffusion current constants above *p*H 2.5, however, are not reproducible at low Versene concentrations. Good reproducibility is obtained when 0.1 *M* Versene is used as a supporting electrolyte. These facts, coupled with the instability of these solutions with respect to time, suggest that equilibrium is difficult to obtain in the region in which the half-wave potential depends on *p*H.

Table IB shows the calculation of K_1 and K_6 from the data which are plotted in Fig. 2. (TiY) was calculated at each *p*H from the equation

$$(\mathrm{TiY}) = 0.890 \times i_d/2.96 \qquad (9)$$

since a solution of 0.890 m*M* titanium(IV) perchlorate, 5.124 m*M* Versene, 0.1 *M* acetate buffer and 0.18 *M* perchloric acid at *p*H 2.0 gave a diffusion current of 2.96 microamperes.

At *p*H values below 2, K_1 varied from 1.56×10^{-23} to 8.53×10^{-20}. However, the value of K_6 from these data is $2 \pm 1 \times 10^{-23}$. It is apparent that this value is in agreement within an order of magnitude with $K_6 (= 7 \pm 5 \times 10^{-23})$ obtained when the Versene concentration rather than the *p*H was varied (see Table IA).

The fact that such agreement is obtained by two different methods in two different supporting electrolytes is considered to be evidence of the existence, at low *p*H, of a hydrolyzed titanium ion whose hydrolysis depends on the square of the hydrogen ion concentration. We believe that the titanyl ion represents the majority or average of the ions or aggregates of titanium(IV) at *p*H values between 0 and 2, in dilute aqueous solutions.

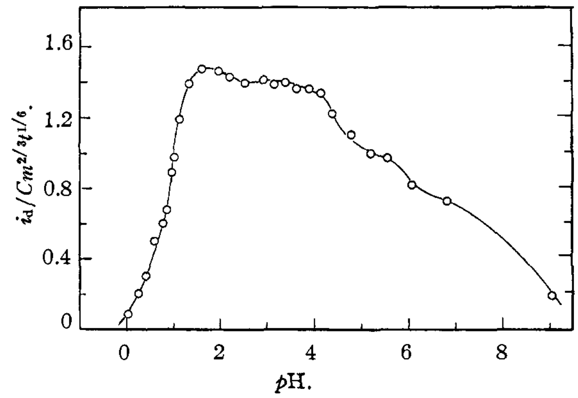

Fig. 2.—$i_d/Cm^{2/3}t^{1/6}$ *vs.* *p*H: 0.894 m*M* titanium(IV) perchlorate, 1.025 m*M* Versene, 0.1 *M* acetic acid, 0.2 *M* perchloric acid.

At *p*H values greater than 2, neither of the above interpretations yields consistent values for the dissociation constants. In view of the facts that the half-wave potential is now *p*H dependent and that the solutions were often visibly colloidal, we suggest that the titanium(IV) Versene complex in this region of *p*H contains oxygen and on dissociation of the complex, colloidal titanic oxide is formed.

$$\mathrm{TiOY^{-2}} = \mathrm{TiO^{+2}} + \mathrm{Y^{-4}} \qquad (10)$$

$$\mathrm{TiO^{+2}} + \mathrm{H_2O} = \mathrm{TiO_2} + 2\mathrm{H^+} \qquad (11)$$

The net dissociation constant in this pH range then is

$$K_{12} = \frac{(\mathrm{TiO_2})(\mathrm{Y}^{-4})(\mathrm{H}^+)^2}{(\mathrm{TiOY}^{-2})} = K_{10}K_{11} \qquad (12)$$

Data and calculations for K_{10} and K_{12} are shown in Table IC. They yield a reasonably constant value for K_{12} rather than K_{10}, which is consistent with the above interpretation.

It has been previously noted that the half-wave potential in the pH range 2.5 to 8, for both the titanium(IV) and titanium(III) Versene complexes, depends approximately on the square of the hydrogen ion concentration, and that below pH 2.5, the half-wave potential is independent of the hydrogen ion concentration. Therefore it is proposed that the electrode reactions are

$$\mathrm{TiY} + e^- = \mathrm{TiY}^- \quad \text{below } p\mathrm{H}\ 2.5 \qquad (13)$$

and

$$\mathrm{TiOY}^{-2} + 2\mathrm{H}^+ + e^- = \mathrm{TiY}^- + \mathrm{H_2O} \quad p\mathrm{H}\ 2.5 \text{ to } 8 \qquad (14)$$

Calculation of Dissociation Constant Ratios from Half-wave Potentials

Since all waves obtained were nearly reversible the half-wave potentials are nearly identical with the electrode potentials of the couples involved. In the pH independent range, the half-wave potential of the complex is -0.22 v. *vs.* the saturated calomel electrode. It follows that

$$E°_{13} - E°_{17} = -0.059 \log \frac{K_{16}}{K_1K_7} \qquad (15)$$

where K_{16} and K_1 are dissociation constants of the TiY^- and TiY complexes, respectively,

$$\mathrm{TiY}^- = \mathrm{Ti}^{+3} + \mathrm{Y}^{-4} \qquad (16)$$

K_7 is the constant for the hydrolysis of titanic ion to titanyl ion, and $E°_{17}$ is the standard potential for the couple

$$\mathrm{TiO}^{+2} + 2\mathrm{H}^+ + e = \mathrm{Ti}^{+3} + \mathrm{H_2O} \qquad (17)$$

which is approximately 0.1 v. *vs.* the normal hydrogen electrode,[11] or -0.15 v. *vs.* the saturated calomel electrode. Therefore

$$K_{16}/K_1K_7 = \text{approximately } 16$$

In the previous section, it has been shown that K_1K_7 is approximately 3×10^{-23}, which yields the result, $K_{16} = 5 \times 10^{-22}$.

In the pH dependent range, from the proposed electrode reaction

$$\mathrm{TiOY}^{-2} + 2\mathrm{H}^+ + e^- = \mathrm{TiY}^- + \mathrm{H_2O} \qquad (14)$$

it would be predicted that

$$E_{1/2} = E°_{14} - 0.059 \times 2\ p\mathrm{H} \qquad (18)$$

The observed dependence of half-wave potential on pH in this region is

$$E_{1/2} = E°_{14} - 0.11\ p\ \mathrm{H} \qquad (19)$$

At pH 4, the half-wave potential is -0.35 v. (see Fig. 1). Extrapolation to zero pH yields a value for $E°_{14}$ of 0.09 v. *vs.* the saturated calomel electrode. From the relation

$$E°_{14} - E°_{17} = -0.059 \log \frac{K_{16}}{K_{10}} \qquad (20)$$

the ratio K_{10}/K_{16} is 1×10^4. Since K_{16} is 5×10^{-22}, the value of K_{10}, which is the dissociation constant of the TiOY^{-2} complex, is 5×10^{-18}.

In Table IC, we have shown that $K_{10}K_{11}$ is about 10^{-21}, and therefore K_{11}, the constant of hydrolysis of the titanyl ion to $\mathrm{TiO_2}$, is approximately 10^{-4}.

Conclusions

The proposed electrode reactions for the titanium-Versene system are

$\mathrm{TiY} + e^- = \mathrm{TiY}^-$	$p\mathrm{H} < 2$
$\mathrm{TiOY}^{-2} + 2\mathrm{H}^+ + e^- = \mathrm{TiY}^- + \mathrm{H_2O}$	pH 2.5 to 8

The following equilibrium constants have been obtained

$\mathrm{TiY}^- = \mathrm{Ti}^{+3} + \mathrm{Y}^{-4}$	5×10^{-22}
$\mathrm{TiOY}^{-2} = \mathrm{TiO}^{+2} + \mathrm{Y}^{-4}$	5×10^{-18}
$\mathrm{TiY} + \mathrm{H_2O} = \mathrm{TiO}^{+2} + 2\mathrm{H}^+ + \mathrm{Y}^{-4}$	3×10^{-23}
$\mathrm{TiO}^{+2} + \mathrm{H_2O} = \mathrm{TiO_2} + 2\mathrm{H}^+$	10^{-4}

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[11] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 268.