

these properties with the relatively large dipole moment differences between amino acids and their isomers. One would expect the oxygen of the -OH group in the acetic acid molecule to undergo hydrogen bonding more

readily than the nitrogen of the -NH<sub>2</sub> group in the acetamide molecule. This may possibly be an explanation of the differences in the behavior of aqueous solutions of these two molecules.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MASSACHUSETTS, AMHERST, MASS., AND DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.]

## On the Standard Potential of the Titanium(III)-Titanium(II) Couple

BY JOHN W. OLVER AND JAMES W. ROSS, JR.

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Data on the potential of the Ti(III)-Ti(II) couple are given and evaluated. These data support the theoretical value of approximately -2 v. *vs.* the n.h.e. as the reduction potential of the couple in aqueous solution.

The standard potential of the Ti(III)-Ti(II) couple is given by Latimer<sup>1</sup> as -0.37 v. based upon measurements reported by Forbes and Hall<sup>2</sup> using a mercury pool cathode on solutions thought to contain Ti(II) in 0.1 M HCl. Other authors<sup>3,4</sup> have been completely unable to prepare stable solutions of Ti(II) not only in aqueous solutions but in low-acidity solvents including acetonitrile and dimethylformamide and have concluded that Ti(II) quickly disproportionates to Ti(III) and Ti(0). We have attempted to clarify this question by polarographic measurements in aqueous and nonaqueous media.

### Experimental

Mixed titanium(II) and titanium(III) halides were prepared according to the procedure described by Forbes and Hall.<sup>2</sup> Aqueous or acetonitrile solutions to be polarographed were prepared by suspending the mixed halides in cold, deaerated solvent and (in a closed nitrogen flushed system) filtering directly into an ice-cold deaerated polarographic cell.

Hexaaquatitanium(III) chloride was prepared by dissolving C.P. titanium in concentrated hydrochloric acid in a hydrogen atmosphere. The crystals were collected and dried in a nitrogen stream and stored in a vacuum desiccator.

Titanium hydride, Grade E, was obtained from Metal Hydrides, Inc. Titanium monoxide, brass-colored, was prepared by the method of Dawihl and Schroter.<sup>5</sup>

Acetonitrile was dried and purified by distillation from P<sub>2</sub>O<sub>5</sub> until a residual current wholly attributable to capacitive charging current was obtained. Polarographic grade tetraethylammonium bromide (Southwestern Analytical Chemicals) was used in acetonitrile when a supporting electrolyte was desired. All reagents used as dissolution agents, complexing agents, or supporting electrolytes in aqueous solution were analytical grade.

Polarograms were obtained using a Sargent Model XXI polarograph without damping. The saturated calomel electrode was used as reference. The reference was connected to the polarographic cell *via* a 1 M KCl salt bridge through a 6-mm. length of porous 6-mm. diameter Vycor rod. Water diffusion into a polarographic cell containing acetonitrile as solvent was felt to be neglectable during the course of a single polarogram. All solutions were deaerated with prepurified tank nitrogen.

### Results and Discussion

Polarograms of solutions prepared by the procedure of Forbes and Hall<sup>2</sup> are shown in Fig. 1. The wave at -0.2 v. is for the oxidation Ti(III) → Ti(IV) + e<sup>-</sup>, while the wave at -0.7 v. is for the irreversible reduction Ti(IV) + e<sup>-</sup> → Ti(III). Curve II is exactly the polarogram obtained when hexaaquatitanium(III), a labile complex, is polarographed, showing conclusively

that Ti(III) does not reduce in this medium at a potential more positive than that at which H<sup>+</sup> is reduced. If Ti(II) existed in such solutions, absence of an anodic wave for the oxidation of that Ti(II) requires that Ti(II) be oxidized irreversibly by at least 0.8 v. If the potential -0.37 v. for the couple were valid the couple would be highly irreversible and not obey the Nernst equation as previously reported.<sup>2</sup> The potential measured at zero current by Forbes and Hall was limited on the negative side by reduction of H<sup>+</sup> rather than reduction of Ti(III) and on the positive side by oxidation of Ti(III) rather than oxidation of Ti(II) and actually represented a mixed potential between those limiting processes. The potential of a mercury cathode in contact with this solution in a potentiometric determination where no current is drawn would depend upon the rates of electrochemical reduction of hydrogen ion and oxidation of titanium(III). That potential would approximate the polarographic zero current in curve II.

Of sixteen trials by Forbes and Hall, ten were discarded because of rapidly falling potentials and reducing capacity less than for Ti(III) alone. The relationship between falling potential and low reducing capacity can be seen from curve III of Fig. 1 since as Ti(IV) is formed the potential of the Hg cathode at zero current falls into the potential range in curve III giving only residual current, a potential more positive than in curve II. Reducing capacity greater than for Ti(III) alone on the remaining six trials suggests the presence of colloidal Ti(0) from disproportionation of Ti(II). Groves and Russell<sup>6</sup> have deposited finely divided titanium on Hg cathodes at high current densities and found such titanium reacts quickly and quantitatively with dichromate (the test used by Forbes and Hall for reducing capacity).

Polarograms of solutions prepared by dissolving titanium metal, TiH<sub>2</sub>, or TiO in mineral acids directly in deaerated polarographic cells showed waves only for Ti(III). Polarograms of Ti(III) in complexing media such as 1 M oxalate, citrate, and thiocyanate at elevated pH where H<sup>+</sup> reduction would not interfere showed no reduction of Ti(III). For example, in 1 M citrate ion at pH 7, Ti(III) could be investigated to -1.8 v. *vs.* s.c.e. without evidence of reduction, at which point electrolyte reduction occurs in the absence of titanium(III). The magnitude of the shift in half-wave potential for Ti(III) as the citrate complex, though indeterminate, is probably several tenths of a volt.

In dry acetonitrile, both hexaaquatitanium(III) chloride and dry mixed titanium halides prepared by the method of Forbes and Hall give similar two-step polarograms with an initial reduction wave at -1.3 v. *vs.* s.c.e. The second step is at a more negative poten-

(1) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(2) G. S. Forbes and L. P. Hall, *J. Am. Chem. Soc.*, **46**, 385 (1924).

(3) O. Ruff and I. Neumann, *Z. anorg. allgem. Chem.*, **128**, 81 (1923).

(4) T. C. Franklin and H. V. Seklemian, *J. Inorg. Nucl. Chem.*, **12**, 181 (1959).

(5) S. W. Dawihl and V. K. Schroter, *Z. anorg. allgem. Chem.*, **233**, 178 (1937).

(6) R. Groves and A. S. Russell, *J. Chem. Soc.*, 2805 (1931).

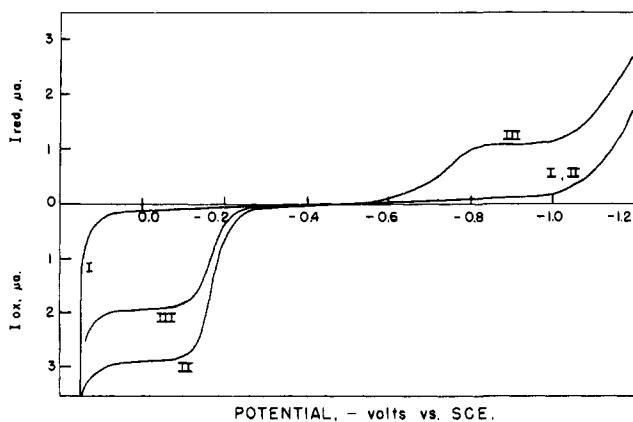


Fig. 1.—Polarograms of titanium in 0.1 *M* HCl: curve I, residual current polarogram for 0.1 *M* HCl; curve II, polarogram of solution of titanium halides prepared after Forbes and Hall,<sup>2</sup> approximately two millimolar in titanium in 0.1 *M* HCl; curve III, polarogram of the same solution with Ti(III) partially oxidized.

tial and approximately twice the size of the first, indicating a one-electron reduction to Ti(II) followed by a two-electron reduction to Ti(0). Considering the dif-

ference in solvation energies of Ti(III) between water and acetonitrile to be expected by analogy with other tripositive transition metals,<sup>7</sup> the aqueous potential corresponding to  $-1.3$  v. *vs.* s.c.e. in acetonitrile would be at least  $-2$  v. *vs.* n.h.e.

This estimate more nearly coincides with the theoretical work of George and McClure,<sup>8</sup> who applied ligand field correction to the hydration energies of di- and tripositive ions of the first transition series in relating standard potentials of the metal ion couples to the third ionization potential of the free metals. Their calculations agreed with known standard potentials for the first transition series except in the case of the Ti(III)–Ti(II) couple. They estimated that the true  $E^0$  of the Ti(III)–Ti(II) couple should be approximately  $-2.3$  v. in aqueous solution. Such a potential would well explain the absence of Ti(II) in aqueous media.

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(7) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1652 (1957)

(8) P. George and D. S. McClure in "Progress in Inorganic Chemistry," F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

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## The Effect of Specific Swamping Electrolytes upon the Formation Constant of the Monochloroiron(III) Complex<sup>1</sup>

BY ROBERT N. HEISTAND<sup>2</sup> AND ABRAHAM CLEARFIELD<sup>3</sup>

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The ultraviolet absorption spectrum of the monochloroiron(III) complex in perchloric acid and sodium perchlorate–perchloric acid mixtures was examined. The formation constant increased with increasing swamping electrolyte concentration but decreased when the ratio of sodium perchlorate to perchloric acid increased at constant total molarity. These results were correlated with the effect of the swamping electrolyte upon the activities of the species involved in the equilibria.

The chloro complexes formed by the hydrated iron(III) cation have been the subject of numerous spectrophotometric studies.<sup>4–9</sup> Gamlen and Jordan<sup>9</sup> reviewed this work in detail and concluded that 4 species,  $\text{FeCl}_2^+$ ,  $\text{FeCl}_2^+$ ,  $\text{FeCl}_3$ , and  $\text{FeCl}_4^-$ , were formed in the system. Desesa and Rogers<sup>10</sup> observed that the absorption spectra of iron(III) solutions containing chloride ion were greatly influenced by changes in hydrogen ion concentration. However, these investigators were interested in developing an analytical method for the determination of iron and did not examine the nature of the acid effect further. Subsequently, Coll, Nauman, and West<sup>11</sup> determined the

effect of perchloric acid concentration and mixtures of perchloric acid and perchlorates upon the absorption spectrum of the monochloroiron(III) complex. They found an enormous increase in the value of the formation constant with increasing perchlorate concentration and attributed this to the dehydration of the hydrated iron(III) cation by perchlorates. However, these authors felt that this was not the only factor responsible for the observed changes in the formation constant. The present study was undertaken to elucidate further the nature of the perchlorate ion effect upon the chloroiron(III) complexes.

### Experimental

**Reagents and Solutions.**—Reagent grade iron(III) chloride was recrystallized from aqueous solution until free of metallic impurities. Iron(III) perchlorate was prepared from the chloride by the method of Mulay and Selwood.<sup>12</sup> The resulting violet crystals were dissolved in 0.1 *M*  $\text{HClO}_4$  and diluted with the acid to a concentration 0.05 *M* total iron. The solution was analyzed for iron(III) and iron(II) by the Zimmerman–Reinhart method and for chloride ion by the Volhard method.<sup>13</sup> There

(11) H. Coll, R. V. Nauman, and P. W. West, *J. Am. Chem. Soc.*, **81**, 1284 (1959).

(12) L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2695 (1955).

(13) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Chemistry," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, pp. 545, 572–573.

(1) Presented before the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1961.

(2) This paper is based upon the thesis submitted by Robert N. Heistand in partial fulfillment of the requirements for the degree of Master of Science, Niagara University.

(3) Address: National Lead Co., Titanium Alloy Mfg. Div., Box C, Bridge Station, Niagara Falls, N. Y., for all inquiries.

(4) A. VonKiss, J. Abraham, and I. Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(5) H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941).

(6) E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

(7) H. Olerup, *Svensk. Kem. Tidskr.*, **66**, 324 (1943).

(8) D. E. Metzler and R. J. Meyers, *J. Am. Chem. Soc.*, **72**, 3772, 3776 (1950).

(9) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(10) M. A. Desesa and L. B. Rogers, *Anal. Chim. Acta*, **6**, 534 (1952).