Ultraviolet Spectroscopic Study of Ferric Equilibria at High Chloride Concentrations

Robert H. Byrne[1] and Dana R. Kester[2]

The equilibria among the species Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$, $FeOH^{2+}$ and $Fe(OH)_2^+$ have been examined by ultraviolet absorption spectroscopy. Our results indicate that previous workers have generally overestimated the stability constant of $FeCl^{2+}$ and that the association of Fe^{3+} and Cl^- is predominantly inner sphere. The formation constant of $FeOH^{2+}$ obtained in 0.68 m NaCl is in good agreement with our earlier results obtained in 0.68 m $NaClO_4$. Our results indicate that formation of $FeOHCl^+$ is much less significant than has been previously reported. Molar absorptivities for the species Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$ and $FeOH^{2+}$ are reported for wavelengths between 220 and 400 nanometers.

KEY WORDS: Hydrolysis; ferric chloride; ferric hydroxide; UV spectroscopy; complexes; ion pairs.

1. INTRODUCTION

A plot of the formation constant for $FeCl^{2+}$ obtained as a function of ionic strength by various workers[1-5] (Fig. 1) shows general agreement in the shapes of the curves, but the formation constants determined at any particular ionic strength are notably different. Uncertainty in this constant is particularly important to studies of the chemistry of iron in natural waters, and it is important also to the interpretation of $FeCl^{2+}$ kinetics of complexation experiments.[6] Our potentiometric investigations at the ionic strength of seawater[7] are essentially in agreement with the potentiometric and spectrophotometric investigations of Woods *et al.*[3] which are among the lower values in Fig. 1. The analyses of Woods *et al.* have been criticized in the more recent work of Rowley and Sutin,[5] whose results correspond to the upper values in Fig. 1. The formation constants obtained spectrophotometrically by Woods *et al.*[3] showed a marked dependence on wavelength. This type of behavior has been described by Kruh[8] to result from assuming that only one complex species exists, when the system actually contains two complex species.

The observed difficulties in the spectrophotometric analyses of

[1]Department of Marine Science, University of South Florida, St. Petersburg, Florida 33701.

[2]Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island 02881.
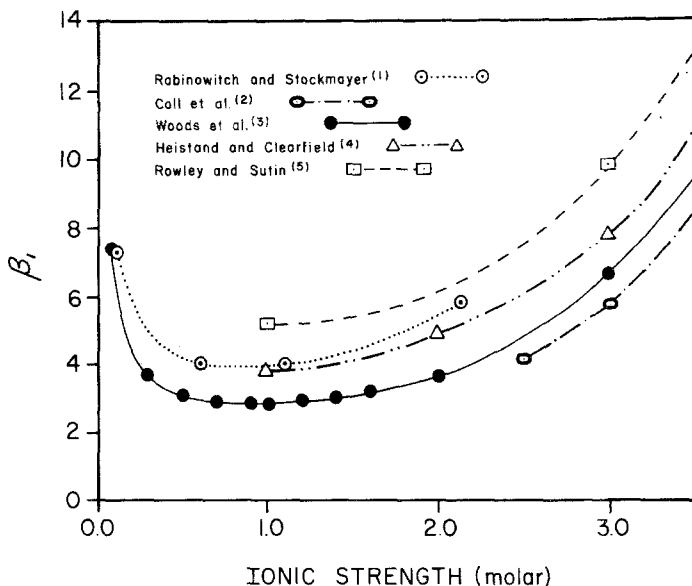
Fig. 1. The formation constant $\beta_1 = [FeCl^{2+}]/[Fe^{3+}]$ [Cl⁻] obtained by various workers is shown as a function of ionic strength.

The observed difficulties in the spectrophotometric analyses of Woods et al.[3] can potentially be overcome by either of two methods. Chloride concentrations can be kept sufficiently low to make the concentration of $FeCl_2^+$ insignificant, or alternatively the existence of this complex can be accounted for quantitatively. Rowley and Sutin[5] used the former method in their analyses. The possibilities of the latter method have become available relatively recently through the use of computer methods. In the present work we have used a non-linear least squares fitting technique[9-11] to analyze spectrophotometric data at a large number of wavelengths simultaneously, greatly diminishing difficulties of the type discussed by Kruh.[8] The data of Woods et al.[12] have been reexamined using this technique, and in addition, our new data at higher chloride concentrations are used to enhance the sensitivity of the analysis to the characteristics of the $FeCl_2^+$ complex.

Ferric chloride complexing experiments at low ionic strength require substantial variation in medium composition. It is difficult to assess whether the metho s of Rowley and Sutin[5] or the methods of Woods et al.[3] more effectively minimize activity coefficient variation at constant total ionic strength. We have adopted the Woods et al. approach in our experiments in order to achieve a relatively high extent
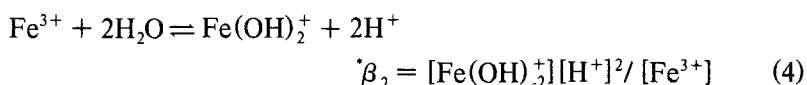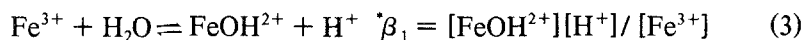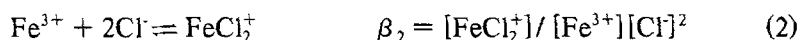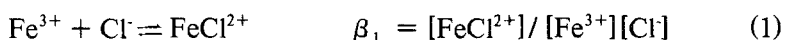
of $FeCl^{2+}$ formation at low total ionic strength, and because new computer techniques greatly diminish the analytical difficulties encountered when treating high ligand number systems. A comparison of our results and the results of Rowley and Sutin[3] provides an assessment of the influence of medium on activity coefficients at constant ionic strength.

As a further means of characterizing ferric chloride equilibria, ferric hydrolysis equilibria have been investigated in 0.68 molal NaCl. In this medium the existence of a mixed ligand complex, $FeOHCl^+$ can be predicted from theoretical considerations.[13] Considerable importance has been attributed to this species as a reaction intermediate.[14] Our studies provide an evaluation of the formation constant and spectral properties of $FeOHCl^+$ at 25°C and 0.68 molal ionic strength.

2. EXPERIMENTAL

2.1. Methods

Spectrophotometric measurements and analyses were conducted according to the methods of Byrne and Kester.[11] In the solutions used in our experiments the significant iron equilibria are represented by:

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \qquad \beta_1 = [FeCl^{2+}]/[Fe^{3+}][Cl^-] \qquad (1)$$

$$Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^+ \qquad \beta_2 = [FeCl_2^+]/[Fe^{3+}][Cl^-]^2 \qquad (2)$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \quad {}^*\beta_1 = [FeOH^{2+}][H^+]/[Fe^{3+}] \qquad (3)$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+$$

$${}^*\beta_2 = [Fe(OH)_2^+][H^+]^2/[Fe^{3+}] \qquad (4)$$

where brackets denote concentration for each chemical species.

The ultraviolet absorbance of a given iron species is related to the species concentration by:

$$_\lambda A_i = l \cdot {}_\lambda\epsilon_i [i] \qquad (5)$$

The absorbance $_\lambda A_i$ of iron species i at wavelength λ is related to the pathlength, l, the absorbance per molar centimeter $_\lambda\epsilon_i$, and the concentration [i]. The total absorbance per molar centimeter, $_\lambda a$, is obtained by summation over all iron species present in the solution, which for this study is:
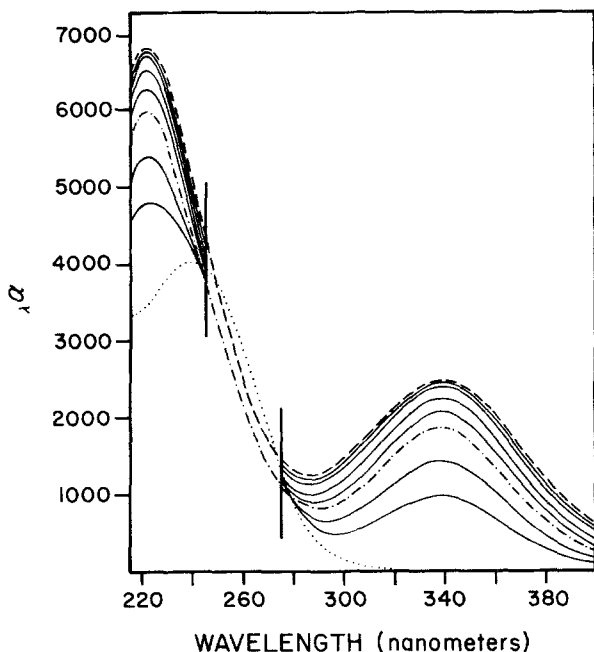
Fig. 2. Absorbance per molar centimeter of Fe(III) is shown as a function of wavelength and chloride concentration for 3 m HCl-HClO$_4$ mixtures. Chloride concentrations for each curve are (from top to bottom for 241 nm $\geq \lambda \geq$ 278 nm): [Cl$^-$] = 2.800 M, 2.323 M, 1.843 M, 0.723 M, 0.482 M, 0.241 M, 0.121 M, 0.0009 M. Only three absorbance curves are shown between 245 nm and 275 nm.

$$_\lambda a = (_\lambda\epsilon_0 + {_\lambda\epsilon_1}\beta_1[Cl^-] + {_\lambda\epsilon_2}\beta_2[Cl^-]^2 + {_\lambda\epsilon_3}^*\beta_1[H^+]^{-1}$$

$$+ {_\lambda\epsilon_4}^*\beta_2[H^+]^{-2})/\{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + {}^*\beta_1[H^+]^{-1}$$

$$+ {}^*\beta_2[H^+]^{-2}\} \tag{6}$$

where $_\lambda\epsilon_0$ applies to the species Fe^{3+} and the coefficients $_\lambda\epsilon_1$ through $_\lambda\epsilon_4$ are for the ferric complexes in Eqs. (1-4).

Eq. (6) is used to analyze absorbance data for solutions having constant total iron but variable [Cl$^-$] or [H$^+$]. In very acidic solutions, terms in [H$^+$] can be neglected and a truncated form of Eq. (6) is used to determine β_1, β_2, $_\lambda\epsilon_0$, $_\lambda\epsilon_1$ and $_\lambda\epsilon_2$ by varying [Cl$^-$].

$$_\lambda a = (_\lambda\epsilon_0 + {_\lambda\epsilon_1}\beta_1[Cl^-] + {_\lambda\epsilon_2}\beta_2[Cl^-]^2)/(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \tag{7}$$

When [Cl$^-$] is constant, Eq. (6) can be rewritten as follows:

$$_\lambda a = (\theta(_\lambda\epsilon_0 + {_\lambda\epsilon_1}\beta_1[Cl^-] + {_\lambda\epsilon_2}\beta_2[Cl^-]^2) + \theta{_\lambda\epsilon_3}^*\beta_1[H^+]^{-1}$$

$$+ \theta_\lambda \epsilon_4 \dot{\beta}_2 [H^+]^{-2})/(1 + \theta \dot{\beta}_1 [H^+]^{-1} + \theta \dot{\beta}_2 [H^+]^{-2}) \qquad (8)$$

where

$$\theta = 1/(1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2) \qquad (9)$$

Eq. (8) was used to analyze absorbance data for solutions having constant total (Fe^{III}), [Cl$^-$], and variable [H$^+$]. Eqs. (7) and (8) both have the general form:

$$_\lambda a = (_\lambda R_0 + {}_\lambda R_1 x + {}_\lambda R_2 x^2)/(1 + R_3 x + R_4 x^2) \qquad (10)$$

where the variable x corresponds to [Cl$^-$] or [H$^+$]$^{-1}$ and the constants R_{0-4}, correspond to constant terms in Eq. (7) or (8).
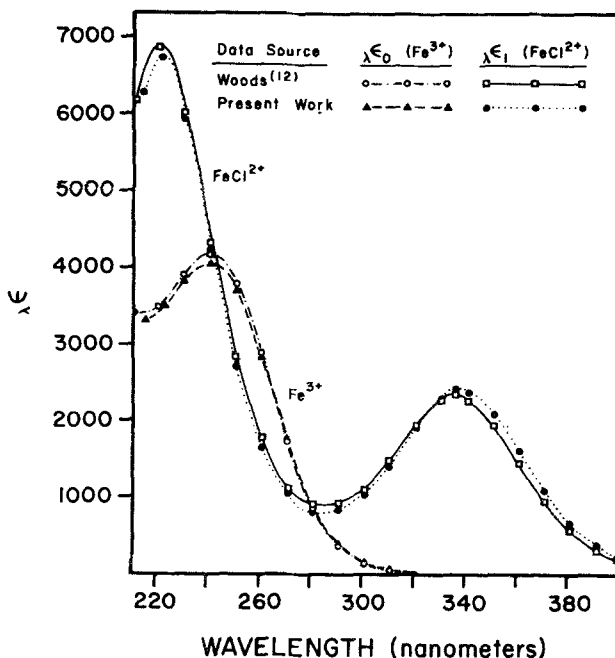
Fig. 3. Molar absorptivities (absorbance per molar centimeter) obtained in our analyses of Wood's data[12] and our own data are shown as a function of wavelength for iron species Fe^{3+} and FeCl^{2+}.

Eq. (10) was used to obtain equilibrium constants and molar absorbances according to the procedures outlined by Byrne and Kester.[11] Absorbance data of the form $(_\lambda a_j, [Cl^-]_j)$ or $(_\lambda a_j, [H^+]_j^{-1})$ were fit using computer methods[9-11] to obtain the constants R_0 through R_4.

The non-linear least squares parameter estimations entailed fitting data pairs $(_\lambda a_j, x_j)$ at as many as 21 wavelengths and 9 values of x simultaneously, resulting in the simultaneous determination of 2 formation constants and as many as 63 $_\lambda\epsilon_i$.

2.2. Materials

Experiments were conducted at 25°C in three molal $HCl-HClO_4$ mixtures and in 0.68 molal $HCl-NaCl$ mixtures. Iron was added to these solutions from acidic stock solutions of ferric chloride. All solutions were prepared from deionized distilled water and chemicals obtained from J. T. Baker. Total iron concentrations were determined by atomic absorption analysis and were within 2.6% of concentrations determined gravimetrically.

Chloride complexation experiments were conducted by mixing 3 molal HCl and $HClO_4$ solutions, each of which had a ferric iron concentration of 3.02×10^{-4} moles/l. These sample solutions were prepared in 1 cm pathlength quartz cuvettes using calibrated micrometer syringes with teflon needles. The absorbances of these solutions were measured against a 3 molal $HClO_4$ reference solution and were corrected for chloride-perchlorate absorbance differences for each mixture.

Hydrolysis equilibria in 0.68 molal NaCl medium were characterized on a hydrogen ion concentration scale.[11,15,16] The potentials developed by a Corning glass pH electrode and a calomel reference electrode with a fiber type liquid junction were measured with a digital pH meter to within 0.1 mv. When calibrated in 0.68 molal NaCl between pH 2.0 and 4.0, the response was within 0.5% of theoretical Nernstian behavior. Sample solutions were 0.68 molal in NaCl and approximately 5×10^{-6} molar in Fe^{III}. The reference solution was 0.68 molal in NaCl and had a pH of four. Absorbance measurements were taken at various pH between 4.2 and 2.0 using 10 cm cells.

All solutions were thermostated at 25 ± 0.1°C. Absorbance measurements were made using Cary 17 and 17D spectrophotometers within the 400 and 190 nanometer wavelength range. In each of our experiments ionic strength is held constant on the molal (m) concentration scale. All analyses were made on the molar (M) concentration scale so that absorptivities and formation constants are expressed in molar units.

3. RESULTS

Absorbance data, $_\lambda a$, obtained in 3 molal $HCl-HClO_4$ mixtures are shown in Fig. 2. For $215 \leq \lambda \leq 241$ nm and $278 \leq \lambda \leq 400$ nm, the
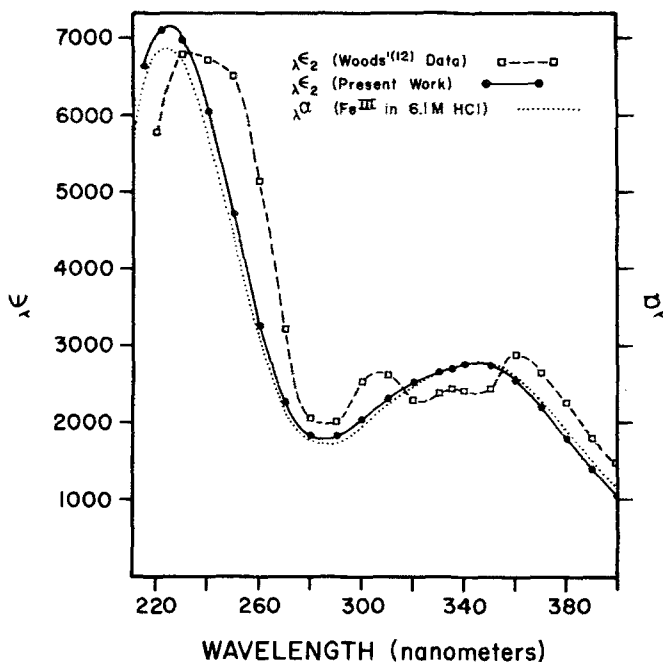
Fig. 4. Molar absorptivities of $FeCl_2^+$ obtained in our analyses of Wood's[12] data and our own are compared. Also shown on the same scale is the absorbance per molar cm of Fe(III) in 6.1 M HCl.

absorbance increases with increasing chloride concentration, whereas, for $241 \leqslant \lambda \leqslant 278$ nm, the absorbance at constant wavelength first decreases and then increases with increasing chloride concentration. This behavior can be explained by the presence of two complex species in solution, $FeCl^{2+}$ and $FeCl_2^+$, with $_\lambda\epsilon_2 > {}_\lambda\epsilon_1 > {}_\lambda\epsilon_0$ outside the limits $241 \leqslant \lambda \leqslant 278$ nm and $_\lambda\epsilon_2 > {}_\lambda\epsilon_1 < {}_\lambda\epsilon_0$ inside these wavelength limits. For low chloride concentrations isosbestic points appear to exist near 242 nm and 278 nm. These isosbestic points disappear at high chloride concentrations, indicating the formation of additional complexed species.

The data shown in Fig. 2 and the data of Woods[12] were analyzed according to the procedures described above. Each analysis was made using molar concentrations for all chemical species. The molar formation constants and molar absorptivities obtained in these analyses are

Table I. Experimental Data for 25°C[a]

λ (nm)	Woods[12] - 1 Molar			Present Work - 2.74 Molar		
	$\lambda\epsilon_0$	$\lambda\epsilon_1$	$\lambda\epsilon_2$	$\lambda\epsilon_0$	$\lambda\epsilon_1$	$\lambda\epsilon_2$
400	0.6	171	1467	0.0	210	1039
390	0.5	327	1781	0.0	392	1382
380	2.4	583	2236	0.0	687	1773
370	2.2	970	2616	0.0	1117	2192
360	3.0	1463	2844	0.0	1632	2558
350	3.0	1968	2432	0.0	2131	2739
340	7.0	2295	2395	0.0	2406	2738
335	10.	2338	2419	0.0	2420	2689
330	10.	2294	2349	2.6	2326	2636
320	25.	1975	2299	17.	1938	2510
310	61.	1494	2605	52.	1447	2291
300	155.	1106	2539	142.	1049	2024
290	355.	923	2000	377.	838	1814
280	855.	929	2056	869.	828	1827
270	1722.	1153	3184	1733.	1059	2256
260	2871.	1778	5136	2811.	1679	3248
250	3782.	2836	6493	3701.	2723	4716
240	4135.	4337	6699	4021.	4238	6037
230	3877.	6025	6778	3903.	5984	6988
222	---	---	---	3460.	6765	7094
220	3445.	6876	5792	---	---	---
215	---	---	---	3298.	6310	6638
210	3390.	5954	14787	---	---	---

$$\beta_1 = 3.06 \pm 0.43 \; M^{-1}$$
$$\beta_2 = 0.28 \pm 0.96 \; M^{-2}$$

$$\beta_1 = 5.34 \pm 0.14 \; M^{-1}$$
$$\beta_2 = 1.82 \pm 0.24 \; M^{-2}$$

[a]Each constant is defined on the molar concentration scale. The uncertainties given with each constant represent the 95% confidence limits.

given in Table I. The molar absorptivities of Fe^{3+}, $FeCl^{2+}$ and $FeCl_2^+$ are also shown graphically in Figs. 3 and 4. A detailed analysis of $\lambda\epsilon_0$ at 0.1 molal ionic strength which resolves the ultraviolet absorption of Fe^{3+} into two Gaussian bands is presented by Brown and Kester.[17]

The data obtained in one of our investigations of ferric hydrolysis in 0.68 molal NaCl are shown in Fig. 5. Within the range $220 \leqslant \lambda \leqslant 400$ three absorbance peaks are observed. The peak near 297 nm is due principally to $FeOH^{2+}$[11] and the peak at 335 nm is identified with $FeCl^{2+}$. The peak at 220 nm is principally a summation of $\lambda\epsilon_1$ and $\lambda\epsilon_0$
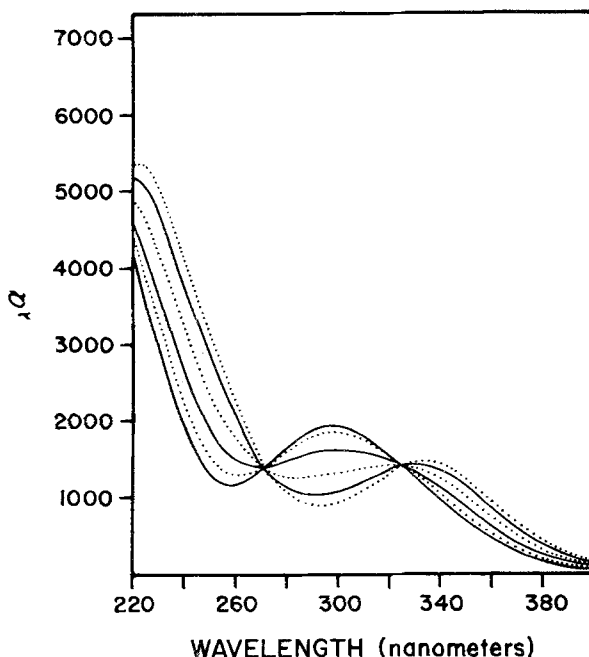
Fig. 5. Absorbance per molar centimeter of Fe(III) is shown as a function of wavelength and pH ($-\log[H^+]$) for iron in 0.68 molal NaCl. The pH values conjugate to each curve are (from top to bottom at 271 nm $\leqslant \lambda \leqslant$ 327 nm): pH = 4.17, 3.87, 3.48, 3.08, 2.64, 2.16. Outside the range 271 nm $\leqslant \lambda \leqslant$ 327 nm this order is inverted.

in approximately a 2:1 ratio. As was the case in our earlier spectrophotometric investigation in 0.68 m NaClO$_4$,[11] an isosbestic point is observed in the vicinity of 271 nm. An additional isosbestic point is observed in these experiments near 327 nm. The results of analyses of the experiment shown in Fig. 5 and two additional experiments over a more limited range of wavelengths are given in Table II.

Using Eq. (10), our analyses directly provide a series of constants R_0 through R_4. In very acidic media, R_3 and R_4 are identified as β_1 and β_2. The parameters R_0, R_1 and R_2 are equal to $_\lambda\epsilon_0$, $_\lambda\epsilon_1\beta_1$ and $_\lambda\epsilon_2\beta_2$. The constants $_\lambda\epsilon_1$ and $_\lambda\epsilon_2$ are then calculated as $_\lambda\epsilon_1 = R_1/R_3$ and $_\lambda\epsilon_2 = R_2/R_4$. When Eq. (10) is applied to weakly acidic media the following identities are established:

$$\mathring{\beta}_1 = R_3\theta^{-1}, \; \mathring{\beta}_2 = R_4\theta^{-1}, \; _\lambda\epsilon_3 = R_1/R_3, \; _\lambda\epsilon_4 = R_2/R_4 \tag{11}$$

and

$$R_0 = \theta\left(_\lambda\epsilon_0 + _\lambda\epsilon_1\beta_1[Cl^-] + _\lambda\epsilon_2\beta_2[Cl^-]^2\right) \tag{12}$$

Table II. Experimental Data for 0.68 m NaCl at 25.0°C[a]

λ (nm)	$_\lambda R_0$-A	$_\lambda R_0$-B	$_\lambda R_0$-C	$_\lambda \epsilon_3$-A	$_\lambda \epsilon_3$-B	$_\lambda \epsilon_3$-C	Average $_\lambda \epsilon_4$
400	---	---	193	---	---	69	0
390	---	---	303	---	---	111	0
380	---	---	470	---	---	181	0
370	---	---	718	---	---	299	0
360	967	1023	1016	498	394	472	385
350	1248	1323	1314	748	623	709	493
340	1374	1516	1508	1043	925	1006	601
330	1428	1510	1494	1377	1270	1334	712
320	1246	1328	1303	1681	1625	1641	968
310	993	1052	1029	1920	1907	1909	1262
300	---	852	835	---	2045	2026	1291
290	---	803	810	---	1992	1979	1245
280	---	888	1012	---	1722	1715	1130
270	---	---	1528	---	---	1386	1370
260	---	---	2379	---	---	1148	708
250	---	---	3384	---	---	1278	447
240	---	---	4395	---	---	1932	0
230	---	---	5312	---	---	3058	1077
220	---	---	5547	---	---	4319	2569

Experiment[b]	$\overset{*}{\beta}_1 = R_3 \theta^{-1}$	$\overset{*}{\beta}_2 = R_4 \theta^{-1}$
A	$(1.97 \pm 0.38) \times 10^{-3}$ M	$(9.5 \pm 17) \times 10^{-8}$ M^2
B	$(1.75 \pm 0.36) \times 10^{-3}$ M	$(0.4 \pm 28) \times 10^{-8}$ M^2
C	$(2.17 \pm 0.60) \times 10^{-3}$ M	$(1.3 \pm 23) \times 10^{-8}$ M^2
Average	$(1.96 \pm 0.54) \times 10^{-3}$ M	$(3.7 \pm 12) \times 10^{-8}$ M^2

[a]Absorptivities are defined on the molar concentration scale. The constant $_\lambda R_0$ is defined in terms of the molar absorptivities of Fe^{3+}, $FeCl^{2+}$ and $FeCl_2^+$ by Eq. (12). [b]The results of three experiments are shown. The uncertainties given with each constant represent the 95% confidence limits. The constants $\overset{*}{\beta}_1$ and $\overset{*}{\beta}_2$ were obtained using Eqs. (10) and (11) and $\theta^{-1} = 3.08$.

In order to calculate the quantities $\overset{*}{\beta}_1$ and $\overset{*}{\beta}_2$ from data obtained in 0.68 molal NaCl, it is necessary to determine the value of θ^{-1} appropriate to 0.68 molal NaCl. Using Eq. (9) and the formation constants $\beta_1 = 2.80 M^{-1}$ and $\beta_2 = 0.45\ M^{-2}$ which we have previously determined at 0.68 molal ionic strength,[7] θ^{-1} is calculated as: $\theta^{-1} = 3.08$. The

parameter $_\lambda R_0$, obtained directly in our data analysis, can be compared with the parameter $_\lambda R_0'$ obtained by independent means. $_\lambda R_0'$ was calculated using $_\lambda \epsilon_0$, $_\lambda \epsilon_1$ and $_\lambda \epsilon_2$ from the data in Figs. 3 and 4; from β_1 and β_2 obtained in 0.68 molal media; and from Eq. (12). The parameters $_\lambda R_0$ and $_\lambda R_0'$ are compared in Fig. 6. This figure also shows $_\lambda \epsilon_3$ determined in 0.68 molal NaCl in the present work, and our previous determinations of $_\lambda \epsilon_3$ in 0.68 molal NaClO$_4$ over a limited range of wavelengths.
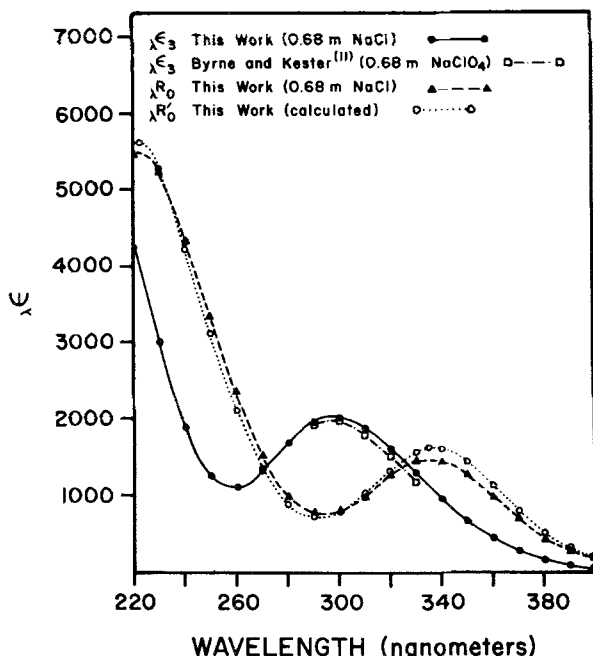

Fig. 6. The molar absorptivity of FeOH^{2+} ($_\lambda \epsilon_3$) obtained in 0.68 m NaCl (this work) and 0.68 m NaClO$_4$[11] are compared. Also shown is the molar absorptivity parameter, $_\lambda R_0$: (a) obtained directly in our ferric hydrolysis experiments in 0.68 m NaCl, and (b) calculated using Eq. (12) and the results of our ferric chloride complexation experiments.

4. DISCUSSION

Our results do not support the argument[5] that unaccounted for higher complexes can explain the discrepancy between the results of Woods et al.[3] and those of Rowley and Sutin.[5] While it is correct that the spectrophotometric analysis of Woods et al.[3] does not account for the existence of significant FeCl$_2^+$ complexation in their test media,

their choice of wavelength apparently minimized the errors present in their single wavelength analysis. Our analyses indicate that when the effects of $FeCl_2^+$ are accounted for, then the potentiometric and spectrophotometric results of Woods et al.[3] are consistent and are in good agreement with the present work, and the potentiometric results of Byrne and Kester.[7]

The formation constants of $FeCl^{2+}$ given in Table I are nearly identical to the results given by the Woods et al.[3] curve in Fig. 1. At 1 M ionic strength Woods et al.[3] obtained $\beta_1 = 2.89$ M^{-1} by potentiometry and $\beta_1 = 2.95$ M^{-1} by spectrophotometry at 335 nm. Our reanalysis of Woods[12] data produced the results $\beta_1 = 3.06 \pm 0.43$ M^{-1} where the uncertainty represents the 95% confidence limits. In a recent potentiometric study, Khachaturyan and Belyakova[18] obtained $\beta_1 = 3.3$ M^{-1} at 1 M ionic strength. In our experiment (shown in Fig. 2) the molal ionic strength was 3.0 molal. The molar scale ionic strength varied slightly under these conditions: $I = 2.74 \pm 0.06$ M. The formation constant which we obtained at this ionic strength is $\beta_1 = 5.34 \pm 0.14$ M^{-1}. The interpolated result of Woods et al.[3] at $I = 2.74$ M is $\beta_1 = 5.6$ M^{-1}. At $I = 3$ M Khachaturan and Belyakova[18] obtained $\beta_1 = 5.7$ M^{-1} and Woods[12] obtained $\beta_1 = 6.6$ M^{-1}.

The formation constant of $FeCl_2^+$ at 1 M ionic strength, $\beta_2 = 0.28 \pm 0.96$ M^{-2}, is not well defined by our analysis. At 2.74 M ionic strength however, the 95% confidence limits given for β_2 are reasonably small: $\beta_2 = 1.82 \pm 0.24$ M^{-2}. These observations are consistent with the general magnitudes of the formation constants in each medium. According to the formation constants given in Table I, $FeCl_2^+$ constitutes as much as 46% of the total iron in the 2.74 M solutions but no more than 6% in the 1 M solutions. It is possible that this is also the reason that $_\lambda\epsilon_2$ produced by analysis of Woods[12] data does not demonstrate a very smooth variation with wavelength, and demonstrates only fair agreement with $_\lambda\epsilon_2$ produced by analysis of our 2.74 M media. Relatively few values of β_2 are available for comparison with the determination in this work. However, the values produced by our potentiometric study,[7] $\beta_2 = 0.45$ M^{-2} at $I = 0.68$ molal, and the study of Khachaturyan and Belyakova,[18] $\beta_2 = 2.45$ M^{-2} at $I = 3.0$ M, are consistent with our spectrophotometric determinations at adjacent ionic strengths. The ionic strength dependence of β_2 is too poorly known to apply corrections to results at different ionic strengths. However, the results of Khachaturyan and Belyakova indicate that such corrections would diminish the differences between their $I = 3.0$ M results and our $I = 2.74$ M results.

The molar absorptivity curves given for Fe^{3+} (Fig. 3) at 1 and 2.74 molar ionic strengths are in good agreement. Within the range $220 \leqslant \lambda \leqslant 400$ nm a single absorbance maximum occurs near 240 nm. The molar absorptivity curves given for $FeCl^{2+}$ at each ionic strength are also in good agreement. The $FeCl^{2+}$ species has an absorbance maximum near 335 nm and a more intense maximum near 220 nm. The molar absorptivity curves shown for $FeCl_2^+$ (Fig. 4) are distinctly different from those of the Fe^{3+} and $FeCl^{2+}$ species. The $FeCl_2^+$ species has an intense absorbance maximum near 220 nm and appears to have two poorly resolved maxima at wavelengths somewhat above and below 335 nm. At all wavelengths $_\lambda\epsilon_0 < _\lambda\epsilon_2$ and $_\lambda\epsilon_1 < _\lambda\epsilon_2$. Due to the poorer alignment between the $_\lambda\epsilon_2$ curves than was obtained for $_\lambda\epsilon_0$ and $_\lambda\epsilon_1$ at each ionic strength an additional evaluation of $_\lambda\epsilon_2$ was made.

Our results indicate that no more than 46% of the total iron in the 2.74 M solution is present as $FeCl_2^+$. If the $FeCl_2^+$ is a major absorbing species at higher chloride concentrations before the $FeCl_3$ and $FeCl_4^-$ become important, our study predicts that the molar absorbance in such a region should approach the characteristics of $_\lambda\epsilon_2$. The Fe(III) spectrum obtained in 6.1 M HCl at 25.0°C closely resembles our computed values of $_\lambda\epsilon_2$ (Fig. 4). This may indicate the Fe(III) in 6.1 M HCl is dominantly $FeCl_2^+$ and higher order complexes which are known to exist at higher chloride concentrations[19,20] are not important under these conditions. This interpretation is consistent with the study of Gamlen and Jordan,[20] in which the ultraviolet absorbance spectra of $FeCl_2^+$, $FeCl_3$, and $FeCl_4^-$ were calculated. The curve $_\lambda\epsilon_2$ which we obtained in 2.74 M media resembles in shape the $_\lambda\epsilon_{FeCl_2^+}$ curve given by Gamlen and Jordan[20] but is notably different from $_\lambda\epsilon FeCl_3$), which has distinct minima at 310 nm and 360 nm and an absorbance maximum at 400 nm. The well established $_\lambda\epsilon_{FeCl_4}$ characteristics given by them are also distinctly different from the absorbance curves which we have obtained.

Our data were quantitatively analyzed for the influence of higher order species using two approaches:

Eq. (7) was used to analyze our 2.74 M absorbance data at chloride concentrations up to only 0.723 M. This analysis produced the following results: $\beta_1 = 5.29 \pm 0.27\ M^{-1}$ and $\beta_2 = 2.39 \pm 1.06\ M^{-2}$. These constants are in quite good agreement with those produced in the analysis using our whole data set. The result for β_1 is essentially unaltered even though the ratio $[FeCl_3]/[FeCl^{2+}]$ is 15 times smaller at $[Cl^-] = 0.723\ M$ than at $[Cl^-] = 2.8\ M$. This indicates that if significant

$FeCl_3$ is present in our solutions, its presence does not influence our determination of β_1. The second approach was based on an expansion of Eq. (7) to assume the presence of $FeCl_3$. Analysis of our 2.74 M absorbance data then produced the following constants: $\beta_1 = 6.01 \pm 1.9\ M^{-1}$, $\beta_2 = 8.3 \pm 12.6\ M^{-2}$, $\beta_3 = 1.5 \pm 3.6\ M^{-3}$. Although the constants β_2 and β_3 are too poorly defined by this analysis to permit a reasonable assessment of their magnitudes, we note that the best estimate for β_1 is near the lower bound of the values shown in Fig. 1, and the upper 95% confidence limit is somewhat less than the upper bound values in Fig. 1.

We conclude that the higher order complexes, $FeCl_3$ and $FeCl_4^-$, do not importantly influence the β_1 values produced in the analyses of our data and the spectrophotometric data of Woods.[12] Potentiometric and spectrophotometric determinations of β_1 at chloride concentrations up to 2.8 M are in good agreement[3,7,18,25] and do not demonstrate a necessity for considering complexes higher than $FeCl_2^+$. The β_2 values produced in our analyses (Table I) are sensitive to assumptions regarding the identity of the highest order ferric species in our solutions, and are therefore less reliable than the values given for β_1.

In the recent work of Strahm et al.[21] an additional requirement is made on the principle of activity coefficient constancy at constant ionic strength. The constant $\beta_1 = 7.6\ M^{-1}$ ($I = 2.6\ M$) determined using Fe(III) concentrations as high as 0.25 M is used in their determinations of β_2 and β_3 at high chloride concentrations. The assumptions inherent in this procedure are thereby propagated into the determinations of the higher order constants. A more immediate difficulty in the determinations of Strahm et al.[21] is the inconsistency of their β_2 and β_3 values. Their β_2 determinations were made in media assumed free of significant $FeCl_3$ formation. However, according to their values of β_2 and β_3, $[FeCl_3] > [FeCl_2^+]$ within the range of conditions they used to determine β_2.

Our experiments conducted at 25°C in weakly acidic 0.68 molal NaCl produced a $FeOH^{2+}$ molal formation constant which is in good agreement with previous results. Our result in the present work $^*\beta_1 = 1.96 \times 10^{-3}\ M$ is the average of three experiments. In our previous spectrophotometric study in 0.68 molal $NaClO_4$ we obtained $^*\beta_1 = 1.84 \times 10^{-3}\ M$. Milburn and Vosburgh[22] obtained $^*\beta_1 = 1.81 \times 10^{-3}\ M$ in 0.68 M $NaClO_4$ at the same temperature. In a potentiometric study at 25°C and 0.68 molal ionic strength[7] we obtained $^*\beta_1 = 1.90 \times 10^{-3}\ M$.

In a study of the aquation kinetics of Fe(III) chloride,[14] Koren and Perlmutter-Hayman predict the existence of $FeOHCl^+$ in weakly

acidic chloride media. When this species is present in significant concentrations, the constant R_3 in Eq. (10) is equal to $({}^*\beta_1 + {}^*\beta_{11}[Cl^-])\theta$ where

$$^*\beta_{11} = [FeOHCl^+][H^+]/[Fe^{3+}][Cl^-] \tag{13}$$

and the constant R_1 is equal to $({}_\lambda\epsilon_3{}^*\beta_1 + {}_\lambda\epsilon_{11}{}^*\beta_{11}[Cl^-])\theta$ where ${}_\lambda\epsilon_{11}$ is the molar absorptivity of $FeOHCl^+$.

Koren and Perlmutter-Haymen[14] calculate that ${}^*K_{11} = [FeOHCl^+][H^+]/[FeCl^{2+}] = (1.2 \pm 0.2) \times 10^{-2}$ M at $I \simeq 0.4$. Using the ferric chloride complexation results in our study we can then calculate ${}^*\beta_{11} \simeq 3.6 \times 10^{-2}$. If the presence of this species in our hydrolysis experiments is assumed it follows that

$$R_3\theta^{-1} = {}^*\beta_1 + {}^*\beta_{11}[Cl^-] \tag{14}$$

We have calculated $R_3\theta^{-1} = (1.96 \pm 0.54) \times 10^{-3}$ M. Using the formation constant ${}^*\beta_1 = (1.84 \pm 0.14) \times 10^{-3}$ M obtained in 0.68 molal $NaClO_4$ yields ${}^*\beta_{11} = 1.8 \times 10^{-4}$ which is 200 times smaller than the value of Koren and Perlmutter-Hayman.[14] Considering the upper 95% confidence limits in this calculation yields ${}^*\beta_{11} \lesssim 1 \times 10^{-3}$. This value is approximately 36 times smaller than the Koren and Perlmutter-Hayman result. Our assessment of ${}^*\beta_{11}$ using Eq. (14) is sensitive to the calculated value of θ^{-1} [Eq. (9)]. If the constants determined and estimated by Rowley and Sutin[5] ($\beta_1 = 5.2$ M^{-1}, $\beta_2 \simeq 5.2$ M^{-2}) are used to determine θ^{-1}, we calculate ${}^*\beta_{11} = 3.7 \times 10^{-3}$. This value is also substantially smaller than the Koren and Perlmutter-Hayman[14] result.

Fig. 6 shows that ${}_\lambda\epsilon_3$ determined in this study and in 0.68 molal $NaClO_4$ are nearly identical. Whereas in $NaClO_4$ the quotient $R_1/R_3 = {}_\lambda\epsilon_3$, in a solution containing $FeOHCl^+$ the same quotient is given by:

$$R_1/R_3 = ({}_\lambda\epsilon_3{}^*\beta_1 + {}_\lambda\epsilon_{11}{}^*\beta_{11}[Cl^-])/({}^*\beta_1 + {}^*\beta_{11}[Cl^-]) \tag{15}$$

This indicates that the agreement shown in Fig. 6 will not be obtained unless ${}^*\beta_1 >> {}^*\beta_{11}[Cl^-]$ or ${}_\lambda\epsilon_3 = {}_\lambda\epsilon_{11}$. Our results indicate that in 0.68 molal NaCl the former condition holds. If ${}^*\beta_{11} \gtrsim 3.7 \times 10^{-3}$, however, then $[FeOHCl^+]/[FeOH^{2+}] \gtrsim 1.3$ at any pH in 0.68 molal NaCl. In this case our observations require that ${}_\lambda\epsilon_{11} \simeq {}_\lambda\epsilon_3$.

Our analysis of Fe(III) hydrolysis in NaCl produced the parameter $\theta({}_\lambda\epsilon_0 + {}_\lambda\epsilon_1\beta_1[Cl^-] + {}_\lambda\epsilon_2\beta_2[Cl^-]^2)$. A comparison of this parameter (a) experimentally determined in our hydrolysis experiments, and (b) calculated using the results of our various ferric chloride complexation experiments, shows reasonably good agreement (Fig. 6), and demonstrates consistency between our determinations in weak and strong acid

media.

Recent kinetic studies have examined the relative importance of inner and outer sphere ferric chloride complexation[6,23,24] at 1 M ionic strength. Perlmutter-Hayman and Tapuhi[24] determined β_1(IN) directly as β_1(IN) = 2.95 ± 0.14 and calculated β_1(OUT) from β_1 = β_1(IN) + β_1(OUT), where β_1 is identified with the formation constant which is obtained in an equilibrium investigation. Using the result of Rowley and Sutin,[5] β_1 = 5.2 M, they calculated β_1(OUT) ⩽ 2.2 M^{-1}. However, they also noted that whereas β_1(OUT) can be determined directly from kinetic measurements if the reciprocal of relaxation time plotted against ([Fe^{3+}] + [Cl$^-$]) is significantly curved, the curvature expected when β_1(OUT) is as large as 2.2 M^{-1} is not observed. Schwarz and Dodson[6] obtained β_1(IN) = 2.9 M^{-1} through kinetic methods and calculated β_1(OUT) = 2.2 M^{-1} by difference using β_1 = 5.2 M^{-1}. Additionally, they obtained $_\lambda\epsilon_1$(IN) = 2500 through kinetic measurements and calculated β_1(OUT) using the relationship

$$_\lambda\epsilon_1 = {_\lambda\epsilon_1}(IN)\beta_1(IN)/(\beta_1(IN) + \beta_1(OUT)) \tag{16}$$

which is obtained by assuming $_\lambda\epsilon_1$(OUT) is negligible at 340nm. They obtained the result β_1(OUT) = 2.3 M^{-1} by using the Rowley and Sutin molar absorbance, $_{340}\epsilon_1$ = 1380, at I = 1 M.

When our result, β_1 = 3.06 ± 0.43 M^{-1}, is used to calculate β_1(OUT) by difference using the β_1(IN) result of Perlmutter-Hayman and Tapuhi[23] we find that:

$$\beta_1(OUT) \leqslant 0.6 \ M^{-1}$$

In addition, if our $_{340}\epsilon_1$ = 2295 result at I = 1 M is used in Eq. (16), we calculate that β_1(OUT) ≃ 0.3 M^{-1}.

From our equilibrium calculations and the kinetic studies of Schwarz and Dodson[6,23] and Perlmutter-Hayman and Tapuhi[24] we conclude that β_1(OUT) is significantly less than the upper bound β_1(OUT) estimates which are dependent on Rowley and Sutin's[5] 1M ionic strength determinations. Our reevaluation of β_1(OUT) based on our β_1 calculations at 1 M ionic strength are in general agreement with the assessment of Rowley and Sutin that β_1(OUT) ⩽ 1M^{-1} at 1 M ionic strength.

ACKNOWLEDGMENTS

REFERENCES

1. E. Rabinowich and W. A. Stockmayer, *J. Am. Chem. Soc.* **64**, 335 (1942).
2. H. Coll, R. V. Nauman, and P. W. West, *ibid.* **81**, 1284 (1959).
3. M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.* **1**, 55 (1962).
4. R. N. Heistand and A. Clearfield, *J. Am. Chem. Soc.* **85**, 2566 (1963).
5. J. K. Rowley and N. Sutin, *J. Phys. Chem.* **74**, 2043 (1970).
6. H. A. Schwarz and R. W. Dodson, *ibid.* **80**, 2801 (1976).
7. R. H. Byrne and D. R. Kester, *Mar. Chem.* **4**, 275 (1976).
8. R. Kruh, *J. Am. Chem. Soc.* **76**, 4865 (1954).
9. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
10. A. Barr, J. Goodnight, J. Sall, and J. Helwig, *A User's Guide to SAS 76*, (Sparks Press, 1976), p. 193.
11. R. H. Byrne and D. R. Kester, *J. Solution Chem.* **7**, 373 (1978).
12. M. J. M. Woods, *Studies of Complex Ion Equilibria I. Iron (III) Chloride System II. Thallium(III) Chloride System.* (University Microfilms, Inc., Ann Arbor, Michigan, 1961), pp. 208.
13. D. Dyrssen, D. Jagner, and F. Wengelin, *Computer Calculation of Ionic Equilibria and Titration Procedures* (Almquest and Wiksell, Stockholm, Sweden, 1969), pp. 250.
14. R. Koren and B. Perlmutter-Hayman, *Inorg. Chem.* **11**, 3055 (1972).
15. W. A. E. McBryde, *Analyst* **94**, 337 (1969).
16. W. A. E. McBryde, *ibid.* **96**, 739 (1971).
17. M. F. Brown and D. R. Kester, *Appl. Spectroscopy* **34**, 377 (1980).
18. O. B. Khachaturyan and A. A. Belyakova, *Russ. J. of Phys. Chem.* **50**, 1424 (1976).
19. M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi, and T. Kitagawa, *Bull. Chem. Soc. Japan* **30**, 433 (1957).
20. G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).
21. U. Strahm, R. C. Patel, and E. Matijevic, *J. Phys. Chem.* **83**, 1689 (1979).
22. R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.* **77**, 1352 (1955).
23. H. A. Schwarz and R. W. Dodson, *J. Phys. Chem.* **80**, 2543 (1976).
24. B. Perlmutter-Hayman and E. Tapuhi, *J. Coord. Chem.* **8**, 75 (1978).
25. A. W. Fordham, *Aust. J. Chem.* **22**, 1111 (1969).