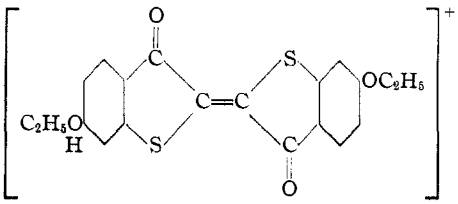
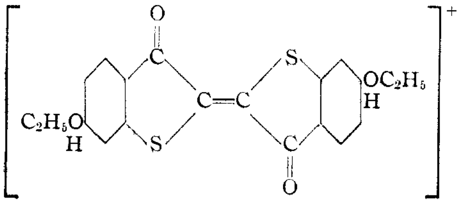


III



IV

when going from solutions in organic solvents to solutions in sulfuric acid, since no additional chelate rings are formed as in the case of structure II above. It is possible, as an alternative, that the strong resonance effect[9] of the ethoxy group in the 6,6′-positions changes the relative basicities of the carbonyl oxygen and the sulfur atoms to such an extent that the structure of these dyes in sulfuric acid solution differs from the dyes of Type I (structure II, above) mainly in the distribution of the electron cloud and, possibly, in the interatomic distances in the chelate rings. This hypothesis is consistent with the observed bathochromic shift and the absence of *cis*- and *trans*-isomers, but it is questionable whether structural differences of this kind will be sufficient to explain the fundamentally different absorption spectra obtained.

Since Vat Scarlet G is a hemi-thioindigoid dye, its spectrum was expected to be considerably different from the other dyes investigated. Bis-4,5-benzothioindigo, however, also shows a spectral absorption curve that is not similar to any of the other thioindigo dyes and there seems to be no adequate explanation available for this observation. The first absorption band in the case of either of these dyes in sulfuric acid solution is at a considerably lower frequency than when dissolved in organic solvents, indicating complex formation with the solvent, perhaps by the formation of one chelated ring (or possibly two in the case of bis-4,5-benzothioindigo), similar to that suggested above for thioindigo.

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[9] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 231.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A Spectrophotometric Study of the Hydrolysis of Iron(III) Ion[1]

BY THOMAS H. SIDDALL, III, AND W. C. VOSBURGH

A method for the determination of the first hydrolysis constant of iron(III) ion has been devised involving measurements of the optical densities of a series of solutions of constant ionic strength, constant total iron concentration, and known variable acidity. Several series of measurements were made at temperatures from 24 to 30° from which the value of the hydrolysis constant at 25° and zero ionic strength was found to be 0.0065 ± 0.0004.

The first hydrolysis constant of the iron(III) ion, has been determined[2–6] by several methods, with results from 2.5 to 11 $\times 10^{-3}$ at 25° and similar lack of agreement at other temperatures. Bray and Hershey[7] calculated $(6.0 \pm 0.5) \times 10^{-3}$ at 25° from the equilibrium measurements of Popoff, Fleharty and Hanson[8] and Noyes and Brann.[9] The two values in best agreement are those of Bray and Hershey and Olson and Simonson if the latter is extrapolated to zero ionic strength. Extrapolation by the method described below gives 5.4×10^{-3}.

In the present investigation the value 6.5×10^{-3} was found by a spectrophotometric method somewhat different from that of Olson and Simonson.

Experimental

Materials and Apparatus.—Iron(III) perchlorate obtained from the G. Frederick Smith Chemical Company was used. For one series of measurements this material was recrystallized as a check on purity.

Standard perchloric acid solutions were prepared from reagent grade acid and standardized against standard sodium hydroxide solutions.

Sodium perchlorate solutions were made from standard perchloric acid and sodium hydroxide solutions. The perchloric acid and sodium perchlorate solutions gave negative tests for chloride and iron(III) ions.

The water used was redistilled from alkaline permanganate in an all-glass still. Iron(III) perchlorate solutions made from the ordinary distilled water available at the time had appreciably higher optical densities at wave length 340 mμ than solutions of the same concentration and acidity made from redistilled water. However, solutions prepared from water redistilled a second time did not differ significantly from solutions prepared from once redistilled water.

Optical density measurements were made by means of a model DU Beckman spectrophotometer. Most of the measurements were made in 10-cm. corex cells; but some were made in 1-cm. quartz cells. Both sets of cells were calibrated. It was found that the measured optical density of iron(III) perchlorate solutions was independent of the slit width in the spectral regions used. There was no provision for automatic temperature control. Considerable care was taken to bring each set of solutions to be measured to room temperature. Just previous to placing a solution in the cell for measurement its temperature was measured and adjusted if necessary to the temperature of the series. The filling of the cells and the measurement were carried out rapidly, requiring only 30 seconds. No changes were observed over an additional 30-second period, and it is believed that errors attributable to temperature differences were not significant.

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[1] Thesis submitted by Thomas H. Siddall, III, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

[2] Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

[3] Brönsted and Volqvartz, *ibid.*, **134**, 97 (1928).

[4] Lamb and Jacques, THIS JOURNAL, **60**, 967, 1215 (1938).

[5] Lindstrand, *Svensk Kem. Tid.*, **56**, 251 (1944).

[6] Olson and Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

[7] Bray and Hershey, THIS JOURNAL, **56**, 1889 (1934).

[8] Popoff, Fleharty and Hanson, *ibid.*, **53**, 1643 (1931); Fleharty, *ibid.*, **55**, 2646 (1933).

[9] Noyes and Brann, *ibid.*, **34**, 1016 (1912).

Absorption Spectrum.—As an aid in choosing or developing a method for the determination of the hydrolysis constant, density measurements were made on solutions containing 1.5 and 4.5 × 10^{-4} *M* iron(III) perchlorate and varying perchloric acid over the range 220 to 350 mμ. In agreement with Olson and Simonson an isosbestic point was observed at 272 mμ; the observed point was at 273 ± 1 mμ with a correction of −0.5 mμ. There was evidence of a second isosbestic point between 220 and 230 mμ, near the end of the range of the instrument. The existence of the isosbestic points makes it probable that there are only two absorbing species under the conditions of the experiments, namely, iron(III) ion and its first hydrolysis product. However, a second hydrolysis product could be present if its absorption spectrum were near enough like that of the first.

The curve for a solution 4.5 × 10^{-4} *M* in iron (III) perchlorate and 1.1 × 10^{-3} *M* in perchloric acid did not pass through the isosbestic point for that total iron concentration, but above it. When prepared, the solution appeared no different from the others, but after three days a precipitate appeared. A solution with 2 × 10^{-3} *M* acid remained clear.

The optical density of a solution 1.25 *M* in perchloric acid and 2 × 10^{-4} *M* in iron(III) perchlorate was very small in the range 340–355 mμ. With allowance for some hydrolysis product, the extinction coefficient of the iron(III) ion was estimated as less than unity while that of the hydrolysis product is shown later to be more than 500 times as large.

Dilution of Stock Solutions.—Lamb and Jacques found it necessary to prepare their dilute iron(III) chloride solutions directly from the solid. Their results were not satisfactory when a stock solution was diluted. Olson and Simonson prepared solutions by dilution of a stock solution, and made their measurements immediately. They were aware that changes took place in the dilute solutions on standing.

Some experiments were made to show which technique is the better. A 0.339 *M* iron(III) perchlorate solution containing some perchloric acid was diluted a thousand-fold with inclusion of enough additional perchloric acid to make the acid concentration 5 × 10^{-3} *M*. The optical density was measured at 272 mμ in a 1-cm. cell immediately and also after a week, giving 0.508 and 0.489, respectively. From this the extinction coefficient at the isosbestic point is 1.45 × 10^3. Two other solutions 0.170 *M* in iron(III) perchlorate and 0.114 and 0.005 *M* in acid, respectively, were diluted, after standing a week, to the same final concentrations of salt and acid, and measured frequently for nine days. The optical density at 272 mμ decreased about 2% within 5 to 10 hours and was constant thereafter. The optical density at 340 mμ decreased from the initial values 0.218 and 0.207 to 0.198 and 0.195, respectively, after 9 days, for the two solutions. There was no sign of precipitation.

While solutions prepared by dilution of a stock solution change, solutions 10^{-4} to 10^{-3} *M* prepared directly from the solid do not. A solution was prepared by the dissolving of 0.2 g. of iron(III) perchlorate in a liter of 0.0025 *M* perchloric acid solution. Its optical density at 272 mμ was measured occasionally for 7 days and found constant from the beginning at 0.683 ± 0.002. The change in solutions prepared by dilution cannot be ascribed to a slow hydrolysis. Accordingly most of the solutions for the more important experiments were made directly from the solid. When made by dilution enough time was allowed for the attainment of equilibrium.

Method.—The method used was based on the observation that in the spectral region 340 to 355 mμ the extinction coefficient of iron(III) ion is negligible compared to that of the first hydrolysis product. If it is assumed that the only significant reaction is

$$Fe^{+3} + H_2O \rightleftharpoons FeOH^{+2} + H^+$$

the condition for equilibrium may be written

$$[FeOH^{+2}][H^+] = k[Fe^{+3}] \qquad (1)$$

where brackets indicate concentrations, and *k* is constant at constant ionic strength. Let C_{Fe} represent the total iron concentration, *d* the optical density for 1 cm. light path and ε the extinction coefficient of $FeOH^{+2}$. Then, since $d = \epsilon[FeOH^{+2}]$ the above equation can be rearranged to give

$$1/d = 1/C_{Fe}\epsilon + (1/C_{Fe}\epsilon k)[H^+] \qquad (2)$$

If the optical densities of a series of solutions of constant total iron and ionic strength and varying acidity are measured and 1/*d* is plotted against the hydrogen ion concentration, the points should lie on a straight line. Division of the intercept of this line on the *Y*-axis by the slope should give *k*. The concentration C_{Fe} needs to be known only accurately enough for the calculation of the ionic strength.

A stock solution was prepared containing 0.3 g. of iron(III) perchlorate in a liter of 0.0025 *M* perchloric acid. The iron perchlorate contained acid, and its composition was estimated by analysis of a more concentrated solution to which no acid was added. The acid concentration in the solution analyzed was 0.673 times the total iron(III) concentration. The iron(III) content of the stock solution was determined by measurement of the optical density at 272 mμ, and since this was found to be 0.880 in a 1-cm. cell, the total iron concentration was 6.1 × 10^{-4} *M*. The extra acid introduced with the salt was therefore taken to be 4 × 10^{-4} *M*. This acid was only a small fraction of the total acid in the more important solutions.

The stock solution was diluted to four times its volume with addition of varying known quantities of acid and sodium perchlorate to make the final solutions. The concentrations of the total added acid varied from 0.95 × 10^{-3} to 14.75 × 10^{-3} *M*, but the ionic strength was kept constant at 0.0166 *M* by inclusion of sodium perchlorate. It can be estimated that the acid liberated in the hydrolysis was less than 1% of the total acid and negligible in the seven solutions of highest acidity, but appreciable in the solutions of lowest acidity.

The optical densities were measured in 10-cm. cells at 26.5°. The values of 1/*d* (with *d* calculated for a 1 cm. cell) were plotted against the total added acid to give line 1 of Fig. 1.

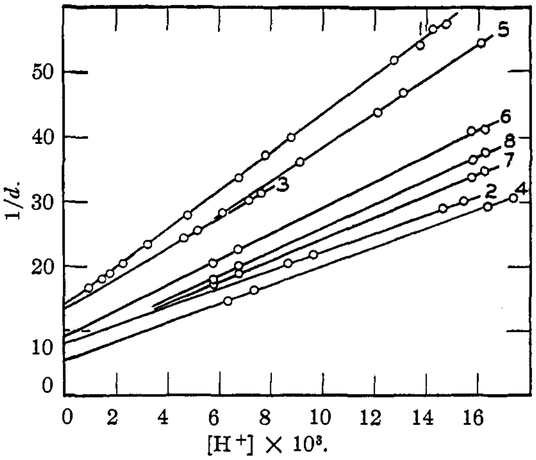

Fig. 1.—Reciprocal of optical density plotted against total perchloric acid concentration at constant total iron concentration and ionic strength.

All twelve points were found by the method of least squares to lie on a straight line with a mean deviation of 0.5%. The seven points of highest acid concentration lie on a straight line with 0.8% mean deviation. The points for the lower acidities would be expected to lie above the line. That they do not may be partly the result of errors, but is probably largely the result of the compensating effects of the acid from the hydrolysis and a little second hydrolysis product.

From the slope and intercept of the line representing the points of highest acidity *k* was calculated to be 4.7 × 10^{-3} at 26.5° for an ionic strength of 0.00166.

This determination was repeated at other temperatures and ionic strengths with the results shown in lines 2 to 8 of

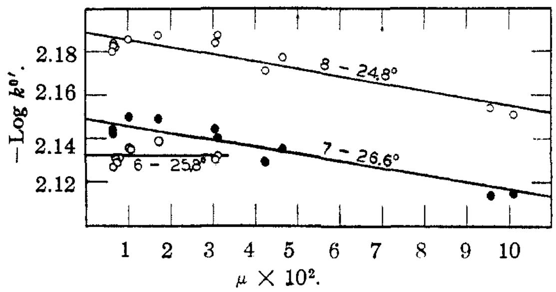

Fig. 2.—Extrapolation to zero ionic strength; left side of Equation 3 ($\log k^{0\prime}$) plotted against ionic strength.

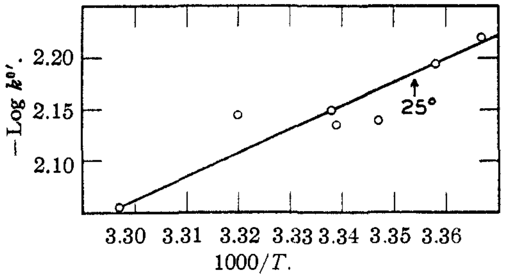

Fig. 3.—Variation of equilibrium constant with temperature from 24 to 30°.

Fig. 1. The values of k calculated from these data are given below in Table I. The respective experiment numbers in the table are the same as the line numbers in Fig. 1. Recrystallized iron(III) perchlorate was used in Experiment 4. In Fig. 3 above the value from this experiment is the farthest to the right and is seen to agree with the others as well as can be expected.

TABLE I

SUMMARY OF DATA

Expt.	$\mu \times 10^2$	λ	T, °C.	$1/C_{A}\epsilon$	fd_i	ϵ/ϵ_i	$k \times 10^3$	$k^\circ \times 10^3$
1	1.66	355	26.5	14.02	0.220	0.324	4.72	7.33
2	1.66	340	30.3	8.09	.211	.586	5.66	8.86
3	1.66	340	30.3	13.33	.127	.591	5.64	8.81
4	1.86	340	24.0	5.44	.290	.632	3.74	6.03
5	1.66	340	28.2	12.16	...	...	4.61	7.01
6	1.73	345	25.8	9.14	.220	.497	4.56	7.26
7	1.73	340	26.6	7.49	.214	.624	4.46	7.10
8	1.73	340	24.8	7.45	.214	.627	4.02	6.40

In the sixth column is given the optical density of the stock solution at 273 mμ, d_i, multiplied by the dilution factor, f. The values of ϵ/ϵ_i in the seventh column are the reciprocals of the products of the intercepts in the fifth and the values of fd_i in the sixth. Since ϵ_i is 1.45×10^3, ϵ is 470 at 355 mμ and 890 at 340 mμ.

In order to be able to calculate the equilibrium constant at zero ionic strength a series of experiments at varying ionic strength was carried out. Four solutions at a single ionic strength, 1.73×10^{-2}, and varying acidity and with a total iron concentration of 1.53×10^{-4} M were prepared. A number of other solutions of constant acidity, 5.73×10^{-3} M, and with the same total iron, but varying ionic strength, were prepared at the same time, and the optical densities were measured at wave length 345 mμ and 25.8°.

Data for the four solutions of varying acidity are shown as line 6 in Fig. 1. From the least-squares equation for this line the value of the intercept at zero acidity, $1/C_{Fe}\epsilon$, was found. From Equation 1 and the fact that $[Fe^{+3}]$ can be set equal to $C_{Fe} - d/\epsilon$ it can be shown that

$$k = [H^+]d/(C_{Fe}\epsilon - d)$$

Accordingly, values of k for the different ionic strengths were calculated from the reciprocal of the intercept, the acid concentrations, and the measured optical densities of the solutions. A similar series of solutions was made and measured at wave length 340 mμ and at two temperatures, 26.6 and 24.8° giving lines 7 and 8 of Fig. 1.

Extrapolation to zero ionic strength for both series was done with the help of the Debye–Hückel equation. If k° represents the equilibrium constant at zero ionic strength, and the temperature is 25°

$$\log k + \frac{2.04\sqrt{\mu}}{1 + 2.5\sqrt{\mu}} = \log k^\circ + B\mu = \log k^{\circ\prime} \quad (3)$$

A plot of the left-hand side of the equation against μ for the two series of measurements was found to give straight lines within the limits of error of the experiments, as shown in Fig. 2. Up to an ionic strength of 0.03 lines parallel to the x-axis would fit the data as well and B could be set equal to zero.

A value for k° was accordingly calculated for each of the k values of Table I, with neglect of the $B\mu$ term of Equation 3 and with the appropriate small alteration of the second term for temperatures 28 and 30°. The values obtained are given in the last column of Table I. A plot of $-\log k^\circ$ against $1/T$ is shown in Fig. 3, according to which the best value of k° at 25° is 0.0065, with an uncertainty estimated to be ±0.0004. This is in agreement with the value of Bray and Hershey at 25° within the limits of uncertainty of the two values. Extrapolation of Fig. 3 to 35° gives $k^\circ = 0.0117$, also in as good agreement with Bray and Hershey as can be expected.

Somewhat previous to the development of the method described above Bjerrum's method of corresponding solutions[10] was tried and found unsatisfactory. It was necessary to use solutions 10^{-3} to 10^{-2} M in total iron, and it is possible that such solutions contain ionic or molecular species not present in appreciable amounts at concentrations of 10^{-4} M. One condition for the applicability of Bjerrum's method is that polynuclear species be absent. The assumption of the presence of polynuclear species in the more concentrated solutions, and that these dissociate slowly on dilution, is in qualitative agreement with both the failure of Bjerrum's method and the slow changes observed on dilution of solutions.

DURHAM, NORTH CAROLINA RECEIVED MARCH 12, 1951

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[10] J. Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.* **21**, 1 (1944).