Ion-Exchange and Spectrophotometric Investigation of Iron(III) Sulfate Complex Ions

By Roy A. Whiteker and Norman Davidson

The distribution equilibria of iron(III) between an ion-exchange resin and solutions at $\mu = 1.0$, $(H^+) = 1.0$, containing $HClO_4$ and H_2SO_4, and $(Fe^{III}) \sim 3 \times 10^{-4} F$ have been measured at 28° and interpreted in terms of the equilibrium constants, $K_1 = (FeSO_4^+)/(Fe^{+++})(SO_4^-) = 95$, $(K_2/K_1) = (Fe(SO_4)_2^-)/(FeSO_4^+)(SO_4^-) = 9.4$. Spectrophotometric studies at 27 $\pm$ 2° of similar solutions show a marked contribution to the absorption spectrum by $FeSO_4^+$ in the 270–350 mμ range, and lead to a value of K_1 of 101–121. The recommended value is therefore 107($\pm$20) liter/mole. The absorption spectra of Fe^{III} solutions at $(H^+) = 4 \times 10^{-3} F$ with $(SO_4^-) = 0.1$–0.9 M are consistent with the value of 9.4 for K_2/K_1. The extinction coefficients of $FeSO_4^+$ and $Fe(SO_4)_2^-$ have been determined. Data on the affinity of sulfate for various cations are tabulated and reviewed.

It is common knowledge that iron(III) is complexed in sodium sulfate and sulfuric acid solutions. A faint yellow color develops upon addition of sulfuric acid to a ferric perchlorate solution in dilute perchloric acid. Spectrophotometric studies show a marked increase in light absorption in the 270–350 mμ range for such solutions, but the published data are not amenable to analysis in terms of the mass action law.[1] Experiments on the Zimmermann–Reinhardt "preventative solution" show that the strong color of a ferric chloride solution is considerably reduced by addition of sulfuric acid; addition of phosphoric acid then causes only a small further diminution of the color.[2] The formal potential of the iron(II)–iron(III) couple at 25° is −0.732 volt in 1 F $HClO_4$[3] and −0.69 volt in 1 F H_2SO_4,[4] indicating complexing of iron(III) in the latter medium.

From a quantitative study of the inhibiting effect of sulfate on the rate of oxidation of iodide by ferric ion, Sykes has deduced a value of 1.04×10^3 liter/mole for the mass action equilibrium constant, $(FeSO_4^+)/(Fe^{+++})(SO_4^-)$, at 18° and an ionic strength of 0.066.[5]

In the present study, further knowledge about the stabilities, the formulas, and the absorption spectra of iron(III) sulfate complex species has been obtained by equilibrium ion-exchange distribution and spectrophotometric experiments. ·

Ion Exchange

Theory.—The method is based on the idea that the distribution coefficient of iron(III) between an aqueous phase and an ion-exchange resin depends on the concentration of ferric ion, Fe^{+++}, in the aqueous phase. At a given formal (total) Fe^{III} concentration, the concentration of Fe^{+++}, and therefore the distribution coefficient, can be affected by the addition of a complexing agent. A convenient method of determining the relative concentration of iron in the aqueous phase before and after equilibration with the resin is to use radioactive iron and counting methods.

The following assumptions are made in analyzing the data. (a) The only iron species adsorbed by the resin is Fe^{+++}. (b) The activity coefficients for the various ionic species in the aqueous phase are constant as the composition of a solution is varied, providing the ionic strength is constant. (c) The amount of Fe^{+++} adsorbed by the resin is sufficiently small so that the activity coefficients of Fe^{+++} and H^+ in the resin are constant. (d) Perchlorate ion is a non-complexing anion.

Using (a), a distribution constant, Q', for the exchange of ferric and hydrogen ion between an aqueous phase and a resin may be written[6]

$$Q' = \frac{(Fe^{+++})_R(H^+)^3 \gamma_{Fe^{+++}R} \gamma^3_{H^+}}{(Fe^{+++})(H^+)^3_R \gamma_{Fe^{+++}} \gamma^3_{H^+R}} \quad (1)$$

where the γ's are activity coefficients, parentheses indicate concentrations in moles per liter of solution or moles per kilogram of resin, and the subscript R indicates that the ion is in the resin.

Using (b) and (c), a mass-action equilibrium constant, Q_0, may be defined for a series of experiments at a fixed ionic strength.

$$Q_0 = \frac{(Fe^{+++})_R(H^+)^3}{(Fe^{+++})(H^+)^3_R} \quad (2)$$

Let c_0 and c_f be the initial and final volume—formal (total) concentrations of Fe^{III} in solution before and after equilibration with the resin, V = volume of solution, g = weight of resin, C' = capacity of resin in equivalents of H^+ per kg. of resin. Using assumption (b) for cases where ferric iron forms complexes with an anion B, such as sulfate

$$(Fe^{+++}) = \frac{c_f}{1 + K_1(B) + K_2(B)^2 + \ldots + K_n(B)^n} \quad (3)$$

where K_n is the mass-action equilibrium constant for the reaction

$$Fe^{+++} + nB = FeB_n \quad (4)$$
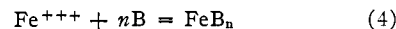
Then

$$Q_0 = \frac{(c_0 - c_f)(V/g)(H^+)^3[1 + K_1(B) + K_2(B)^2 + \ldots]}{c_f[C' - 3(c_0 - c_f)(V/g)]^3} \quad (5)$$

The apparent distribution coefficient, Q_A, is defined in terms of experimentally determinable quantities.

$$Q_A = \frac{(c_0 - c_f)(V/g)(H^+)^3}{c_f[C' - 3(c_0 - c_f)(V/g)]^3} \quad (6)$$

Then

$$(Q_0/Q_A) = 1 + K_1(B) + K_2(B)^2 + \ldots \quad (7)$$

Q_0 is measured in perchloric acid solutions with (B)

(1) A. v. Kiss, J. Abraham and I. Hegedüs, Z. anorg. allgem. Chem., 244, 98 (1940).

(2) O. L. Barneby, This Journal, 36, 1429 (1914).

(3) E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 509.

(4) G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, This Journal, 56, 57 (1934).

(5) K. W. Sykes, J. Chem. Soc., 124 (1952).

(6) R. E. Connick and S. W. Mayer, This Journal, 73, 1176 (1951).

= 0 and an effort is made to deduce the values of the K's from the variation of Q_A with (B).

Experimental

The cation-exchange resin, Dowex-50, 100–200 mesh, in the sodium form was washed with hydrochloric acid and then with distilled water until free of chloride. It was partially dried in air and then allowed to equilibrate with the vapor over a one formal sodium perchlorate solution for several weeks in an evacuated desiccator. The capacity of four different batches of resin varied from 2.99 to 3.02 eq./kg. of resin. This was determined by titration with sodium hydroxide and a pH meter, using vigorous stirring, to a pH of 7–8. Iron(III) solutions were prepared from reagent grade ferrous ammonium sulfate by oxidizing with liquid bromine, boiling, and dilution with perchloric acid. Sulfuric and perchloric acids were prepared from the concentrated reagent grade acids and standardized with sodium hydroxide.

The radioactive isotope used was the 46.3 day Fe^{59}. Because of its reasonably penetrating β and γ radiations, it is much easier to assay than the longer lived Fe^{55} isotope. It was supplied by the Oak Ridge National Laboratory as catalog item 26 PX with a specific activity of 1450 millicurie per gram, and no significant chemical or radioactive impurities.[7]
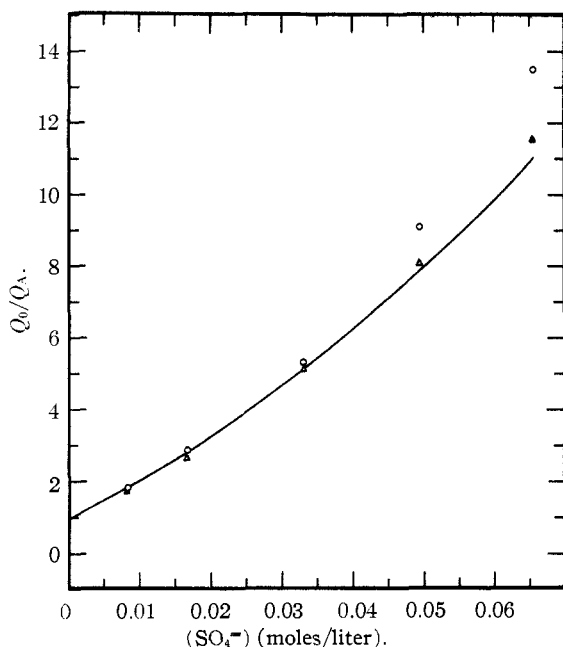

Fig. 1.—Q_0/Q_A vs. (SO_4^-) for two experiments ($\triangle$ and $\bigcirc$). The solid line is the theoretical curve for $K_1 = 95$, $K_2 = 893$. For each experiment, $c_0 = 3 \times 10^{-4}$ F, and 100 ml. of sample was equilibrated with 2.00 g. of resin. For the $\triangle$ experiment, the detailed experimental conditions are listed in the table below. Q_0, in this case, was 8.05.

(HClO₄)	(H₂SO₄)	(SO₄⁻)	(H⁺)	μ	Activity of aqueous phase, counts/ min.[a]
formula wt./l.		moles/liter			
1.003[b]	0.0	0.0	1.003	1.00	700
1.008	.0	.0	1.008	1.01	133
0.875	.112	.0084	1.004	1.01	205
.751	.224	.0167	1.008	1.03	270
.501	.449	.0331	1.016	1.05	383
.250	.723	.0495	1.023	1.07	459
.0	.964	.0655	1.030	1.10	512

[a] Four-ml. sample of aqueous phase counted in solution counter.   [b] Sample not contacted with resin.

(7) "Catalog and Price List No. 4," Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee, March, 1951, p. 13.

Radioassay was performed directly on the aqueous solutions using a Mark 1, Model 70 Radiation Counter Laboratories thin wall jacketed counter, with an annulus volume of ca. 4 ml. The observed counting efficiency was 150 disintegrations per count.

Solutions used for the distribution equilibrium experiments typically contained 3–6 $\times$ 10^{-4} F inactive iron(III), sufficient active iron to give counting rates of 500–1000 counts/min., and perchloric and sulfuric acid such that the ionic strength and hydrogen ion concentration were 1.0. The procedure for a run was to prepare seven 100-ml. solutions in 125-ml. glass-stoppered conical flasks, all containing the same amount of iron, but with varying amounts of sulfuric and perchloric acids. One of the two solutions that contained only perchloric acid was used to measure the initial amount of radioactivity. Two (2.00) grams of resin was added to each of the other six solutions, the stoppers were sealed with paraffin, and the flasks were rotated in a thermostated water-bath at 28.3° for 20–24 hours. The solutions were then radioassayed.

Check radioassays showed that the sample preparation and counting procedures were reproducible to 1–2%, although the resin distribution experiments were less satisfactory.

Results.—Figure 1 exhibits a plot of the values of Q_0/Q_A as a function of (SO_4^-) for several typical runs. Qualitatively, there is a marked decrease in the distribution coefficient when sulfuric acid is substituted for perchloric acid. Since all experiments were at an ionic strength of 1.0 and at $(H^+) = 1.0$, they cannot reveal whether sulfuric acid, bisulfate ion, or sulfate ion is the complexing species. The spectrophotometric studies reported below show that the first complex is $FeSO_4^+$; therefore, the ion-exchange data are analyzed in terms of the assumption that (SO_4^-) is the (B) of equations 3–7. We have used 0.075 mole/liter for the mass action dissociation constant of HSO_4^- at 28° in a solution of ionic strength 1.0.[8]

The data have been analyzed in terms of a simplified version of equation (7), $(Q_0/Q_A) = 1 + K_1(SO_4^-) + K_2(SO_4^-)^2$. K_1 was deduced from the limiting slope of plots like Fig. 1 and K_2 from the limiting slope of a plot of $(Q_0/Q_A) - 1 - K_1 \cdot (SO_4^-)$ vs. $(SO_4^-)^2$. The resulting values of the association constants are shown in Table I.

TABLE I

ASSOCIATION CONSTANTS FOR IRON(III) SULFATE COMPLEXES AT 28°, μ = 1.0

c_0, formula wt./l.	Q_0	K_1, l./mole	K_2, l./mole
3 × 10⁻⁴	7.88	95.5	562
3 × 10⁻⁴	8.80	98.0	927
3 × 10⁻⁴	7.85	87.8	905
3 × 10⁻⁴	8.05	92.4	964
6 × 10⁻⁴	8.80	99.6	1232
3 × 10⁻⁴	8.45	97.0	800
Av.	8.31	95.1	898
Av. dev.	0.41	3.6	159

We can offer no satisfactory explanation for the variation of Q_0 from experiment to experiment displayed in Table I. Furthermore, in experiments in which no inactive iron was added to the Fe^{59} solution, i.e., with $c_0 \sim 2$–6×10^{-7} F, values of Q_0 that ranged from 2–4 were obtained. It was suspected, but never completely proved, that these low values of the distribution coefficient were due to reduction of the Fe^{III} to Fe^{II} by the resin.

It is evident from Fig. 1 that the Q_A values for high values of (SO_4^-) were not reproducible, and that some of the experiments indicate that the formation of higher complexes, such as $Fe(SO_4)_3^-$ should be considered. However, it is unlikely that the assumptions that the mass action law is valid at constant ionic strength and the resin behaves ideally and absorbs only Fe^{+++} and not $FeSO_4^+$ are sufficiently good to justify a more elaborate analysis of the data, even

(8) G. J. Doyle and N. Davidson, THIS JOURNAL, 71, 3491 (1949). This value is based on the value of 0.0101 for the thermodynamic ionization constant of HSO_4^-. (H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 430.)

if the experiments were more reproducible. The amount of Fe^{+++} adsorbed by the resin was always less than 0.07 equivalent per kg. so that assumption (c) is probably valid.[6]

It is difficult to estimate the absolute accuracy of the constants presented in Table I. The qualitative fact of complexing by sulfate is unmistakably demonstrated by these experiments; confirmation to 10% of the value of K_1 is obtained by the spectrophotometric studies. Confirming evidence for the formation of a negative complex like $Fe(SO_4)_2^-$ is the observation that the anion-exchange resin, Amberlite IRA-400, absorbs significant quantities of ferric iron from sulfate solutions.[9]

Spectrophotometry

Experimental.—Hydrated ferric perchlorate was prepared by heating ferric chloride with excess perchloric acid, evaporating to fumes and then until incipient precipitation. The pale violet crystals which separated on cooling were recrystallized twice from a minimum amount of water and then dissolved to give a solution that was 1 F in $HClO_4$. The solution was standardized iodometrically.[10]

Measurements were made at room temperature, 27 $\pm$ 2°, with a Beckman Model DU ultraviolet spectrophotometer using a hydrogen lamp and quartz cells with a path length of 1.00 cm. Solutions used were at an ionic strength of 1.06 $\pm$ 0.07 unless otherwise specified.

Results.—As shown in Fig. 2, there is a marked increase in the light absorption, due to Fe^{III}, in the 270–350 $m\mu$ wave length range, when sulfuric acid or sodium sulfate is added. The light absorption is much greater in 0.9 F Na_2SO_4 than in 1.0 F H_2SO_4, suggesting that the species which complexes the iron is SO_4^-, not HSO_4^-. The following experiment shows conclusively that this is the case. A series of solutions were prepared from $Fe(ClO_4)_3$, $NaClO_4$, $HClO_4$ and H_2SO_4 with $(Fe^{III}) = 5.12 \times 10^{-4}$ F, $\mu = 1.0$, but with variable amounts of total sulfate and acid so that the free sulfate ion was fixed at 0.0193 ± 0.0002 M (calculated assuming $K_{HSO_4^-} = 0.075$) although the hydrogen and bisulfate ion concentrations varied from 0.08 to 1.0 and 0.021 to 0.26 M, respectively. The absorption spectra of the several solutions were almost identical. Figure 2, curves 4 and 5, illustrates this for the extreme values of (H^+) used. The small difference in the two spectra is attributed to different concentrations of $FeOH^{++}$. The spectra in Fig. 2 are in qualitative agreement with those presented by Kiss, *et al.*[1]

A quantitative study of the equilibria involved was made for two series of solutions at $\mu = 1.0$, $(H^+) = 1.0$, $(Fe^{III}) = 5.12 \times 10^{-4}$ F, with the formal concentration of sulfuric acid varying from 0.021 to 1.0 F. The data have been analyzed by plotting D *vs.* $(D - D_0)/(SO_4^-)$, where $D =$ observed optical density; $D_0 = \epsilon_0(Fe^{+++})_0 =$ optical density of a solution *sans* sulfate, but having the same formal concentration of ferric ion, $(Fe^{+++})_0$, and hydrogen ion as all the other solutions; ϵ_0 is the formal extinction coefficient of Fe^{III} at this acidity, in the absence of sulfate. If $FeSO_4^+$ is the only important complex species

$$D = \epsilon_1(Fe^{+++})_0 - (D - D_0)/(K_1(SO_4^-)), \quad (8)$$

where ϵ_1 is the extinction coefficient of $FeSO_4^+$.[11]

Examples of the analysis of the data for the two experiments are exhibited in Fig. 3 for the wave length 295 $m\mu$. The plots give reasonably good straight lines, showing that the principal complex species formed in the concentration range used for these experiments is $FeSO_4^+$. For the experiment in which the sulfate ion concentration was varied from 0.066 to 0.0028, the points for $(SO_4^-) > 0.011$ fall above the best straight line through the points of lower concentration. This is due to the formation of significant amounts of $Fe(SO_4)_2^-$; the points at lower sulfate concentration are therefore used to compute ϵ_1 and K_1 of equation (8). The plots for all wave lengths at 5 $m\mu$ intervals between 290 and 340 $m\mu$ showed the same features as those for 295 $m\mu$. The values of K_1 and their average deviation for the two series of experiments were 101 ($\pm$2.3) and 121 ($\pm$2.3). There is a systematic error between the two experiments which is larger than the random errors of either

(9) Unpublished experiments by M. Czerczewski in this Laboratory.

(10) E. H. Swift, This Journal, **51**, 2682 (1929).

(11) This method of analysis is due to W. B. Lewis, Thesis, University of California at Los Angeles, 1942; we learned of it from T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).
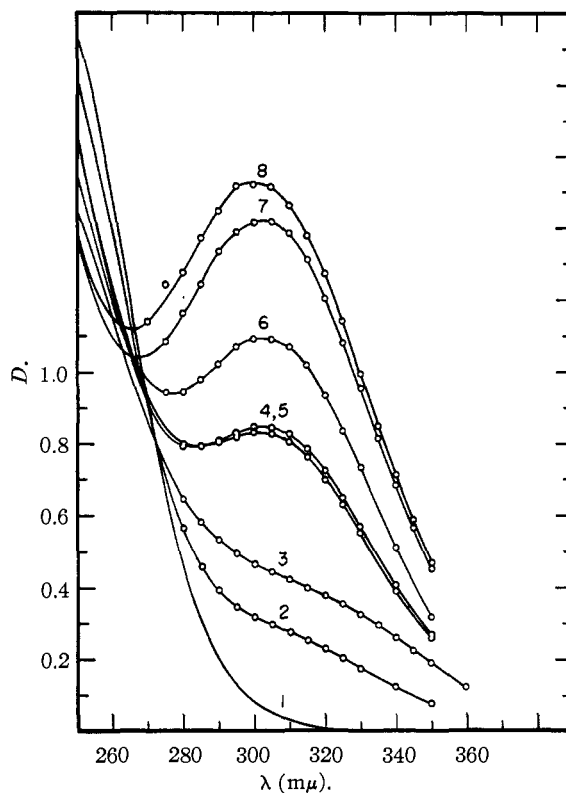
Fig. 2.—Absorption spectra of iron(III) in solutions containing sulfuric acid and sulfate ion, $D = \log_{10}(I_0/I)$, 1-cm. cells. (1) Calculated curve for solutions which are 5.12×10^{-4} F in Fe^{III} and 1 F in $HClO_4$. The values of D have been calculated from the best values of ϵ obtained from solutions varying from 1.28×10^{-2} F to 3.20×10^{-4} F in Fe^{III}, all 1 F in $HClO_4$. (2) 5.12×10^{-4} F Fe^{III}, 1.003 M H^+, 0.00275 M SO_4^-. (3) 5.12×10^{-4} F Fe^{III}, 4×10^{-3} F $HClO_4$, 0.94 F $NaClO_4$. (4) 5.12×10^{-4} F Fe^{III}, 1.0 M H^+, 0.0194 M SO_4^-. (5) 5.12×10^{-4} F Fe^{III}, 0.08 M H^+, 0.0194 M SO_4^-. (6) 5.12×10^{-4} F Fe^{III}, 1.068 M H^+, 0.0655 M SO_4^-. (7) 5.12×10^{-4} F Fe^{III}, 4×10^{-3} F $HClO_4$, 0.333 F Na_2SO_4. (8) 5.12×10^{-4} F Fe^{III}, 4×10^{-3} F $HClO_4$, 0.920 F Na_2SO_4. The order of increasing optical density at the extreme left-hand edge of the plot ($\lambda = 250$ $m\mu$) is 7, 8, 3, 6, 4 and 5, 2, 1.

one. The extinction coefficients, ϵ_1 (λ), obtained from the two experiments agreed to $\pm$7%; the average values are plotted in Fig. 4.

The use of equation (8) for the analysis of spectrophotometric data for complex ions is rather uncommon in the literature; it is therefore worthy of mention that we have treated our data by the more familiar equation[12]

$$(Fe^{+++})_0/(D - D_0) = [1/(\epsilon_1 - \epsilon_0)][1 + 1/(K_1(SO_4^-))] \quad (9)$$

and obtained essentially the same results. Equation (8) appears to be more attractive than (9) in that K_1 is directly determined from the slope of the plot, whereas in (9), the ratio of intercept to slope must be calculated.

In order to obtain larger relative concentrations of $Fe(SO_4)_2^-$, solutions with higher concentrations of free sulfate ion were prepared. These contained: $(Fe^{III}) = 5.12 \times 10^{-4}$ F, $(H^+) = 4 \times 10^{-3}$ F, and (a) 0.92 F Na_2SO_4, (b) 0.333 F Na_2SO_4, and (c) 0.100 F Na_2SO_4, 0.70 F $NaClO_4$. The absorption spectra of (a) and (b) are given in Fig. 2. The spectra showed a saturation effect as the sulfate ion concentration increased. Accordingly, an effort was made to analyze them according to the mass-action law, even though (a) had an ionic strength of 2.76, using $K_1 = 107$, and $(K_2/K_1) = 9.4$, and ϵ_1 from Fig. 4. The calculated ex-
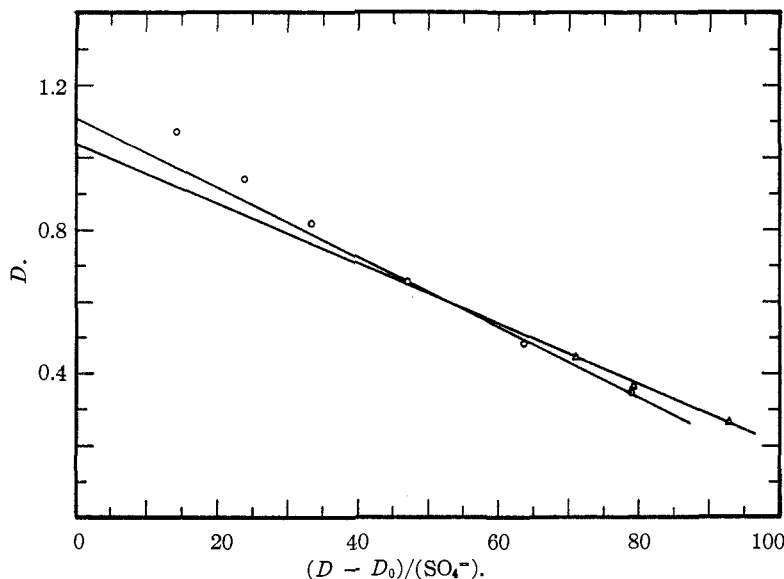
(12) H. McConnell and N. Davidson, *ibid.*, **72**, 3164 (1950).

Fig. 3.—Plots of D vs. $(D - D_0)/(SO_4^-)$ for λ = 295 mμ for solutions at μ = 1.0, (H$^+$) = 1.0. O and Δ are for two different experiments. For the O experiment, the experimental conditions for the six points, reading from left to right, are

H$_2$SO$_4$ (f)	0.998	0.501	0.301	0.161	0.0798	0.0396
HClO$_4$ (f)	.004	.501	.703	.841	.924	.961
(SO$_4^-$) (calcd.)	.0655	.0338	.0205	.0111	.00552	.00275

tinction coefficients of Fe(SO$_4$)$_2^-$, ϵ_2, from the three solutions agreed to ±5%; the average values of ϵ_2 are shown in Fig. 4. The deviations of the calculated ϵ's from the average were systematic and indicate a small contribution to the optical density by a more strongly colored Fe(SO$_4$)$_3^=$ species.

Incidental to the main purposes of this investigation, the absorption spectra of Fe^{III} at μ = 1 and (H$^+$) = 1.0 M and 4 × 10^{-3} M have been obtained. The absorption spectra of Fe^{+++} and FeOH^{++} have been calculated, using 2.0 × 10^{-3} for the first hydrolysis constant of Fe^{+++} at μ = 1 and 27°.[13] The results for ϵ of FeOH^{++} fall between the two sets of values given by Rabinowitch and Stockmayer[14] and Olson and Simonson.[15] It should be recalled that the former authors rather arbitrarily selected 1 × 10^{-3} for the hydrolysis constant of Fe^{+++}; their spectrophotometric data gave values of $K_{HFeOH^{++}}$ only.

Discussion

In conclusion, the value of the association constant K_1 = (FeSO$_4^+$)/(Fe^{+++})(SO$_4^-$) at μ = 1 and 28° has been measured as 95 ± 4 (average deviation) (liter/mole) by the equilibrium ion-exchange method, and as 101(±2) and 121(±2) in two spectrophotometric experiments. The agreement between the two methods of measuring K_1 is satisfactory, in view of experimental error and the limited validity of the assumptions used to interpret the data. We accordingly recommend the value 107 ± 20 for K_1.[16] The ion-exchange method gives a value of 9.4 for (K_2/K_1) = (Fe(SO$_4$)$_2^-$)/(Fe(SO$_4$)$^+$)(SO$_4^=$), and this value is consistent with spectrophotometric data for Fe^{III} solutions at high sulfate concentrations.

(13) W. C. Bray and A. V. Hershey, THIS JOURNAL, **56**, 1889 (1934).

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

(15) A. R. Olson and T. R. Simonson, J. Chem. Phys., **17**, 1322 (1949).

(16) Any fractional error in the assumed value of 0.075 for $K_{HSO_4^-}$ used in the calculations results in an approximately equal fractional error in the calculated values of K_1 and K_2/K_1.

The value of K_1 = 107 is not directly comparable to the value of 1.04 × 10^3 at μ = 0.06 and 18° determined by Sykes,[5] because of the differences in ionic strength and temperature. According to the equation

$$- \log_{10}\gamma = 0.5z^2 \left[\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu\right] \quad (10)$$

used by him to estimate a thermodynamic constant, the present investigation gives 6.8 × 10^3 for the thermodynamic formation constant of FeSO$_4^+$ at 27° as compared to 1.5 × 10^4 calculated by Sykes.

Table II displays some of the measured values of the association constants of sulfate with several cations. The results shown are for ionic strengths in the range 0.5–3.5, where the constants should not be strongly dependent on ionic strength. The data are too sparse and their reliability too uncertain to justify an extensive discussion. We note however the increase in association constants with increasing charge on the cation. For most of the cases studied, the ratio (K_1^2/K_2) is about 10. For those cases where the question has been examined, the complexing anion is always
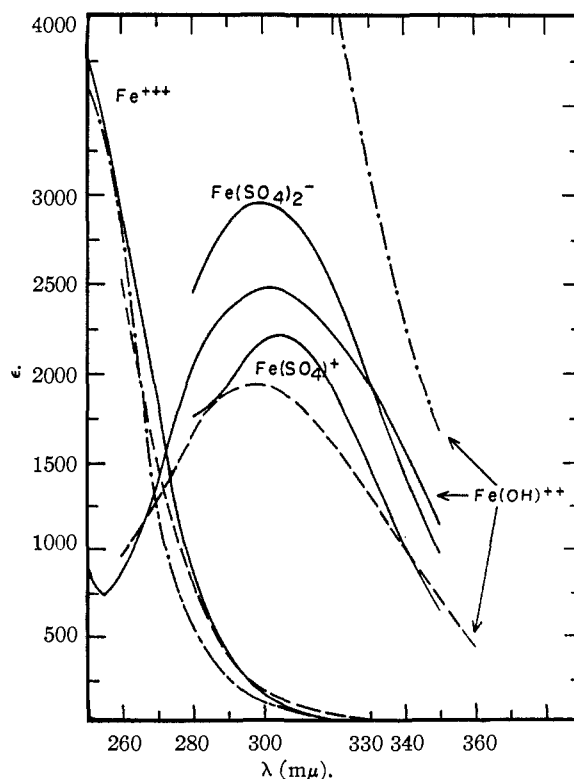

Fig. 4.—Extinction coefficients of some complex iron species. ϵ = $(1/cl)\log_{10}(I_0/I)$. ——, this research; — — —, Olson and Simonson; — · — · — ·, Rabinowitch and Stockmayer.

TABLE II

ASSOCIATION CONSTANTS OF SOME COMPLEX SULFATES[a]

Ion	K_1, (MSO₄)/ (M)(SO₄)	K_2/K_1, M(SO₄)₂/ (MSO₄) (SO₄)	Remarks
U⁺⁴ [17]	1740	150	25°, μ = 3.5, (H⁺) = 2.0
Th⁺⁴ [18],[b]	2100	240	25°, μ = 2.0, (H⁺) varied
Zr⁺⁴ [19],[c]	6140	708	25°, μ = 2.0, (H⁺) = 2.0
Fe⁺³	107	9	28°, μ = 1.0, (H⁺) varied
Ce⁺³ [6]	60		25°, μ = 0.5–0.9, (H⁺) ~ 10⁻³
Ce⁺³ [20]	34		25°, μ = 0.5, (H⁺) ~ 10⁻²
	17.5		μ = 1.0, (H⁺) ~ 10⁻²
Cu⁺⁺ [21]	4		25°, μ = 1.0
Cu⁺⁺ [22],[d]	9		20°, μ = 1.0
Cd⁺⁺ [23]	7		μ = 3.0
VO₂⁺⁺ [24]	67		25°, μ = 3.5, (H⁺) = 2.0
Ag⁺ [23]	1.7	1	μ = 3.0

[a] For the sake of intercomparison of results, equilibrium constants for the reaction M + HSO₄⁻ → MSO₄ + H⁺ have been converted to the form presented here using $K_{HSO_4^-}$ = 0.075. [b] The authors use 0.084 for $K_{HSO_4^-}$; for comparative purposes, the results have been recalculated for $K_{HSO_4^-}$ = 0.075. There is evidence for the formation of Th(SO₄)·(HSO₄)⁺ at high acidity. [c] A value for [Zr(SO₄)₃⁻]/[Zr(SO₄)₂](SO₄⁻) of 1 was also measured. [d] The formation of Cu(SO₄)₃⁻⁴ was also inferred.

(17) Data of R. H. Betts and R. Leigh (*Can. J. Research*, **B28**, 514 (1950)) reinterpreted by J. C. Sullivan and J. C. Hindman (THIS JOURNAL, **74**, 6091 (1952)).

(18) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

(19) R. E. Connick and W. H. McVey, *ibid.*, **71**, 3182 (1949).

(20) T. W. Newton and G. M. Arcand, ref. 10.

(21) R. Näsänen, *Acta Chem. Scand.*, **3**, 179 (1949).

(22) S. Fronaeus, *ibid.*, **4**, 72 (1950).

(23) I. Leden, *ibid.*, **6**, 97 (1952).

(24) R. H. Betts and R. K. Michels, *J. Chem. Soc.*, S286 (1949).

sulfate, not bisulfate (see however footnote (b) of Table II).

The ionic radii of Ce⁺³ and Fe⁺³ are quite different, 1.02 and 0.60 Å., respectively.[25],[26] Nevertheless, these two tripositive cations have about the same affinity for SO₄⁻. They also have about the same affinities for Cl⁻ and NO₃⁻: $K_{CeCl^{++}}$ = 0.8–1.1 (μ = 0.4–1.5)[6]; $K_{FeCl^{++}}$ = 4, (μ = 1.0)[14]; $K_{CeNO_3^{++}}$ ~ 1, (μ = 0.89)[6]; $K_{FeNO_3^{++}}$ = 6.8–0.6, (μ = 0.066–0.6, 18°),[5] 0.3, (μ = 1, 25°).[27] On the other hand, the relative affinities of Fe⁺³ and Ce⁺³ for OH⁻ are quite different, their hydrolysis constants being 2.0 × 10⁻³ and 5 × 10⁻⁸, respectively, at μ = 1.[28]

It may be noted that, at present, there is no decisive evidence on the question of whether, in some of these complexes, the complexing anion is in the first coördination sphere of the cation, displacing water molecules, or whether the anion and cation are separated by a layer of water molecules, in which case these are pure "ion-pair" complexes.

(25) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

(26) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 330.

(27) J. A. Ibers and N. Davidson, THIS JOURNAL, **73**, 476 (1951).

(28) T. Moeller, *J. Phys. Chem.*, **50**, 242 (1946). We have multiplied the value of 1 × 10⁻⁹ given by Moeller by 50 to correct for the estimated effect of sulfate on his hydrolysis experiments.

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Complex Ions of Chromium. III. Reactions between Hexaquochromium(III) and Oxalate Ions[1]

BY RANDALL E. HAMM AND ROBERT E. DAVIS

The formation of dioxalatodiaquochromate(III) ion from hexaquochromium(III) and oxalate ions was shown to be rate limited by two consecutive slow reactions. The slowly reacting species could be reduced at a dropping mercury electrode at half-wave potentials of −0.90 and −1.15 volts vs. the saturated calomel electrode. The rates of reaction of the two species were determined by measuring currents at the diffusion plateaus. The reactions were found to be consecutive and first order with respect to the reacting species. The first reaction rate was inversely proportional to hydrogen ion concentration, and the second reaction rate was independent of hydrogen ion concentration. Both rates were independent of oxalate ion concentration. Mechanisms for the reactions were postulated, and some of the intermediates were isolated and identified. Rate constants, heats and entropies of activation for the two slow reactions were reported.

In the study of the oxidation of oxalic acid by potassium dichromate, Werner[2] showed that for potassium dichromate–oxalic acid ratios between 1:1 and 1:9, potassium dioxalatodiaquochromate(III) was always a product. Croft[3] demonstrated that addition of alkali oxalate to a boiling solution of the dioxalatodiaquochromate(III) gave trioxalatochromate(III) ion. These facts suggested that it might be interesting to investigate the formation of the oxalate complexes by direct reaction of oxalate and chromium(III) ions. The existence of a monoxa-

(2) E. A. Werner, *J. Chem. Soc.*, **53**, 602 (1888).

(3) H. Croft, *Phil. Mag.*, **21**, 197 (1842).

late complex would also be investigated, even though no mention has been made of it in the literature. Wyrouboff[4] showed that addition of neutral alkali oxalates to chromium(III) salt solutions resulted in the formation of a "practically insoluble" chromium oxalate, indicating that in order to study the direct reaction of hexaquochromium(III) and oxalate ions, dilute solutions would be necessary in order to avoid precipitation. Polarographic measurements were found to be ideal for following the course of such reactions in dilute solutions.

Preliminary polarograms of solutions of approximately 10⁻³ M hexaquochromium(III) ion in excess oxalate ion showed the formation of two re-

(4) A. Wyrouboff, *Bull. soc. mineral. Franc.*, **24**, 86 (1901).