[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Investigation of Oxalate, Citrate and Tartrate Complexes of Ferric and Ferrous Iron

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The standard potential of the reaction $Fe^{+++} + e = Fe^{++}$ (+0.76 v.) is so close to that of the reaction $Hg_2^{++} + 2e = 2Hg$ (+0.80 v.) that the reduction of simple ferric ion at the dropping electrode produces a wave that starts from zero applied e.m.f.[1] The half-wave potential of this wave corresponds to the oxidation of the mercury of the dropping electrode and hence it is not characteristic of ferric ion; any other substance which is a stronger oxidant than mercurous ion in a given solution will produce a similar wave. Although the diffusion current of simple ferric ion is well developed and can be applied to the determination of iron,[2] the fact that many other substances produce a similar diffusion current limits its practical application to cases in which it is known that such substances are absent.

In order to obtain a true polarographic wave whose half-wave potential is characteristic of the ferric-ferrous couple, it is necessary to employ a supporting electrolyte that forms a more stable complex with ferric ion than with ferrous and mercurous (or mercuric) ions, so that the potential of the ferric–ferrous system is decreased to a greater extent than that of the mercurous–mercury system. This condition is fulfilled in solutions containing oxalate,[3,4] citrate,[1] tartrate,[5] or fluoride[3] ions, and in strongly alkaline solutions containing mannitol.[6]

This study was undertaken to obtain systematic data on the polarographic characteristics of ferric and ferrous iron in citrate, tartrate, and oxalate solutions, since from the few data in the literature these complexing agents appeared to be most promising for the determination of iron. Particular attention was paid to the *p*H of the various solutions, a factor whose importance has frequently been overlooked in polarographic studies of the complex ions formed between weak acids and metal ions.

Experimental

The photographically recording polarograph used, which was of the Heyrovsky-Shikata[1,7] type, was constructed by the author. The chief novelty of this instrument is that its camera is large enough to accommodate ordinary 8 × 10 inch paper (Eastman Kodabromide E-1), which is not only much less expensive than the special size paper required for commercial polarographs but its larger size also permits the recording of large polarograms with a resultant increase in precision. The Ayrton shunt used to control the galvanometer sensitivity consisted of two decade resistance boxes in series; this arrangement provided 1000 different sensitivity settings so that wave heights could be precisely adjusted to any desired value. The period of the recording galvanometer (Leeds and Northrup Type R) was adjusted to about 12 sec. by a damping resistance across its terminals in parallel with the Ayrton shunt. The instrument was calibrated at frequent intervals as previously described[8]; its maximum sensitivity was 0.0164 microamp./mm. The potentiometer bridge (Leeds and Northrup slide wire) was calibrated and the applied potential could be read to ±0.2%, corresponding to an accuracy of about ±4 mv. in the measurement of half-wave potentials when the total voltage across the bridge was 2 v., or ±2 mv. when the total bridge voltage was 1 v. The recording camera and bridge were driven by a synchronous motor, and the drive mechanism was arranged so that either could be activated while the other remained stationary.

An H-type cell with saturated calomel anode[9] was used, and all measurements were made at 25.0 ± 0.1°. Hydrogen was used to remove dissolved air from the solutions. The *m*-value of the dropping electrode was measured frequently by means of the automatic stop-clock device previously described[10]; slight variations were noted from day to day but all the values were between 1.50 and 1.52 mg./sec. The drop time ranged between 2.5 and 3.8 sec. depending on the potential of the dropping electrode.

*p*H measurements were made with a glass electrode. All solutions contained 0.005% gelatin as a maximum suppressor.

Results and Discussion

Citrate Media.—The stability of a complex ion formed between a metal ion and a weak acid will, in general, be dependent on the *p*H, and hence this factor has a pronounced influence on the polarographic characteristics of such complexes. The effect of *p*H on the polarogram of ferric iron in 0.5 *M* citrate solutions is demonstrated in Fig. 1. In recording each successive polarogram the galvanometer zero was shifted progressively downward but the same voltage scale was used for all the curves.

In 0.5 *M* citrate solutions of *p*H less than 11 the polarogram consists of only a single wave, with an excellent diffusion current, corresponding to the reduction of the ferric complex to the ferrous complex, and no wave for the further reduction of the ferrous complex to the metal is observed before the reduction of hydrogen or sodium ion. However, in a 0.5 *M* sodium citrate solution containing 0.05 *M* excess hydroxide ion (curve e in Fig. 1) a second wave due to reduction of the ferrous complex to metallic iron does clearly develop, the half-wave potential being −1.62 v. *vs.* the saturated calomel electrode. Solutions of *p*H smaller

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 276.

[2] I. M. Kolthoff and George Matsuyama, *Ind. Eng. Chem., Anal. Ed.*, **17**, 615 (1945).

[3] M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[4] J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

[5] E. T. Verdier, *Coll. Czechoslov. Chem. Commun.*, **11**, 240 (1939).

[6] K. Komarek, *ibid.*, **10**, 466 (1938).

[7] J. Heyrovsky and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

[8] Ref. 1, p. 227.

[9] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[10] J. J. Lingane, *ibid.*, **16**, 329 (1944).

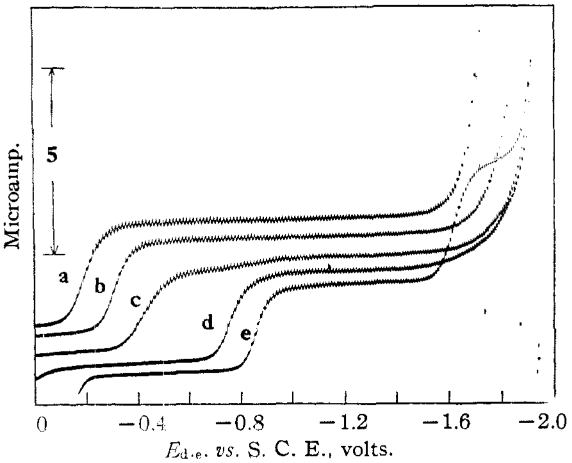

Fig. 1.—Influence of *p*H on the polarogram of ferric iron in citrate medium. In all cases the total concentration of sodium citrate was 0.5 *M*. Curve a was obtained with 50 cc. of 1.99 millimolar ferric iron, and the other curves were recorded after addition of small increments of 2 *N* potassium hydroxide. The *p*H was measured after each addition. The *p*H values were: (a) 5.6, (b) 6.8, (c) 7.7, (d) 10.9 and (e) 12.0, the latter two values being corrected for the alkaline error of the glass electrode.

than about 10 had a pale yellow color but the strongly alkaline solutions were virtually colorless.

The fact that the second stage of reduction is not observed up to a *p*H of about 11 (which is only slightly beyond the equivalence point in the neutralization of the monohydrogen citrate ion) signifies that the citrato ferrous complex is so stable that it is not reduced before the potential at which sodium ion is reduced. It is remarkable that the second wave does appear when a large excess of hydroxide is present, and this is a clear indication that a different ferrous complex is formed in strongly alkaline solutions. In very strongly alkaline solutions some of the coördinating citrate ions are probably either replaced by hydroxide ions or else the hydroxyl groups in the citrate ion undergo acidic ionization. Assuming the first alternative, the resulting hydroxo citrato ferrous complex must be more stable thermodynamically than the citrato ferrous complex, or it would not form, and the fact that no reduction wave is obtained with the less stable citrato complex shows that the overvoltage (activation energy) required for its reduction is much larger than that required to reduce the more stable hydroxo citrato complex. Judging from the slope of the second wave in curve e the reduction of the hydroxo citrato complex does not proceed with strict thermodynamic reversibility, $E_{3/4} - E_{1/4} =$ 0.070 v. compared to 0.028 v. for a reversible 2-electron reduction,[1,4] but the overvoltage probably is not very great.

Over a *p*H range from 4 to 12, and with a total concentration of sodium citrate of 0.5 *M* and 0.005% gelatin, the half-wave potential of the ferric–ferrous wave is a linear function of *p*H, the relation being

$$E_{1/2} = 0.426 - 0.108\,p\text{H} \qquad (1)$$

The reversibility of the ferric–ferrous couple in both acidic and alkaline citrate solutions was investigated by obtaining the polarograms in Fig. 2.

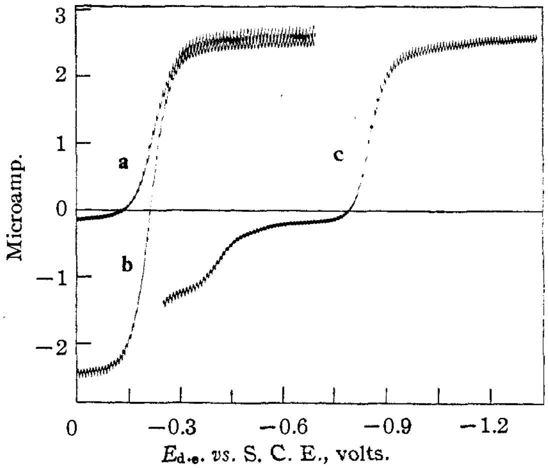

Fig. 2.—Test of the reversibility of the ferric–ferrous couple in citrate medium.

Curve a in Fig. 2 was recorded with 50 cc. of 1.99 millimolar ferric iron in 0.5 *M* sodium citrate of *p*H 6.1 containing 0.005% gelatin; curve b was obtained after adding 10 cc. of freshly prepared 10 millimolar ferrous ammonium sulfate, so that the concentrations of ferric and ferrous iron were both 1.66 millimolar; and curve c resulted after adding 3 cc. of 5 *N* sodium hydroxide so that the solution contained 0.14 *M* excess hydroxide ion. Curve b demonstrates conclusively that the ferric–ferrous couple is strictly reversible at a *p*H of 6, and very probably also at lower *p*H values and up to a *p*H of about 7; below *p*H 7 the citrato ferrous complex produces an anodic wave whose half-wave potential is the same as that of the cathodic wave of the ferric complex. It is equally clear from curve c that the ferric–ferrous couple is not reversible in strongly alkaline citrate solutions; the poorly developed anodic wave has a half-wave potential of −0.40 v. compared to −0.85 v. for the cathodic wave. The slope of the cathodic wave in curve c is very close to the expected value for a reversible 1-electron reduction ($E_{3/4} - E_{1/4} =$ 0.063 v. compared to the theoretical 0.056 v.), and therefore the irreversibility of the couple in strongly alkaline solution must be attributed to irreversibility in the oxidation of the ferrous complex rather than in reduction of the ferric complex.

In 0.5 *M* sodium citrate containing 0.005% gelatin the cathodic diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ is constant to ±1.5% over a range of *p*H values from 5 to 12 and equal to 0.93 ± 0.01 microamp./millimole/liter/mg.$^{2/3}$ sec.$^{-1/2}$ at 25°. In 0.5 *M* sodium citrate and 0.005% gelatin the diffusion current constant of the anodic wave at *p*H 6 is 0.90 at 25°, only slightly smaller than that for the cathodic wave. Varying the concentration of sodium citrate between 0.25 and 0.5 *M* at *p*H 6 had no appreciable effect on the diffusion current constants. The relatively small values of the diffusion current constants reflect the relatively large size of the complex ions and the fact that only 1 electron is involved in the electrode reaction. This is somewhat disadvantageous in practical analyses because it decreases the accuracy with which very small concentrations of iron can be determined.

It is evident that ferric iron may be determined in either acidic or alkaline citrate solutions, but for the determination of ferrous iron from its anodic wave the *p*H of the citrate solution should be between about 5 and 7.5 and the optimum *p*H is between 6 and 7. A 0.5 *M* citrate solution of *p*H between 6 and 7 should be very useful for analyzing mixtures of ferric and ferrous iron. Since ferrous iron in citrate (and tartrate and oxalate) solutions is easily air-oxidized it is necessary to add a measured volume of the ferrous solution to a known volume of the supporting electrolyte which has been freed from dissolved air by hydrogen or nitrogen in order to obtain reproducible results.

Tartrate Media.—Polarograms of ferric iron in tartrate media of various *p*H values are shown in Fig. 3. In all cases the total concentration of sodium tartrate was 0.5 *M*, the concentration of ferric iron was 1.99 millimolar, and 0.005% gelatin was present as a maximum suppressor.

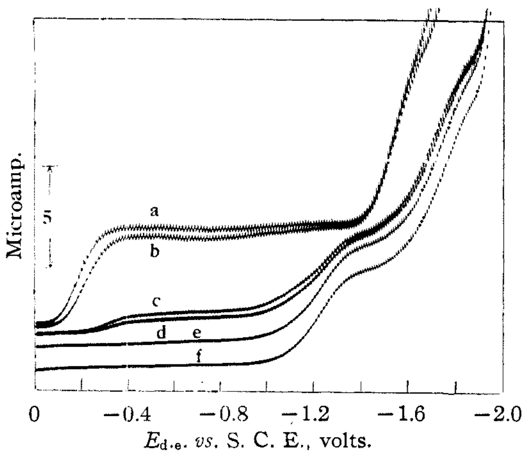

Fig. 3.—Effect of *p*H on the polarogram of ferric iron in tartrate media. The *p*H values were: (a) 5.8, (b) 6.2, (c) 6.8, (d) 7.4, (e) 8.2 and (f) 9.4.

Both stages of reduction are observed at all *p*H values between 5.8 and 9.4, but the second wave (reduction of the tartrato ferrous complex to the metal) is so close to the final current rise that the diffusion current is not distinctly developed. At *p*H values smaller than 6.2 the diffusion current due to reduction of the tartrato ferric complex to the ferrous complex is very well defined, and in this *p*H range the characteristics of this first wave are very similar to the first wave in citrate solutions.

Between a *p*H of 6.2 and about 8 the first wave divides into two separate waves, and as the *p*H is increased the relative height of the first of these waves decreases although the total height of both waves remains constant (curves c and d in Fig. 3). The transition is complete at *p*H 8.2 as shown by curve e. The doublet wave between *p*H 6.2 and 8 obviously cannot be caused by reduction of a single tartrato ferric complex to two different oxidation states, since the sum of both parts represents only a 1-electron reduction, and it must result from the reduction of two different tartrato ferric complexes. The occurrence of a divided wave shows that the equilibrium between the two species is established slowly, as otherwise at potentials at which the first diffusion current is observed the more difficultly reducible species would simply be transformed to the more easily reducible form at the electrode surface as the concentration of the latter is decreased by its reduction and only a single wave would result. It is significant that the divided wave is observed over the *p*H range in which the concentration of hydrogen tartrate ion decreases from a value several times that of the ferric iron to virtually zero. From the second ionization constant of tartaric acid (6.9×10^{-5}), and the fact that the total concentration of sodium tartrate was 0.5 *M*, the concentration of hydrogen tartrate ion at a *p*H of 6.2 is 4.6 millimolar, at *p*H 6.8 it is 1.1 millimolar, at *p*H 7.4 it is 0.29 millimolar, and at a *p*H of 8.2 it is only 0.05 millimolar. The concentration of ferric iron was 1.99 millimolar. It seems reasonable to conclude that at *p*H values smaller than about 6.2 the ferric complex involves the hydrogen tartrate ion, at *p*H values between 6.2 and 8 two species are present, one comprising the hydrogen tartrate ion and the other the tartrate ion, and at *p*H values above 8 only the complex containing the tartrate ion remains.

At *p*H 6.8 the diffusion current of the first part of the divided wave in curve c of Fig. 3 is 0.65 microamp. and the total diffusion current is 3.48 microamp., the ratio being 0.19. At this *p*H the concentration of hydrogen tartrate ion is 1.1 millimolar, and assuming that three hydrogen tartrate ions are combined with one ferric ion, the equilibrium concentration of the hydrogen tartrato complex would be 0.37 millimolar, and the ratio to the total concentration of ferric iron would be $0.37/1.99 = 0.19$. The agreement of the relative wave heights with the calculated equilibrium ratio of the two complexes is good evidence that the rate of conversion of the tartrato into the hydrogen tartrato complex is so small that no appreciable transformation occurs at the surface of the dropping electrode during the life of a drop.

The half-wave potentials of the several waves referred to the saturated calomel electrode, and with a total tartrate concentration of 0.5 *M*, are

*p*H	5.8	6.2	6.8	7.4	8.2	9.4
$E_{1/2}$	−0.17	−0.21	−0.29	−0.33	−1.19	−1.20
	−1.50	−1.53	−1.15	−1.18	−1.72	−1.73
			−1.68	−1.71		

At *p*H values smaller than 6.2 the half-wave potentials of the ferric to ferrous wave are almost identical with the values in citrate media (eq. 1), showing that the ferric complexes in the two media have virtually equal stabilities.

Between *p*H 4 and 6 in 0.5 *M* sodium tartrate containing 0.005% gelatin the diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ of the cathodic ferric wave is 1.11 ± 0.03 microamp./millimole/liter/mg.$^{2/3}$ sec.$^{-1/2}$ at 25°. This value is somewhat larger than that in acidic citrate solution because the tartrato ferric ion is smaller, and therefore has a larger diffusion coefficient, than the citrato complex.

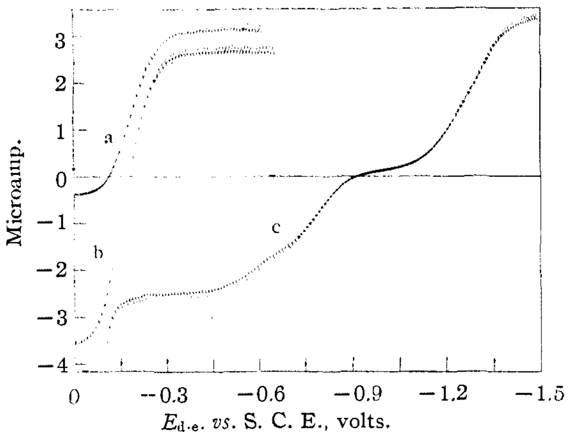

Fig. 4.—Test of the reversibility of the ferric–ferrous couple in tartrate medium. Curve a was recorded with 50 cc. of a 1.99 millimolar solution of ferric iron in 0.5 *M* sodium tartrate of *p*H 5.6. Curve b resulted after addition of 10 cc. of freshly prepared 10 millimolar ferrous ammonium sulfate solution. Curve c was obtained after addition of 1 cc. of 5 *N* sodium hydroxide solution, and the solution contained approximately 0.1 *M* excess hydroxide ion.

Polarograms a and b in Fig. 4 demonstrate that the ferric–ferrous couple is reversible in a tartrate solution of *p*H 5.6, and very probably at lower *p*H values and up to a *p*H of about 6.2, but, contrary to the conclusions of Verdier,[1,5] the couple does not behave reversibly in strongly alkaline tartrate solution. This behavior parallels that in citrate solutions. Note that the anodic wave in strongly alkaline tartrate solution (curve c in Fig. 4) comprises two distinct parts; this points to the existence of two different ferrous complexes, probably a tartrato ferrous ion and a hydroxy tartrato ferrous ion, in sluggish equilibrium.

Figure 5 is a polarogram of a mixture of ferric and ferrous iron in an *ammoniacal* tartrate solution of *p*H 9.7. Part a is the anodic wave due to the oxidation of the ferrous complex to the ferric state, part b results from the reduction of the ferric complex to the ferrous complex, and part c corresponds to the reduction of the ferrous complex to the metallic state.

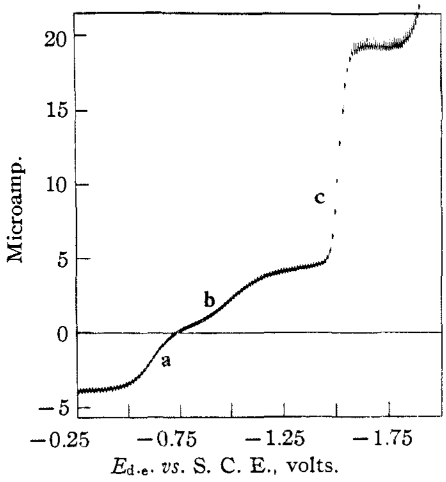

Fig. 5.—Polarogram of a mixture of 2 millimolar each of ferric and ferrous iron in ammoniacal tartrate solution of *p*H 9.7. The solution contained 0.5 *M* ammonium tartrate, 1 *M* excess ammonia and 0.005% gelatin.

The chief noteworthy difference between the polarogram in ammoniacal tartrate solution and in sodium tartrate solution of the same *p*H is the well-defined reduction wave of the ferrous complex in the ammoniacal medium (wave c in Fig. 5). The fact that the half-wave potential of this wave (−1.53 v.) is 0.2 v. more positive than that of the corresponding wave in sodium tartrate medium of the same *p*H (−1.73 v.) is a clear indication of different ferrous complexes in the two media. It is significant that the half-wave potential of wave c is very nearly the same as that (−1.49 v.) reported by Voriskova[11] for the reduction of the complex *ammino* ferrous ion from 1 *M* ammonia–1 *M* ammonium chloride. Very probably ferrous iron in ammoniacal tartrate solution exists as an ammino tartrato complex, which is thermodynamically more stable, but more reversibly reduced, than the tartrato complex. This conclusion is supported by the fact that the half-wave potential (−0.98 v.) of the cathodic ferric–ferrous wave in ammoniacal tartrate solution (curve b in Fig. 5) is more than 0.2 v. more *positive* than that of the corresponding wave in a sodium tartrate solution of the same *p*H. The easier reduction in ammoniacal tartrate could result either from increased stability of the ferrous state or decreased stability of the ferric state, but in view of the character of curve c there is little doubt that the first alternative is correct.

It will be noted that the ferric–ferrous couple does not behave reversibly in ammoniacal tartrate solution, the half-wave potential of curve *a* (−0.62 v.) being 0.36 v. more positive than that of curve b (−0.98 v.).

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[11] M. Voriskova, *Coll. Czechoslov. Chem. Commun.*, **11**, 580 (1939).

An ammoniacal tartrate supporting electrolyte presents more opportunities for analytical applications than a sodium tartrate medium, because at *p*H values in the neighborhood of 9 all three diffusion currents are accurately measurable, and the solution is well buffered which facilitates the *p*H adjustment.

Since the tartrato ferric ion readily undergoes photochemical reduction the solution must be freshly prepared when it is desired to measure only the cathodic wave. The same is true of the citrate and oxalate complexes. Fortunately the cathodic and anodic diffusion current constants are virtually identical, so photochemical reduction will cause no significant error in the determination of total iron provided one records the entire curve and measures the total cathodic-anodic wave height.

The polarograms in Fig. 6 demonstrate the effect of the photocatalyzed reduction of the tartrato ferric ion by tartrate ion. Curve a was obtained with a freshly prepared solution containing 2 millimolar ferric iron in a 0.5 *M* sodium tartrate solution of *p*H 5.8. Curve b was recorded after the solution stood in a stoppered flask for four weeks exposed to diffuse northern daylight. It is seen that the cathodic wave disappeared completely and was replaced by the anodic wave of the ferrous complex. The reduction was probably completed long before the four weeks elapsed. The curves in Fig. 6 suggest the possibility of developing a polarographic actinometer.

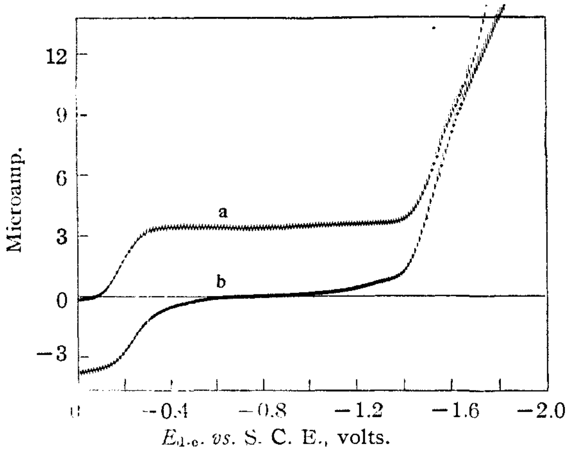

Fig. 6.—Photochemical reduction of ferric iron in tartrate solution. Curve a was obtained with a freshly prepared solution containing 2 millimolar ferric iron in 0.5 *M* sodium tartrate solution of *p*H 5.8, and curve b was recorded after four weeks exposure to diffuse northern daylight.

Oxalate Media.—Typical polarograms of ferric iron in 0.2 *M* sodium and potassium oxalate solutions of various *p*H values are shown in Figs. 7 and 8.

At *p*H values less than 7.9 the diffusion current for the reduction of the ferric to the ferrous complex is very clearly developed. The reversibility of the ferric–ferrous couple in oxalate media of *p*H less than about 7.9 has already been established.[1,3,4] The second reduction stage is observable only at *p*H 7.9, the half-wave potential being −1.72 v. *vs.* the saturated calomel electrode (curve c in Fig. 7).

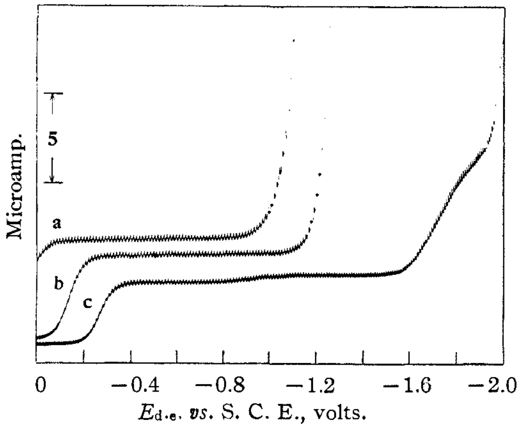

Fig. 7.—Influence of *p*H on the polarogram of ferric iron in oxalate medium. Curve a was obtained with 50 cc. of a 2 millimolar solution of ferric iron in 0.2 *M* oxalic acid solution whose *p*H had been adjusted to 1.3 by dilute potassium hydroxide, and the other curves were recorded after addition of increments of 2 *N* potassium hydroxide. The *p*H values were: (a) 1.3, (b) 2.3 and (c) 7.9.

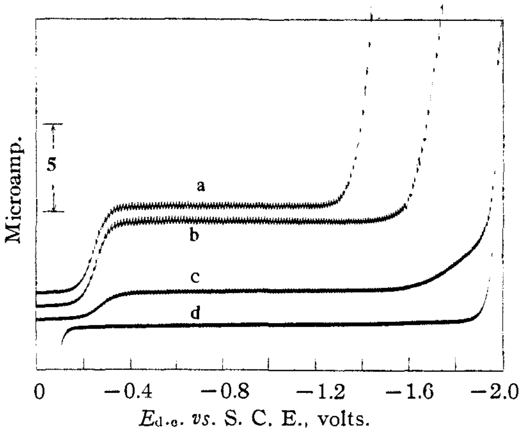

Fig. 8.—Influence of *p*H on the polarogram of ferric iron in oxalate medium. Curve a was obtained with 50 cc. of a 2 millimolar solution of ferric iron in 0.2 *M* sodium oxalate solution whose *p*H had been adjusted to 3.7 by addition of dilute hydrochloric acid, and the other curves were recorded after adding small increments of 5 *N* sodium hydroxide. The *p*H values were: (a) 3.7, (b) 5.3, (c) 8.3 and (d) 0.1 *M* excess hydroxide ion. A precipitate of hydrous ferric oxide formed in solutions c and d.

When the *p*H is smaller than about 2 the ferric–ferrous wave starts at zero applied e.m.f. The half-wave potentials of this wave at various *p*H values, and with a total oxalate concentration of 0.2 *M*, are

*p*H	2.3	3.7	5.25	7.9	8.3
$E_{1/2}$ *vs.* S. C. E.	−0.140	−0.240	−0.245	−0.270	−0.275

As the *p*H is increased from 2 to 3.7 the half-wave potential shifts markedly to more negative values, but between a *p*H of 3.7 and 8.3 it changes relatively very little; in this latter *p*H range $\Delta E_{1/2}/\Delta p\text{H}$ amounts to only −0.008 v.

Up to a *p*H of 3.7 the predominant oxalate species is the hydrogen oxalate ion, and the oxalate ion concentration is small, but above *p*H 3.7 the oxalate ion predominates and is present at a much larger concentration than the ferric iron. It was shown in a previous paper[4] that with relatively small concentrations of excess oxalate ion the half-wave potential of the ferric–ferrous couple shifts to more negative values as the oxalate ion concentration is increased, but when the oxalate ion concentration is large compared to that of the ferric iron further increases in its concentration have virtually no effect on the half-wave potential because the ferric and ferrous complexes both contain the same number of oxalate ions. The above data are in accord with these previous conclusions.

When the *p*H is increased above 7.9 ferric iron precipitates, apparently as the hydrous oxide. From curve c in Fig. 8 it may be concluded that at *p*H 8.3 the solubility of ferric iron in a 0.2 *M* oxalate solution is 0.39 millimolar, and in 0.2 *M* sodium oxalate containing 0.1 *M* excess sodium hydroxide the solubility is so small that no wave is observable (curve d in Fig. 8). The smaller stability in alkaline medium of the oxalato ferric ion compared to the citrato and tartrato complexes must reflect the fact that the bonds in the latter two complexes directly involve hydroxyl ions, which are absent in the oxalate ion. It appears that the bond between the central ferric ion and oxygen of the hydroxyl group is stronger than that with the oxygen of the carboxyl group.

After a 2 millimolar solution of ferric iron in a 0.5 *M* oxalate solution of *p*H 1.3 stood in diffuse daylight for several days a bright yellow precipitate appeared, and a polarogram of the solution showed no wave for either ferric or ferrous ion. It is evident that in practical applications of an acidic oxalate supporting electrolyte the solution must be freshly prepared.

Over the *p*H range between 2 and 6 in 0.2 *M* sodium oxalate containing 0.005% gelatin the diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ of the cathodic ferric wave is constant and equal to 1.50 ± 0.03 microamp./millimole/liter/mg.$^{2/3}$ sec.$^{-1/2}$ at 25°. This value is considerably larger than in acidic citrate or tartrate media, reflecting the fact that the oxalato ferric ion is much smaller, and hence has a much larger diffusion coefficient, than the citrato and tartrato complexes.

Summary

A photographically recording polarograph, which has several advantages over commercially available instruments, is described.

In acidic citrate, tartrate and oxalate supporting electrolytes ferric iron produces very similar polarograms; only the first stage of reduction of the ferric complexes to the ferrous state is observed at *p*H values smaller than about 6 and the diffusion currents are very well developed. The second stage of reduction of the ferrous complexes to the metal is clearly shown only in strongly alkaline citrate medium and in ammoniacal tartrate solution. In oxalate solutions of *p*H greater than 7.9 ferric iron precipitates as the hydrous oxide.

In all three media the ferric–ferrous couple behaves reversibly only when the *p*H is smaller than about 7, and under these conditions the ferrous complexes produce anodic waves whose half-wave potentials are identical with the cathodic half-wave potentials of the ferric complexes. In alkaline citrate and tartrate solutions the ferric–ferrous couple is irreversible, the anodic ferrous waves occurring at a much more positive potential than the cathodic ferric waves. The ferri-ferrous couple is also irreversible in ammoniacal tartrate medium.

Evidence is presented that in strongly alkaline citrate solution ferrous iron (and possibly also ferric iron) exists as a hydroxo citrato complex. In tartrate solutions of *p*H between about 6.2 and 8 two different complex of ferric iron appear to be present, one involving the hydrogen tartrate ion and the other the tartrate ion. In ammoniacal tartrate solutions ferrous iron apparently exists as an ammino tartrato complex.

The photochemical reduction of ferric iron in tartrate and citrate solutions can be accurately followed from the disappearance of the cathodic wave of the ferric complex and the appearance of the anodic wave of the ferrous complex. This fact might be made the basis of a polarographic actinometer.

An acidic citrate supporting electrolyte of *p*H between 5 and 7 offers more analytical possibilities than any of the other solutions investigated.

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