A Study of the Ferric-Tartrate Complex in Alkaline Solution

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A STUDY OF THE FERRIC-TARTRATE COMPLEX IN
ALKALINE SOLUTION

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Senior Thesis
Western Michigan University
June 1965
Submitted to:
Mr. Raymond Janes
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INTRODUCTION

For a number of years, the study of the hydrodynamic behavior of cellulose has been limited by the lack of a solvent capable of dissolving this high polymer without degrading its degree of polymerization. The consequence of the degradation is the marked change in the properties of the cellulose molecule in solution. Investigations to improve this problem have generally taken two directions.

The first involves the substitution of derivatives on the reactive alcoholic sites of the molecule (substitution method). This allows the molecule to be dissolved, in appropriate solvents, without degradation during dissolution.

The second involves the search for compounds capable of solvating the unsubstituted cellulose molecule without reducing its degree of polymerization (direct solvation method). The copper-based cuprammonium hydroxide and cupriethylenediamine coordinating agents are perhaps the best examples of such compounds.

Each of these methods is not without limitations. Common to both methods is the problem of reduction of the degree of polymerization. It has been found that even the mildest conditions in substitution of derivatives causes some degradation of the cellulose molecule. Furthermore, nearly all reagents capable of dissolving cellulose directly are degrading agents. Exceptions to this are cuprammonium hydroxide and cupriethylenediamine. However, the degree of polymerization is severely reduced in these alkaline solutions by the action of atmospheric oxygen, especially with cuprammonium hydroxide. With careful exclusion of atmospheric oxygen from these solutions,
consistent results can be obtained. This explains the wide application of these reagents in cellulose analysis.

A problem associated only with the substitution method is the indirect relation of the substituted derivative to the original cellulose. Furthermore, deviation in the degree of substitution does not permit comparison of substituted samples.

A problem associated with copper-based solvents of the direct solvation method, in addition to their degradation by oxygen, is their intense blue color. This limits the use of spectrophotometric methods of analysis. Furthermore, it is difficult to reproduce the component composition in preparations of the copper-based solvents.

In the early 1950's, Jayme(1) began research to solve the problems which had reduced the value of the copper-based solvents. This research included substitution of other metal ions for copper in the copper-based solvents, and the investigation of other coordination compounds. Two new cellulose solvents were the result of this research; the cadmium-ethylenediamine and the ferric-tartrate complexes. Of these, the ferric-tartrate complex in highly alkaline solution is the most important. Not only is the cellulose dissolved without degradation, but its solutions are stable to atmospheric oxygen. Subsequent studies of the ferric-tartrate solvent have been directed mainly toward the determination of the optimum composition of the complex for cellulose dissolution. In addition, the properties of the solutions with these compositions were studied(2-15).

Some work has also been done to determine the structure of the ferric-tartrate complex in aqueous alkaline solutions, and the mechanism by which this reagent dissolves cellulose. This work has been sketchy
and incomplete, with conclusions being drawn without the support of adequate experimental evidence.

It is the aim of this author to determine the structure of the ferric-tartrate complex in a solution 2.0 M in excess sodium hydroxide and also to determine what effect the total molality of iron (III) and tartrate have on the complex. Such information is necessary for an understanding of the mechanism of cellulose dissolution.
LITERATURE SURVEY

The Ferric-Tartrate Complex

Investigations of the ferric-tartrate complex in alkaline solutions have been limited. Frankel was one of the first to study its behavior in aqueous alkaline solution. He proposed a structure in which three tartrate anions were coordinated with a central ferric ion. He speculated that the six coordinating sites of the iron were satisfied by coordination with the hydroxyl groups of the tartrate. The driving force behind this coordination being the strong alkali which strips a proton from one of the hydroxyl groups, forming a diolate anion. This structure was suggested on the basis of color changes in the solution as the molar ratios of iron, tartrate and alkali were changed. At a ratio of \( \text{NaOH}/\text{Fe}^{3+} = 3 \), a color change from brown to yellow-green occurred. The suggested reaction was:

\[
3C_2O_2H_4(CO_2Na)_2 + \text{Fe(NO}_3)_3 + 3\text{NaOH} \rightarrow \text{C}_6\text{H}_6\text{Fe(CO}_2)_6\text{Na}_6 + 3\text{H}_2\text{O}
\]

Since the color change was only slightly dependent on total iron concentration, the 1:3, ferric:tartrate structure was assumed.

![Figure 1](image)

Franke's model of the 1:3, ferric:tartrate complex
According to Jayme (1), this complex (Figure 1) forms the dark-green cellulose solvent when dissolved in a two to four normal excess of alkali. Jayme assumes that the excess alkali does not change the structure of the complex.

Jayme and Bergmann (10) report another ferric-tartrate complex which has greater solvating power than the 1:3 complex. This solvent is brown in color and has a molar composition of 1:1, ferric:tartrate, in an excess of sodium hydroxide. After the initial formation of the complex however, the complex stability is not greatly affected by a lowering of the hydroxide ion concentration. Jayme suggests a structure in which the two hydroxyl oxygens and a carboxylate oxygen of a single tartrate are coordinated to a ferric ion. The remaining coordinating sites of the iron are hydrated. No supporting evidence for this structure was given. Franke (16) has indicated a similar structure, which Jayme undoubtedly assumed to be the correct structure. Special reference was given to the light sensitivity of this complex. (17)

\[
\begin{align*}
\text{[} & \begin{array}{c}
\text{Fe} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array} \\
\text{Na}^+ \\
\text{[} & \begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{O}
\end{array} \\
\text{[} & \begin{array}{c}
\text{H}_2\text{O}
\end{array}
\end{align*}
\]

Figure 2
Franke's model of the 1:1, ferric:tartrate complex
Still another structure was proposed by Pyatnitskii, who found the composition of the ferric-tartrate complex to be 1:2 in aqueous alkaline solutions having a pH above 10. Although no clue was given as to which hydroxyl and/or carboxylate groups participated in the coordination, it was proposed that each tartrate ion forms one five-membered ring with the ferric ion. The composition and relative degrees of complexation were determined from equilibrium relations in the distribution of ferric ions between a quinolinol complex in chloroform and the alkaline solution.

A more recent investigation has been done by Bayer in which the method of continuous variation was used to study the complex. Using optical rotation and optical absorbance measurements at 546 μm and 440 μm respectively, the optimum ferric:tartrate mole ratio was found to be 1:4.5 in a 2 M excess of sodium hydroxide. No structure was proposed.

Studies of the ferric-tartrate complex in aqueous solutions, indicate the importance of the following experimental conditions on the type of complex formed:

1. pH of the solution.
2. source of the tartrate ligand (free acid or tartrate salt)
3. molar composition.

Therefore, to determine the structure of the cellulose solvent, it is necessary to prepare the complex by the same method as is used in cellulose studies.
Preparation of the Ferric-Tartrate Cellulose Solvent

Two methods are currently used to prepare the ferric-tartrate cellulose solvent. The first is a two step method developed by Jayme and Lang.\(^{(12)}\) Equimolar quantities of ferric nitrate and sodium tartrate are mixed, resulting in the formation of an insoluble brown precipitate. The precipitate, which is assumed to be a 1:1 complex of ferric-tartrate, is isolated and washed. The solid is then reacted with concentrated alkali and more sodium tartrate to form the 1:3 complex. All the above operations must be done in light protected equipment or in a darkroom because of the extreme sensitivity to light of the intermediate 1:1 complex.

The second method of preparation, often referred to as the direct preparation method, was developed by Valtasaari.\(^{(15)}\) Sufficient sodium hydroxide, to prepare the complex and provide the required excess alkali, is added with cooling to proper amounts of ferric nitrate and sodium tartrate. Bayer\(^{(19)}\) recommends the substitution of tartaric acid for the sodium tartrate because of its greater solubility. These operations must also be done in light protected equipment or in a darkroom. The stability of the complex is maintained by cold storage.

Solvents prepared by the Jayme and Lang method\(^{(12)}\) have indeterminate ferric and tartrate ion concentrations due to the washing of the intermediate product. Jedlinska and Nadziakiewicz\(^{(13)}\) report that the Valtasaari solvent did not dissolve all cellulose samples, but should be used where applicable, since it is more readily prepared.
EXPERIMENTAL

The experimental program was designed to determine: (1) the structure of the ferric-tartrate complex in a solution 2.0 M in excess sodium hydroxide; and (2) the effect of the total molality of iron (III) and tartrate ligand on the stability of the complex.

The spectrum of a ferric-tartrate solution, 0.5 M and 1.5 M with respect to iron (III) and tartrate, was studied in the wavelength interval, 200 μm to 2000 μm, to determine whether optical absorption peaks were associated with the complex. Spectrophotometric measurements are frequently used as an additive property in continuous variation studies of complexes. In fact, a continuous variation study using spectrophotometric measurements was planned, but could not be carried out due to the extreme optical density of the absorption peak. The extreme optical density prevented quantitative measurements from being made.

Magnetic measurements of the complex were made to determine the number of unpaired electrons in the iron (III) ion. This information was used to determine whether certain types of bridged complex types were present.

The stability of the complex was studied by preparing ferric-tartrate solutions having the same mole ratio of iron (III) and tartrate, and the same sodium hydroxide concentration, but different total molalities of iron (III) and tartrate ligand.

Experimental Procedures and Calculations

Preparation of Ferric-Tartrate Solutions

Solutions having a mole ratio of 1:3 with respect to iron (III)
and tartrate, and 2.0 M with respect to excess sodium hydroxide, were prepared according to the method of Valtasaari. Reagent grade ferric nitrate (Fe(NO₃)₃ • 9H₂O), sodium hydroxide (50% by weight solution) and L(+) tartaric acid were used. A stock solution of ferric nitrate was made, which on analysis, by a modification of a standard method, was found to be 2.198 M with respect to iron (III). The 50% solution of sodium hydroxide contained 0.7737 grams reagent per milliliter.

A solution having a mole ratio of 1:3, ferric:tartrate, and a total molality of 2.0 M with respect to iron (III) and tartrate was prepared in a light-protected reaction assembly. The special assembly was necessary to protect certain light sensitive species formed during the preparation. The reaction assembly consisted of a 200 ml., three-necked, round bottom flask equipped with a glass stirring rod, a thermometer, and a three-way buret fitted with a plastic stopper. The entire assembly was painted black except for the thermometer and the buret above the stopcock. The three-way buret allowed sodium hydroxide to be added to the reaction flask without excessive contamination by carbon dioxide from the air.

L(+) tartaric acid (22.5135 grams; 0.15 mole) was weighed into a plastic beaker and ferric nitrate (22.75 ml.; 0.05 mole) stock solution added. This solution was transferred to the light-protected reaction flask with as small a volume of water as necessary for complete transfer of reagents. The reaction flask was cooled to 5° and sodium hydroxide solution (33.66 ml.; 1.5 moles) slowly added with stirring. The temperature was kept below 15° at all times.
This amount of sodium hydroxide provided for the neutralization of three hydrogen ions for each tartaric acid molecule plus enough for a solution 2.0 M in sodium hydroxide. The resulting clear green solution was transferred carefully from the reaction flask to a 100 ml. volumetric flask, using a small volume of water to rinse the reaction flask. The solution was thermostated at 20.0 ± 0.2° in a temperature bath and diluted to the correct volume. The solution was thoroughly mixed and transferred to a polyethylene flask for storage at 5°.

Solutions of 1:3, ferric:tartrate, having a total molality of 1.0 M, 0.5 M, 0.25 M, 0.125 M and 0.0625 M with respect to iron (III) and tartrate ligand were prepared by diluting 25 ml. aliquots of the previously prepared solution to 50 ml. in a volumetric flask.

Blank solutions corresponding to the 1:3, ferric:tartrate solutions above were prepared. These solutions contained no iron (III) but had the same concentration of tartrate and sodium hydroxide.

A blank solution of 1:3 mole ratio iron (III) to tartaric acid and containing no sodium hydroxide was also prepared. This solution was prepared by adding 5.69 ml. (0.0125 mole) of iron (III) solution to 5.6284 grams (0.0375 mole) of tartaric acid and diluting at 20 ± 0.2° to 25 ml. in a volumetric flask.

Spectrophotometric Measurements

The spectrum of a 2.0 M solution having a mole ratio of 1:3, ferric:tartrate, was studied in the wave length interval, 200 µm to 2000 µm. A matched pair of 1 cm. quartz rectangular cells with matching quartz inserts were used. The quartz inserts were used to
obtain different path widths. A variable slit width was used.

A Beckman DU spectrophotometer was used to obtain measurements from 700 μ to 2000 μ. A light path of 1 cm. was used. A Beckman DB recording spectrophotometer was used to obtain measurements from 480 μ to 700 μ. A light path of 0.11 cm. was used in this wavelength interval. A qualitative examination of the spectrum from 200 μ to 480 μ was made by forming a thin film-like layer of the solution between one wall of the 1 cm. quartz cell and the quartz insert. Measurements in this case were made on the Beckman DB also. A quartz cell and insert providing a 0.01 cm. path length was used. This cell was the property of The Upjohn Company and the measurements were made on a Cary 14 recording spectrophotometer at The Upjohn Company.

**Magnetic Measurements and Calculations**

Magnetic measurements were made with a Gouy magnetic balance. The apparatus consisted of a glass sample tube suspended from the beam of an analytical balance by means of a nylon line, and a permanent magnet having a constant field intensity of approximately 10,000 gauss.

Magnetic measurements included: finding the change in weight of a sample on application of the magnetic field; the weight of the sample; its height in the sample tube; and the calibration of the Gouy apparatus. The Gouy apparatus was calibrated by means of an aqueous nickel chloride solution. The susceptibility per gram, \( \chi_s \), of aqueous nickel chloride solutions has been given as:
\[ 10^6 \chi_g = (10,030/T) \left( \frac{y}{100} \right) - 0.72 \left( 1 - \frac{y}{100} \right) \]

where \( y \) is the weight percent of nickel chloride in the solution, and \( T \) is the absolute temperature. The accuracy is about 0.5 percent. The percent nickel chloride was determined by electrodeposition of nickel from the solution.

The susceptibility per gram, \( \chi_g' \), of iron (III) in a solution is given by the equation:

\[ (\chi_g') = (k)(h)(\Delta m)/m - \chi_1 \]

where \( k \) is a constant dependent on the dimensions and volume of the sample tube, and the magnetic field intensity; \( h \) is the height in cm. of the sample in the sample tube; \( \Delta m \) is the change in weight of the sample in grams caused by the application of the magnetic field; \( m \) is the weight of the sample in grams; \( f \) is the weight fraction of iron (III) in the sample; and \( \chi_1 \) is the susceptibility of a blank solution containing only ligand. Although the diamagnetic susceptibility of the ligand is small, a large number of ligand atoms in a complex may form an appreciable portion of the susceptibility of the complex. This is especially true where large organic molecules form the ligand.

The susceptibility per gram atom of iron (III), \( \chi_A' \), is given by

\[ \chi_A' = 55.85 \chi_g' \]

where 55.85 is the atomic weight of iron. The prime indicates that the susceptibility has been corrected for the presence of diamagnetic components. The magnetic moment of the iron (III) ion, \( u_{\text{eff}}' \), is given by the equation:

\[ u_{\text{eff}}' = 2.84(\chi_A' T)^{\frac{1}{2}} \]

In this equation, 2.84 = \((NB^2/3k)^{\frac{1}{2}}\), where \( N \) is Avogadro's number;
B is the Bohr Magneton \((0.927 \times 10^{-20} \text{erg/gauss})\); \(k\) is Boltzmann's constant; and \(T\) is the absolute temperature.

The magnetic moment of the ion is in turn used to calculate the number of unpaired electrons, \(n\), in the unfilled atomic shell of the atom, by the relation:

\[
 u_{\text{eff}} = \left( n(n+2) \right)^{\frac{1}{2}}.
\]
RESULTS AND DISCUSSION

Spectrophotometric Results

The spectrum and color of the ferric-tartrate complex in 2.0 M excess sodium hydroxide are somewhat irregular. No characteristic absorption bands appear in the 500 µm to 2000 µm region of the spectrum, as is the case with most iron (III) complexes. Also, most ferric complexes are brown to red in color, whereas the ferric-tartrate complex is brilliant green. These results apparently indicate there is something unique about the bonding in the complex.

A very strong absorption edge begins at 440 µm. This absorption maxima is so strong that it could not be kept on scale in a cell having a path length of 0.01 cm. Measurements using a film-like layer of the solution indicate an absorption maxima, due to the complex, at 280 µm. These measurements were only qualitative, however, being obtained by pressing a drop of solution between the cell wall of a rectangular quartz cell and a cell insert. This absorption maxima is an additive property of the complex, which could be used in continuous variation studies if a quantitative method of measurement is devised.

Magnetic Results

The molar susceptibility 1.458 x 10^{-2} cgs units at 25° observed for the iron (III) ion in 1:3, ferric:tartrate, corresponds to a magnetic moments of 5.93 Bohr Magnetons. This value corresponds to the theoretical moment calculated for 5 unpaired d electrons. The ferric-tartrate complex in 2.0 M excess sodium hydroxide is, therefore, an outer orbital complex having six sp^3d^2 bonds with
the 3d shell in iron (III) half filled. This result disallows the existence of olated and oxolated complex species in which the iron (III) atoms are linked through bridging OH groups. Olation and oxolation (26) would bring the iron (III) atoms close enough to give rise to exchange effects between the anti-parallel spins of unpaired electrons and make the complex species nearly diamagnetic.

**Stability Results**

Solutions of 1:3, ferric:tartrate having a total molality of 2.0 M, 1.0 M, 0.5 M, 0.25 M, 0.125 M and 0.0625 M with respect to iron (III) and tartrate ligand were stored in polyethylene bottles and refrigerated at 5°C. Except for the 2.0 M and 1.0 M samples, all solutions had precipitated ferric hydroxide within one week. The solutions having a total molality of 2.0 M and 1.0 M were stable over the entire test period (3 months). These results indicate that a 1:3, ferric:tartrate, cellulose solvent must have a total molality greater than 1.0 M. The instability of solutions having a total molality less than 1.0 M suggests a polymeric type complex structure which becomes unstable on dilution.
SUMMARY

A study was made of the ferric-tartrate cellulose solvent to determine the structure of this complex and what effect the total molality of iron (III) and tartrate ligand have on the coordination.

The spectrum of a 1:3 ferric:tartrate, solution having a total molality of 2.0 M and a 2.0 M excess of sodium hydroxide was studied in the wavelength interval 200 mu to 2000 mu. No absorption maxima were noted beyond 500 mu. A strong absorption edge appears at 440 mu, but is so strong that it cannot be kept on scale in cells having a path length of only 0.01 cm. A qualitative measurement of the spectrum below 440 mu indicates an absorption maxima at 280 mu.

Solutions of 1:3, ferric:tartrate, 2.0 M with respect to excess sodium hydroxide, were prepared which had total molalities of 2.0 M, 1.0 M, 0.5 M, 0.25 M, 0.125 M and 0.0625 M with respect to iron (III) and tartrate ligand. Except for the 2.0 M and 1.0 M solutions, all were unstable, precipitating ferric hydroxide within one week.

Magnetic susceptibility measurements were made on ferric-tartrate solutions having a mole ratio of 1:3, ferric:tartrate, and a 2.0 M excess of sodium hydroxide. An outer orbital complex having five unpaired electrons was shown, indicating the absence of olated and/or oxolated complex types.
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