Chemical analysis of the original recrystallized product showed that oven drying may be omitted if the biiodate is washed with ethyl alcohol and air dried.

Summary

The results of this investigation show that the solubility relations in this system are the same over a range of temperatures as those found by Meerburg at 30° and confirm the fact that potassium biiodate can be recrystallized safely from aqueous solution.

In using potassium biiodate as a volumetric standard, care should be exercised in drying the sample. Either an alcohol-washed, air-dried sample should be used or a sample which has been dried sufficiently to convert the compound to the anhydride.

HARTFORD, CONN. RECEIVED APRIL 11, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY OF THE HEBREW UNIVERSITY]

The Structure and Behavior of Ferric Tartrate and Citrate Complexes in Dilute Solutions[1]

BY M. BOBTELSKY AND J. JORDAN

It is hard to find a problem of complex chemistry which has been studied with as much stubbornness as the behavior and structure of the various metallic tartrates and citrates. This is apparently due to the fact that these complexes are met with simultaneously in various fields of the natural sciences: analytical chemistry, both qualitative and quantitative, makes use of these complexes, though not to a sufficient extent; the properties of the various tartrates and citrates, their solubility and their behavior in the presence of alkali seem to be well suited for the analytical separation of metals without using hydrogen sulfide; oxy-complexes (especially the citrates of iron and of the alkaline earths) are of considerable interest in physiological chemistry, too.

The structure of tartrates and citrates of bivalent cations has been discussed in a previous paper.[1a] There, we have postulated formulas assuming that the organic (tartrate and citrate) radicals occupy *three* coördination positions, though some tartrates of bivalent cations have been prepared which crystallize with two molecules of water[2,3] (thus suggesting coördination number four for the tartrate radical). Apparently, the structure of the various complexes depends not only on the organic radical, but also on the cation concerned. Furthermore, a regrouping of the radicals may occur, while the complexes are neutralized by alkali.

In this paper we should like to discuss the complexes of a tervalent cation: we have chosen the ferric complexes, because they are the most important ones and are easily accessible to photometric, conductometric, potentiometric and polarographic research. Some "thermometric titrations"[4] were also carried out by us, to confirm results obtained by other methods.

It should be borne in mind that it is extremely difficult to crystallize out citrate or tartrate complexes of iron.[5] The citrates are very soluble and the tartrates are mostly precipitated as basic salts.[5,6,7] Even the structure of the well-known crystallized "green ferric citrate" is still controversial.[8,9] And, generally, there is no finally accepted view about the structure of the ferric citrate and tartrate complexes, though many papers have been published on this subject.[5−17]

Contrary to bivalent cations, tervalent iron forms complexes not only with trisodium citrate and disodium tartrate but even with *free* citric and tartaric acid. We have found that in the most stable complexes the molar ratio between iron and the tartrate or citrate radicals is $2Fe^{III}$: 3Cit (or 3Ta).[17a]

Experimental

Conductometric, photometric and **polarographic** measurements were carried out as described in the previous paper.[1]

Potentiometric titrations were made with a Hellige "electron-tube-potentiometer" using a bright platinum

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(1) This paper was presented before the Division of Physical and Inorganic Chemistry at the 110th Meeting of the American Chemical Society, Chicago, September, 1946.

(1a) M. Bobtelsky and J. Jordan, THIS JOURNAL, **67**, 1824 (1945).

(2) Fr. Bullnheimer and E. Seitz, *Ber.*, **33**, 817 (1900).

(3) S. U. Pickering, *J. Chem. Soc.*, **96**, 1409 (1909); **97**, 1837, 1851 (1910); **99**, 169 (1911); **101**, 174, 1614 (1912); **103**, 1354 (1913); **107**, 942, 955 (1915); **109**, 235 (1916).

(4) W. Swietoslawski, "Thermochemie" (Part VII of Ostwald-Drucker's Handbuch), p. 108 (1928).

(5) S. U. Pickering, *J. Chem. Soc.*, **103**, 1358 (1913); **105**, 644 (1914).

(6) W. Franke, *Ann.*, **486**, 242 (1931).

(7) Eliane Poulenc-Ferrand, *Compt. rend.*, **210**, 299 (1940).

(8) E. Belloni, *C. A.*, **15**, 839 (1921).

(9) W. D. Treadwell and E. Wettstein, *Helv. Chim. Acta*, **18**, 200, 981 (1935).

(10) C. Morton, *Chem. Zentr.*, **102**, II, 3569 (1931); **104**, I, 753 (1933).

(11) E. E. Wark and J. W. Wark, *Z. physik. Chem.*, **157**, 310 (1931).

(12) Shin'ichiro Hakomori, *Chem. Zentr.*, **99**, I, 1385 (1928).

(13) N. L. Galvez, *C. A.*, **32**, 7183 (1938).

(14) H. Grossmann and A. Loeb, *Z. physik. Chem.*, **72**, 93 (1910).

(15) Pariselle and Delsal, *Compt. rend.*, **198**, 83 (1934).

(16) Delsal, *J. chim. phys.*, **35**, 350 (1938).

(17) Yeu-Ki-Heng, *ibid.*, **33**, 356 (1936).

(17a) In this paper, the abbreviations "Cit" and "Ta" are generally used for citrate and tartrate and do not denote any particular acid or ion.

indicator electrode and a saturated calomel reference electrode.

pH-measurements were performed with a Beckman pH-meter, laboratory model G, using a Beckman glass electrode.

The temperature, at which the various measurements were carried out, had been selected with a view to avoid the formation of precipitates. Most satisfactory results were obtained from conductometric titrations at 0° in aqueous solution and at 30° in 50% ethanol. Photometric measurements were made at room temperature (20–25°). The use of a thermostat would have complicated the technique unnecessarily.

The pH-measurements, too, were carried out at room temperature, the potentiometric titrations at 0°.

As the ferric complexes were sensitive to light, all experiments were carried out in darkness; filtered deep-red light (which proved to have no action whatever upon the solution concerned) was used occasionally.

The **thermometric titrations** were carried out according to the technique described by Mayr and Fisch.[18]

Results

The experimental results were mostly summed up in graphs. The actually measured values are plotted in continuous curves and the extrapolations in dotted lines (........). With each conductometric titration curve the corresponding "theoretical curve" (calculated by the summation of the conductivities of the various single components, under the assumption that there was not any interaction between them) is plotted in broken lines (--- or -·-·-).

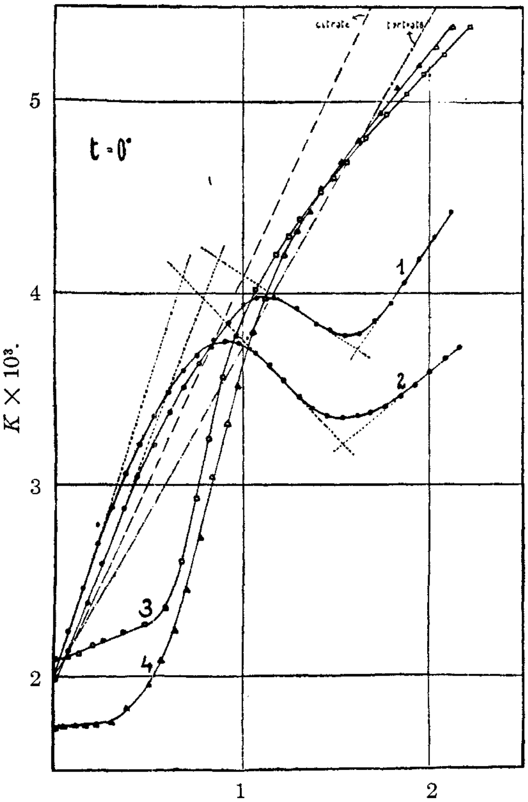

Fig. 1.—Conductimetric titration curves: (1) 1 cc. 3 N $Fe_2(SO_4)_3$ + 49 cc. H_2O + x cc. 1 M Na_3Ci; (2) 1 cc. 3 N $Fe_2(SO_4)_3$ + 49 cc. H_2O + x cc. 1 M Na_2T; (3) 1 cc. 1 M Na_3Ci + 49 cc. H_2O + x cc. 3 N $Fe_2(SO_4)_3$; (4) 1 cc. 1 M Na_2T + 49 cc. H_2O + x cc. 3 N $Fe_2(SO_4)_3$.

Conductometric titration curves of ferric sulfate with sodium citrate (= trisodium citrate) and disodium tartrate (disodium tartrate), in aqueous solution, are plotted in Fig. 1 (curves 1 and 2). Both these curves, as well as those of the reverse titrations (curves 3 and 4 of Fig. 1) show breaks at the approximate molar ratios 1 Fe^{III}:1.5Cit; 1Fe^{III}:0.8Cit; and 1Fe^{III}:1.5Ta; 1Fe^{III}:0.7Ta. This suggests that complexes of the composition Fe_2Cit_3, Fe_5Cit_4 (?) and Fe_2Ta_3, Fe_3Ta_2 are formed. Analogous experiments with *free citric* (H_3Ci) *and tartaric* (H_2T) *acid*, both in aqueous solution (Fig. 2, curves 1 and 2) and in 50% ethanol (Fig. 2, curves 3 and 4), show that complexes of the composition Fe_3Cit_2 and Fe_3Ta_2 are formed.[18a]

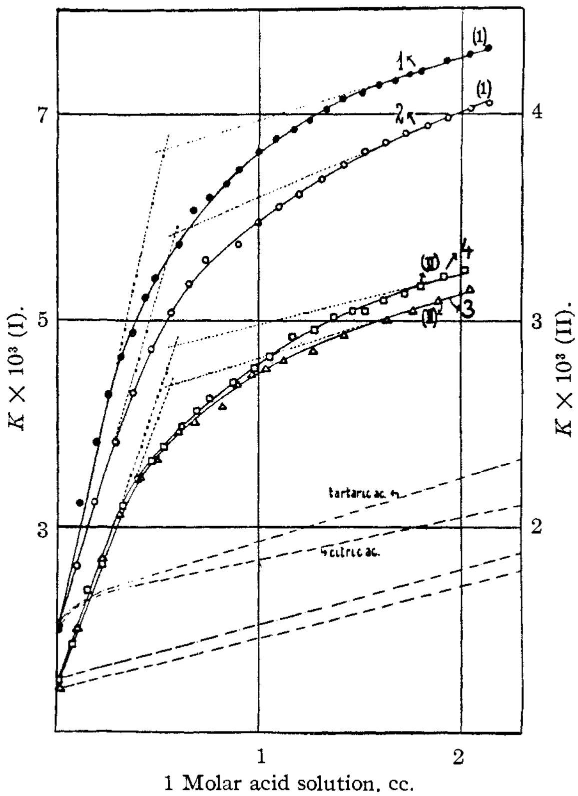

Fig. 2.—Conductimetric titration curves: (1) 1 cc. $Fe_2(SO_4)$ + 49 cc. H_2O + x cc. 1 M H_3Ci; t = 0°; (2) 1 cc. 3 N $Fe_2(SO_4)_3$ + 49 cc. H_2O + x cc. 1 M H_2T; t = 0°; (3) 1 cc. 3 N $Fe_2(SO_4)_3$ + 24 cc. H_2O + 25 cc. C_2H_5OH + x cc. 1 M H_3Ci; t = 30°; (4) 1 cc. 3 N $Fe_2(SO_4)_3$ + 24 cc. H_2O + 25 cc. C_2H_5OH + x cc. 1 M H_2T; t = 30°.

Results of *photometric measurements* are plotted in Fig. 3. The curves show the changes in the

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[18] C. Mayr and J. Fisch, *Z. anal. Chem.*, **76**, 418 (1929).

[18a] In order to distinguish between the two different complexes of the composition Fe_3Ta_2 we shall denote the one formed with Na_2T:Fe_3Ta_2 salt; and the complex formed with H_2T·/Fe_3Ta_2 acid. We shall distinguish between different citrate complexes, too, using a similar notation whenever required.

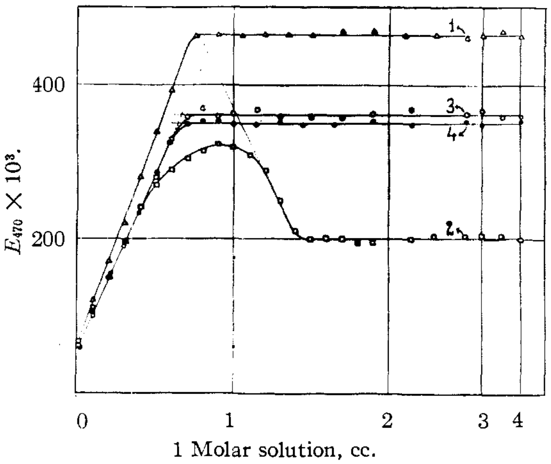


Fig. 3.—Extinction curves of aqueous solutions (filter 470; layer of 5 mm.; vol. of sol. 50 cc.): (1) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + *x* cc. 1 *M* Na_2T; (2) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + *x* cc. 1 *M* Na_3Ci; (3) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + *x* cc. 1 *M* H_2T; (4) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + *x* cc. 1 *M* H_3Ci.

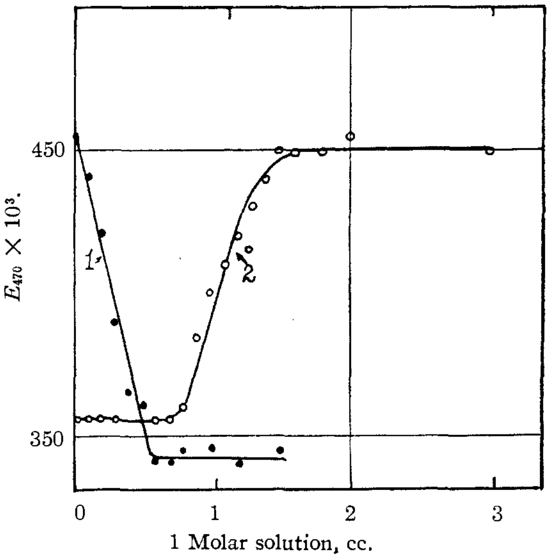


Fig. 4.—Extinction curves of aqueous solutions (filter 470; layer of 5 mm.; vol. of sol. 50 cc.): (1) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + 0.65 cc. 1 *M* Na_2T + *x* cc. 1 *M* H_2T; (2) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + 5 cc. 1 *M* H_2T + *x* cc. 1 *M* NaOH.

extinction (filter of 470 mμ) of aqueous ferric sulfate solutions, on addition of disodium tartrate, trisodium citrate and the *free* acids. The curves with disodium tartrate (1), tartaric acid (3) and citric acid (4) show one neat break each, at the upper limit of the extinction value. These breaks confirm the existence of the complexes $Fe_3Ta_{2\,\mathrm{acid}}$ and $Fe_3Cit_{2\,\mathrm{acid}}$, respectively. The curve with Na_3Ci (2) shows breaks corresponding to the compounds $Fe_3Cit_{2\,\mathrm{salt}}$ or Fe_5Cit_4 (?), and Fe_2Cit_3.

Some photometric experiments were made in order to investigate the relation between the various complexes and their stability. Results are plotted in Figs. 4 (tartrate) and 5 (citrate). As curve 1 of Fig. 4 shows, $Fe_3Ta_{2\,\mathrm{salt}}$ is transformed upon addition of tartaric acid into $Fe_3Ta_{2\,\mathrm{acid}}$. The extinction decreases linearly until the value of $Fe_3Ta_{3\,\mathrm{acid}}$ is reached. Hence, $Fe_3Ta_{2\,\mathrm{acid}}$ is considerably more stable than $Fe_3Ta_{2\,\mathrm{salt}}$.

It is worth while mentioning that the change in *p*H, parallel to the transformation of $Fe_3Ta_{2\,\mathrm{salt}}$ into $Fe_3Ta_{2\,\mathrm{acid}}$, was found to be very small: from 2.15 to 1.90.

As shown by curve 2 of Fig. 4, the extinction of solutions containing iron and an excess of tartaric acid remains first unchanged on adding sodium hydroxide; then, it gradually increases as more and more Fe_2Ta_3 is formed. Thus, this curve confirms photometrically the existence of the complex Fe_2Ta_3. (The shape of the curve, with the abrupt inflexion, may be due to the cubic dependence of the reaction on the concentration of disodium tartrate.)

Experiments similar to those in curve 1 could not be made with citrate, owing to the small difference between the extinctions of $Fe_3Cit_{2\,\mathrm{acid}}$ and $Fe_3Cit_{2\,\mathrm{salt}}$ (*cf.* Fig. 3, curves 2 and 4). Photometric measurements were carried out, however, with solutions containing iron and an excess of citric acid to which sodium hydroxide was added and the results are shown in Fig. 5. The curves obtained are analogous to the corresponding curve with tartrate (Fig. 4, curve 2), discussed above.

The existence of the complex Fe_2Ta_3 is also confirmed by *thermometric titrations*. The corresponding curve (2) is plotted in Fig. 6. Curve 1 of Fig. 6 shows an analogous thermometric titra-

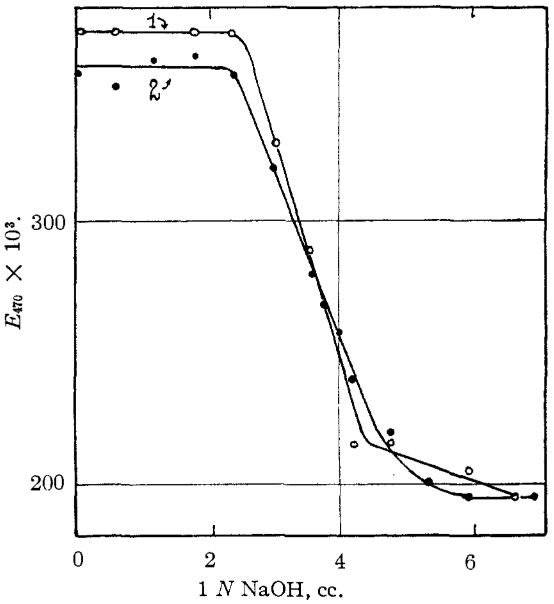


Fig. 5.—Thermometric titration curves: (1) 4 cc. 3 *N* $Fe_2(SO_4)_3$ + 196 cc. H_2O + *x* cc. 1 *M* Na_3Ci; (2) 4 cc. 3 *N* $Fe_2(SO_4)_3$ + 196 cc. H_2O + *x* cc. 1 *M* Na_2T.

tion of ferric sulfate with trisodium citrate. There are breaks at $3[Fe^{III}]:2[Cit]$ and $2[Fe^{III}]:3[Cit]$.

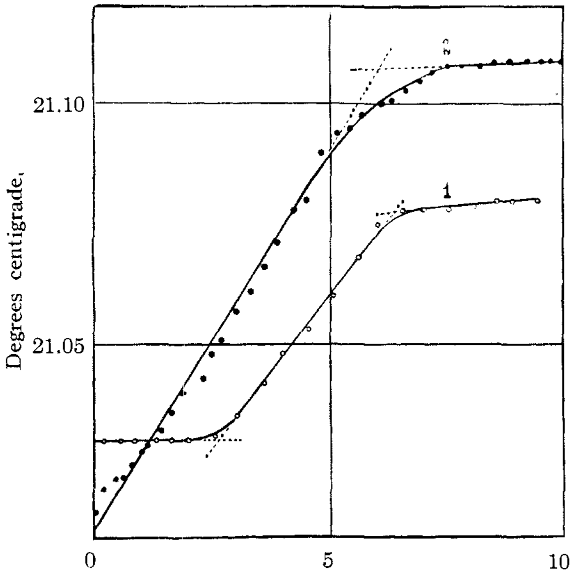


Fig. 6.—Extinction curves of aqueous solutions (filter 470; layer of 5 mm.; vol. of sol. 50 cc.): (1) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + 2 cc. 1 *M* H_3Ci + *x* cc. 1 *N* NaOH; (2) mixture of 1 cc. 3 *N* $Fe_2(SO_4)_3$ + 5 cc. 1 *M* H_3Ci + *x* cc. 1 *N* NaOH.

Potentiometric titration curves show *one* inflexion each, at the ratio $2[Fe^{III}]:3[Cit]$ and $2[Fe^{III}]:3[Ta]$, respectively. The results are plotted in Fig. 7.

It has been reported that ferric ion gives well-defined *polarographic* waves in alkaline tartrate and citrate solutions.[19] We have studied the shift of the half-wave potential with varying amounts of trisodium citrate and of free citric and tartaric acid. A rather irregular curve was obtained by plotting the logarithms of the trisodium citrate concentration against the shift of the half wave potential. In the case of free citric and tartaric acid the half wave potential could not be estimated as very large diffusion currents were obtained, probably because the hydrogen-ion discharge could not be separated from the ferric wave.

Discussion

The experimental results seem to indicate that *three* different kinds of ferric citrate and tartrate complexes may exist in *dilute solutions*. The structures, proposed below, are based on the ratio between iron and citrate (or tartrate) established by various measurements and on the behavior of the complexes. We assume that water molecules occupy those coördination positions of the central ferric ion which are not bound to groups of the

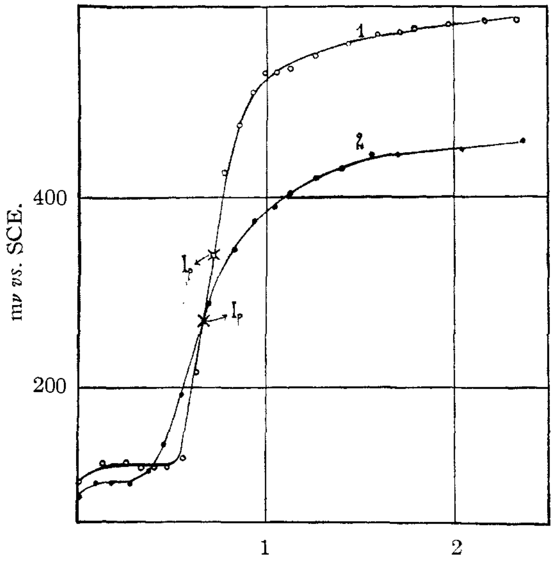
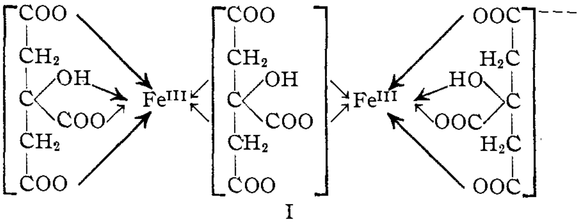


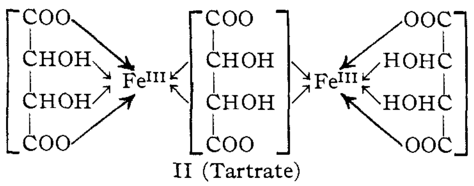
Fig. 7.—Potentiometric titration curves: (1) 1 cc. 1 *M* Na_3Ci + 49 cc. H_2O + *x* cc. 3 *N* $Fe_2(SO_4)_3$; (2) 1 cc. 1 *M* Na_2T + 24 cc. H_2O + 25 cc. C_2H_5OH + *x* cc. 3 *N* $Fe_2(SO_4)_3$.

organic radicals. It was supposed that the degree of dehydration of the iron nuclei depends on the stability of the chelate complex formed, and that in the most stable complexes, Fe_2Cit_3 and Fe_2Ta_3, all the coördination positions are occupied by citrate and tartrate radical, respectively.

The existence of these stable complexes, Fe_2Cit_3 and Fe_2Ta_3, formed in solutions containing *excess of trisodium citrate and disodium tartrate*, was confirmed by conductometric, photometric, calorimetric and potentiometric measurements. They do not show the usual reactions of the ferric ion (*e.g.* thiocyanate). Their solutions are of greenish color and it is of interest that the "green trisodium ferricitrate" $Na_3Fe_2Cit_3$, prepared by Belloni,[8] is *anhydrous*. The most simple formulas, consistent with all the experimental facts, are



I
(Citrate)



II (Tartrate)

The molar extinction of the citrate complex is much smaller than that of the corresponding tar-

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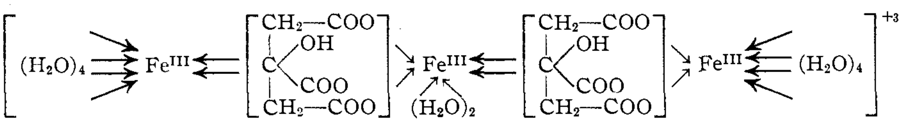
[19] I. M. Kolthoff and J. J. Lingane, "Polarography," New York, N. Y., 1941, p. 227.

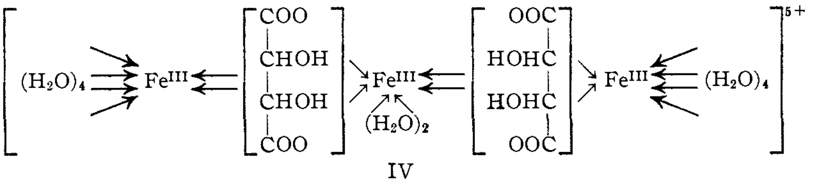
trate. This is probably due to the linkage between the central ferric ion and the third carboxylic group of the citrate radical.

Another type of complexes is apparently formed with disodium tartrate and trisodium citrate in solutions containing an *excess of iron.* The tartrate complex has the composition 3 Fe/2 Ta (= "$Fe_3Ta_{2\,\text{salt}}$"). The existence of an analogous $Fe_3Cit_{2\,\text{salt}}$ complex was confirmed by thermometric measurements and possibly also by photometric experiments: Both the tartrate and citrate complexes have probably similar molar extinctions (*cf.* Fig. 3, curves 1 and 2; extinction value for the citrate complex is extrapolated). These are much larger than those of $Fe_3Ta_{2\,\text{acid}}$ and $Fe_3Cit_{2\,\text{acid}}$, *complexes formed in solutions containing free citric and tartaric acid.* The stability of $Fe_3Ta_{2\,\text{salt}}$ and $Fe_3Cit_{2\,\text{salt}}$ (see Figs. 4 and 5) is much smaller than of $Fe_3Ta_{2\,\text{acid}}$ and $Fe_3Cit_{2\,\text{acid}}$. (The considerable stability of the latter is also shown by the neat breaks in photometric curves 3 and 4 of Fig. 3.) Notwithstanding this, the usual reactions of the ferric ion are obtained with all these complexes.

For $Fe_3Cit_{2\,\text{salt}}$ and $Fe_3Ta_{2\,\text{salt}}$, formed with *trisodium citrate and disodium tartrate,* we propose the formulas



III
(Citrate)



IV
(Tartrate)

These complexes should be hydrated. Actually, a highly hydrated compound of approximately the same composition as III, $Fe_3Ci_{2\frac{1}{2}}(OH)_2\cdot 8H_2O$, has been isolated and analyzed by Belloni.[8] (Conductometric experiments with trisodium citrate—shown in Fig. 1—suggest a compound $Fe_5Cit_{4\,\text{salt}}$; this, as well as $Fe_3Cit_{2\,\text{salt}}$ may be represented by the general formula $[Fe_nCi_{n-1}]^{3+}$ and they differ from each other only by the value of n[20].)

The complexes with the free acids, $Fe_3Cit_{2\,\text{acid}}$ and $Fe_3Ta_{2\,\text{acid}}$ have *equal molar extinctions.* Assuming that their configuration is identical and that the ferric nuclei are bound to similar groups, we propose the formulas V and VI.

The remarkable increase of conductivity (*cf.* Fig. 2), as compared with the calculated one (about 200%), which is observed during the formation of the complexes V and VI, suggests considerable dissociation of hydrogen ions.

Acknowledgment.—The authors wish to thank Mr. M. P. Seinfeld for carrying out the thermometric titrations reported in this paper.

Summary

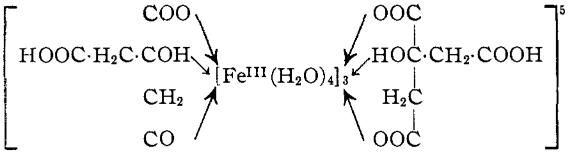
1. Ferric citrate and tartrate complexes, formed in dilute solutions, have been studied by photometric, conductometric, potentiometric, polarographic and calorimetric methods. The respective citrate and tartrate complexes are of analogous behavior.

2. Trisodium citrate and disodium tartrate form complexes, in which the molar ratio between iron and citrate (or tartrate) is 2:3. It is assumed that, in these complexes, the central ferric cations are *anhydrous*, *i.e.*, all their coördination valences are saturated with the chelate radicals.

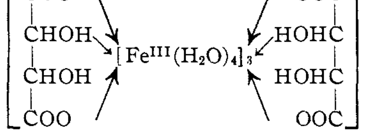
3. In solutions containing excess iron some less stable complexes are formed with trisodium citrate and disodium tartrate. In these complexes the molar ratio is $n[Fe^{III}]:(n-1)[\text{citrate}]$ and $3[Fe^{III}]:2[\text{tartrate}]$. Their ferric nuclei are supposed to be *hydrated.* They are easily transformed into the more stable complexes mentioned in paragraph 2 above, by addition of more citrate or tartrate.

4. *Free* citric and tartaric acid form complexes in which the molar ratio between ferric iron and organic radical is 3:2. The molar extinctions of both the citric and tartaric complexes are identical. In these complexes, too, the ferric nuclei are supposed to be *hydrated.*

5. For all complexes structural formulas are proposed.



V
(Citrate)



VI
(Tartrate)

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[20] "Ci" is use to denote the ion: $COOCH_2C(OH)COOCH_2$-COO^{---}.