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# Spectrophotometric Determination of Formation Constants of Iron(III) Complexes with Chloride Ion in Dimethyl Sulfoxide[*1]

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The formation constants of $FeCl^{2+}$ and $FeCl_2{}^+$ have been measured in dimethyl sulfoxide (DMSO) containing $Fe(ClO_4)_3$, NaCl, $HClO_4$ and $NaClO_4$. Some spectrophotometric methods giving the formation constants and molar extinction coefficients of the complexes were developed and gave, on the average, $\log K_1 = 3.62$ and $\log K_2 = 2.10$, at 0.02 M $HClO_4$ and an ionic strength of 0.10 M at 25°C. It is rather surprising that these values are only slightly larger than those in *N*-methylacetamide, which is expected, however, to give much smaller values than DMSO, due to its extraordinarily large dielectric constant. The species formed between Fe(III) and $Cl^-$ ion is reasonably supposed to be a true complex bonded directly with each other and not an ion-pair association product. At higher concentrations of Fe(III), formation of polynuclear complexes can occur.

Dimethyl sulfoxide (DMSO) has recently come to be widely used as an advantageous medium for inorganic chemical reactions. Spectrophotometric and electron magnetic resonance studies showed that a small amount of tetrachloroferrate(III) ion was present in solution of iron(III) chloride in a number of organic solvents including DMSO, the formation being the smallest in the case of DMSO.[1] On the other hand, the predominant iron(III)

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[*1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, No. 2B104, April, 1967.

[1] T. B. Swanson and V. W. Laurie, *J. Phys. Chem.*, **69**, 244 (1965).

ion in DMSO was found to exist in the form of monochloroiron(III) complex ion in solutions of hexa-solvated iron(III) perchlorate and tetraethylammonium chloride at the concentration ratios of 1 and 2 between iron(III) and chloride ion when the concentration of iron(III) was $1.52 \times 10^{-4}$ M.[2,3]

In an investigation of the electron transfer reaction between iron(III) and iron(II) in DMSO catalyzed by chloride ion, the formation constants for the chloride ion-containing complexes were required to be known in order to estimate the individual rate constants, which have been already reported.[4] Consequently, the present work was undertaken to obtain formation constants, and a couple of methods of calculation based on spectrophotometrically observed data were developed for the purpose.

## Experimental

**Materials.** Commercial DMSO of analytical reagent grade was distilled under a reduced nitrogen atmosphere, shaken with activated alumina overnight, and redistilled under the same conditions. The purified DMSO contained water approximately at the concentration of 0.025 M at the highest, found using Karl Fischer reagent.

Crystals of $Fe(ClO_4)_3 \cdot 6DMSO$,[5] anhydrous sodium perchlorate and solutions of perchloric acid in DMSO were prepared by a procedure described previously.[6] Sodium chloride was twice recrystallized from water and dried.

**Apparatus.** A Beckman Model DU spectrophotometer with a thermostated cell compartment and quartz cells was used for the measurement of optical density.

## Results and Calculations

**Absorption Spectra.** Figure 1 shows the absorption spectra of iron(III) species in the absence and the presence of chloride ion in DMSO. Curve A is the spectrum of $Fe(DMSO)_6{}^{3+}$ (written $Fe^{3+}$ for simplicity), which agrees well with that of Drago and others.[3] Curve B represents the apparent spectrum of the mixture of $Fe^{3+}$ and $Fe(DMSO)_5Cl^{2+}$ ($FeCl^{2+}$ for simplicity). By using the values of $K_1$ as will be obtained below, the true molar extinction coefficients of $FeCl^{2+}$ at various wavelengths were calculated from Curves A and B, and then Curve C was drawn as the true spectrum of $FeCl^{2+}$. There is an absorption peak at 340 mμ in the spectrum of $FeCl^{2+}$, whereas none is observed in that of $Fe^{3+}$, and an isosbestic point at about 280 mμ is also recognized for the two spectra. The apparent spectra of iron(III) complexes in both solutions are not affected by acid concentration, indicating that the solvating DMSO molecule of iron(III) undergoes no appreciable solvolysis (proton donation), because DMSO is aprotic,[7] or rather slightly basic.[8]

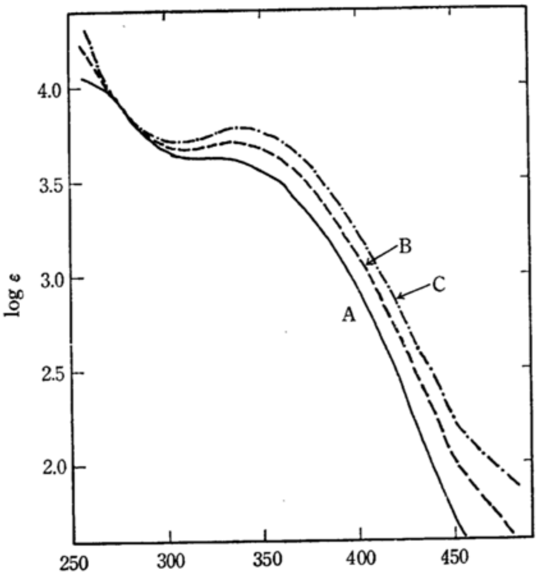

Fig. 1. Absorption spectra of $Fe^{3+}$ and $FeCl^{2+}$ in DMSO, $[HClO_4]=0.02$ M, $\mu=0.10$, 25°C.
A: ——— $Fe^{3+}$
B: – – – $[Fe(III)]=7.0\times10^{-5}$ M, $[Cl]=6.3\times10^{-4}$ M
C: —·—· $FeCl^{2+}$

**Continuous Variation Method.** Job's method of continuous variations[9] was used to indicate the formula of the prominent species, if any. Figure 2 shows the Job's curves at 450, 460 and 470 mμ with $C=[Fe(III)]+[Cl]=1.00\times10^{-2}$ M, $[HClO_4]=0.02$ M and $\mu=0.10$ M at 25°C, where [Fe(III)] and [Cl] stand for the total concentrations of iron(III) and chloride ion employed, respectively. The ordinate $Y$ is defined as the difference between the observed optical density and the optical density which would have been obtained if no complex formation had occurred. At the wavelengths used here, absorption caused by the free ligand was negligible. The abscissa $x$ is defined as $x=[Fe(III)]/C$.

Figure 3 shows the Job's curves at 400 mμ with $C_a=1.00\times10^{-3}$ M and $C_b=0.70\times10^{-3}$ M for

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[2] R. L. Carlson, Ph. D. Thesis, University of Illionis, 1962.

[3] R. S. Drago, D. M. Hart and R. L. Carlson, *J. Am. Chem. Soc.*, **87**, 1900 (1965).

[4] G. Wada and W. L. Reynolds, *Inorg. Chem.*, **5**, 1354 (1966).

[5] J. Selbin, W. E. Bull and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **16**, 219 (1961).

[6] J. Menashi, W. L. Reynolds and G. Van Auken, *Inorg. Chem.*, **4**, 299 (1965).

[7] T. B. Reddy, Ph. D. Thesis, University of Minnesota, 1960; I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).

[8] G. Wada and W. L. Reynolds, unpublished.

[9] P. Job, *Ann. Chim.*, 10E series, **9**, 113 (1928); *ibid.*, 11E series, **6**, 97 (1936).

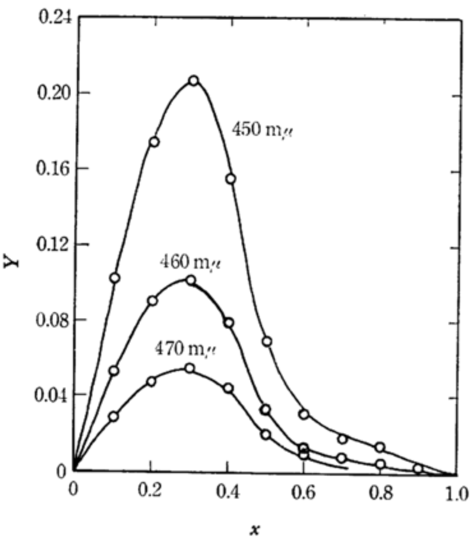

Fig. 2. Job's curves of Fe(III)+Cl$^-$ system in DMSO. $C=1.00\times10^{-2}$ M, [HClO$_4$]=0.02 M, $\mu=0.10$, 25°C.

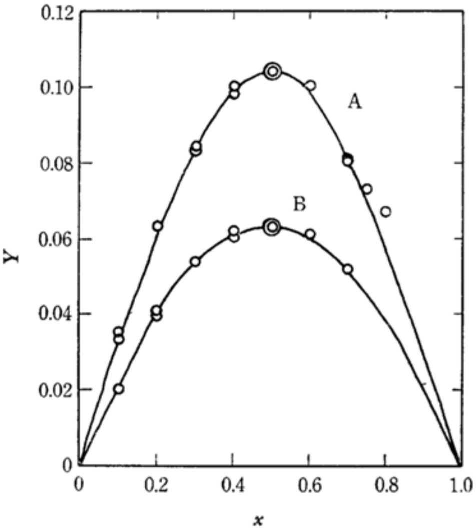

Fig. 3. Job's curves of Fe(III)+Cl$^-$ systems in DMSO. [HClO$_4$]=0.02 M, $\mu=0.10$, 25°C, 400 mμ.
A: $C_a=1.00\times10^{-3}$ M B: $C_b=0.70\times10^{-3}$ M

Curves A and B, respectively, as well. Other conditions were the same as in Fig. 2. Quite similar plots to those in Fig. 3 but with smaller $Y$ values, were obtained at 410 mμ, although they are omitted in the figure.

It would be reasonably concluded from Figs. 2 and 3 that, at a lower total concentration $C$, the 1 : 1 complex FeCl$^{2+}$ is predominantly formed, while, at a higher $C$, the system is more complicated, with the probable formation of polynuclear chloroiron(III) complexes, as well as polychloromononuclear iron(III) complexes. This is because the shift of the maximum point of $Y$ from $x=0.5$ to approximately 0.3 as $C$ is increased tenfold indicates the occurrence of polychloroiron(III) complexes, probably FeCl$_2{}^+$, and the sudden decrease in $Y$ values at $x>0.4$ in Fig. 2 suggests the formation of polynuclear iron(III) complexes containing chloride ion, with smaller molar extinction coefficients than those of FeCl$^{2+}$ and FeCl$_2{}^+$, although their formulas are unknown.

In the following part of the text, simpler systems will be mainly taken into account, where FeCl$^{2+}$ plays the leading role, except as otherwise noted.

**Calculation of $K_1$ from Job's Curves.** In the system where simply FeCl$^{2+}$ complex is formed, $Y$ and $K_1$ are expressed by the following relations, according to their definitions,

$$Y=\varepsilon_0[\mathrm{Fe}^{3+}]+\varepsilon_1[\mathrm{FeCl}^{2+}]-\varepsilon_0[\mathrm{Fe(III)}] \quad (1)$$

$$K_1=[\mathrm{FeCl}^{2+}]/[\mathrm{Fe}^{3+}][\mathrm{Cl}^-] \quad (2)$$

in which $\varepsilon_0$ and $\varepsilon_1$ are the molar extinction coefficients of Fe$^{3+}$ and FeCl$^{2+}$, respectively. By using the following relation

$$[\mathrm{Fe(III)}]=[\mathrm{Fe}^{3+}]+[\mathrm{FeCl}^{2+}] \quad (3)$$

Eq. (1) is rewritten as

$$Y=(\varepsilon_1-\varepsilon_0)[\mathrm{FeCl}^{2+}] \quad (4)$$

*Method I of Common Y.* In Fig. 3, consider a set of two points ($x_a$, $Y$) and ($x_b$, $Y$) on the Curves A and B, respectively, which have a common value of $Y$. Then, the following relation is established, where subscripts $a$ and $b$ correspond to the respective points on the Curves A and B,

$$K_1=\frac{[\mathrm{FeCl}^{2+}]_a}{[\mathrm{Fe}^{3+}]_a[\mathrm{Cl}^-]_a}=\frac{[\mathrm{FeCl}^{2+}]_b}{[\mathrm{Fe}^{3+}]_b[\mathrm{Cl}^-]_b} \quad (5)$$

By solving Eq. (5),

$$[\mathrm{FeCl}^{2+}]_a=[\mathrm{FeCl}^{2+}]_b=\frac{x_a(1-x_a)C_a{}^2-x_b(1-x_b)C_b{}^2}{C_a-C_b} \quad (6)$$

$$[\mathrm{Fe}^{3+}]_a=x_aC_a-[\mathrm{FeCl}^{2+}]_a \quad (7)$$

$$[\mathrm{Cl}^-]_a=(1-x_a)C_a-[\mathrm{FeCl}^{2+}]_a \quad (8)$$

and substituting for Eq. (5) the values from Eqs. (6), (7) and (8), the value of $K_1$ can be calculated. And $\varepsilon_1$ is also known from the following equation.

$$\varepsilon_1=\frac{Y}{[\mathrm{FeCl}^{2+}]_a}+\varepsilon_0 \quad (9)$$

Similar, but less complete methods have been reported by several researchers.(10) Table 1 shows an example of this method under the conditions $C_a=1.00\times10^{-3}$ M, $C_b=0.70\times10^{-3}$ M, [HClO$_4$]= 0.02 M and $\mu=0.10$ M at 25°C and gives the

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10) For instance, S. E. Turner and R. C. Anderson, *J. Am. Chem., Soc.*, **71**, 912 (1949); A. K. Mukerji and A. K. Dey, *J. Inorg. Nucl. Chem.*, **6**, 314 (1958); P. Sanyal, S. P. Sangal and S. P. Mushran, This Bulletin, **40**, 217 (1967).

TABLE 1. DERIVATION OF $K_1$ AND $\varepsilon_1$ BY THE METHOD I OF COMMON $Y$
$C_a=1.00\times10^{-3}$ M, $C_b=0.70\times10^{-3}$ M, $[HClO_4]=0.02$ M, $\mu=0.10$ M at 25°C.
$\varepsilon_0^{400}=845$, $\varepsilon_0^{410}=520$ $\text{M}^{-1}\,\text{cm}^{-1}$

| $\lambda$ m$\mu$ | $Y$ | $x_a$ | $x_b$ | $K_1\times10^{-3}$ $\text{M}^{-1}$ | $\varepsilon_1\times10^{-3}$ $\text{M}^{-1}\,\text{cm}^{-1}$ |
|---|---|---|---|---|---|
| 400 | 0.060 | 0.18 | 0.36 | 2.6 | 1.36 |
| 400 | 0.055 | 0.17 | 0.30 | 4.2 | 1.28 |
| 400 | 0.050 | 0.15 | 0.26 | 3.9 | 1.30 |
| 400 | 0.045 | 0.14 | 0.23 | 5.4 | 1.25 |
| | | | | Mean | 1.30±0.05 |
| 410 | 0.035 | 0.16 | 0.31 | 2.2 | 0.88 |
| 410 | 0.030 | 0.14 | 0.24 | 3.7 | 0.81 |
| | | | Mean | 3.7±1.2 | 0.85±0.04 |

averaged values of $K_1=(3.7\pm1.2)\times10^3\ \text{M}^{-1}$ and $\varepsilon_1^{400}=(1.30\pm0.05)\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ and $\varepsilon_1^{410}=(0.85\pm0.04)\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$.

In considering $Y$ values for this method, such ranges of $Y$ had better be avoided as where the differences between $x_a$ and $x_b$ are too small ($x_a<0.1$) or where the lower curve is too broad near its maximum point ($x_b>0.4$). In addition, only the left halves of the curves must be used, otherwise polynuclear iron(III) species might become effective.

Similarly, at the concentration of acid $[HClO_4]=0.07$ M, other conditions being the same, the method gave $K_1=(3.8\pm0.6)\times10^3\ \text{M}^{-1}$ and $\varepsilon_1^{400}=(1.24\pm0.02)\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$. No dependence of $K_1$ upon acid concentration was recognized.

At 41.1°C and $[HClO_4]=0.02$ M, $K_1=(6.3\pm1.5)\times10^3\ \text{M}^{-1}$ and $\varepsilon_1^{400}=(1.29\pm0.02)\times10^3\ \text{M}^{-1}$ $\text{cm}^{-1}$ were obtained, which gave approximate values of $\Delta H_1=7$ kcal/mol and $\Delta S_1=40$ cal $\text{deg}^{-1}$ $\text{mol}^{-1}$, in association with data at 25°C.

Other possible methods for obtaining $K_1$ from Job's curves will be described briefly in the following.

*Method II Using Two Maxima.* The $Y$ values of the two maximum points on the two curves in Fig. 3 are denoted as $Y_a^m$ and $Y_b^m$, respectively. At these points, as $[Fe^{3+}]=[Cl^-]$, the following relation holds.

$$K_1=\frac{Y_a^m/(\varepsilon_1-\varepsilon_0)}{\{(C_a/2)-Y_a^m/(\varepsilon_1-\varepsilon_0)\}^2}=\frac{Y_b^m/(\varepsilon_1-\varepsilon_0)}{\{(C_b/2)-Y_b^m/(\varepsilon_1-\varepsilon_0)\}^2}\qquad(10)$$

By solving this equation, the values of $\varepsilon_1$ and therefore $K_1$ will be obtained.

$$\varepsilon_1=\frac{2(Y_a^m\sqrt{Y_b^m}-Y_b^m\sqrt{Y_a^m})}{C_a\sqrt{Y_b^m}-C_b\sqrt{Y_a^m}}+\varepsilon_0\qquad(11)$$

The results of the numerical calculation at $[HClO_4]=0.02$ M and $\mu=0.10$ M are that $K_1=3.1\times10^3\ \text{M}^{-1}$, $\varepsilon_1^{400}=1.30\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ and $\varepsilon_1^{410}=0.81\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ at 25°C, and $K_1=6.7\times10^3$ $\text{M}^{-1}$, $\varepsilon_1^{400}=1.27\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ and $\varepsilon_1^{410}=0.79\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$ at 41°C. This method is less accurate than the previous one.

*Method III using a Single Curve.* Taking a pair of points $(x_1, Y_1)$ and $(x_2, Y_2)$ on a single Job's curve, and defining the ratio $Y_1/Y_2=[FeCl^{2+}]_1/[FeCl^{2+}]_2$ as $\alpha$, the following relation is established.

$$K_1=\frac{\alpha[FeCl^{2+}]_2}{(x_1C-\alpha[FeCl^{2+}]_2)\{(1-x_1)C-\alpha[FeCl^{2+}]_2\}}=\frac{[FeCl^{2+}]_2}{(x_2C-[FeCl^{2+}]_2)\{(1-x_2)C-[FeCl^{2+}]_2\}}\qquad(12)$$

Solving Eq. (12), a value for $[FeCl^{2+}]_2$ is obtained and therefore $K_1$.

$$[FeCl^{2+}]_2=\left\{\frac{\alpha x_2(1-x_2)-x_1(1-x_1)}{\alpha(\alpha-1)}\right\}^{1/2}C\qquad(13)$$

Then $\varepsilon_1$ is known from Eq. (9).

The results of the numerical calculation from 9 sets of data at $[HClO_4]=0.02$ M, $\mu=0.1$ M at 25°C when $C=1.00\times10^{-3}$ M are $K_1=(3.7\pm0.7)\times10^3\ \text{M}^{-1}$ and $\varepsilon_1^{400}=(1.28\pm0.03)\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}$.

**Determination of $K_1$ and $K_2$ from Linear Relations of $\bar{\varepsilon}$.** *Determination of* $K_1$. At concentrations of iron(III) and chloride ion low enough so that the amount of $FeCl_2^+$ formed is negligible, the apparent molar extinction coefficient of iron(III), $\bar{\varepsilon}$, is defined as

$$\bar{\varepsilon}[Fe(III)]=\varepsilon_0[Fe^{3+}]+\varepsilon_1[FeCl^{2+}]\qquad(14)$$

By combining Eq. (14) with Eqs. (2) and (3), $\bar{\varepsilon}$ is expressed by a relationship linear with respect to $(\bar{\varepsilon}-\varepsilon_0)/[Cl^-]$.

$$\bar{\varepsilon}=\varepsilon_1-\frac{1}{K_1}\frac{\bar{\varepsilon}-\varepsilon_0}{[Cl^-]}\qquad(15)$$

Accordingly, plotting $\bar{\varepsilon}$ *vs.* $(\bar{\varepsilon}-\varepsilon_0)/[Cl^-]$ will give $-1/K_1$ as the slope and $\varepsilon_1$ as the intercept. Figure 4 shows this relation when $[Fe(III)]=3.00\times10^{-4}$ M and $[Cl]=8.0\times10^{-5}$—$6.5\times10^{-3}$ M were used at $[HClO_4]=0.02$ M and $\mu=0.10$ M at 25°C, observed at 400 m$\mu$. As the concentration of chloride ion is raised, corresponding to a point moving from right to left on the abscissa, the observed $\bar{\varepsilon}$ goes off the straight line, indicating that the occurrence of $FeCl_2^+$ is no longer negligible. Only the linear part is to be taken account of so far as the calculation of $K_1$ is concerned. At first, [Cl] is used in place of $[Cl^-]$ and a rough value of $K_1$ is estimated from the slope. By using the first approximate $K_1$, a second approximate $[Cl^-]$ is calculated at the corresponding [Cl], and a more accurate straight line is drawn, followed by the recalculation of a more accurate $K_1$. On repeating the cycles until a self-consistent $K_1$ and $[Cl^-]$'s are obtained, the most reliable $K_1$ is finally decided. Actually, two cycles were enough for

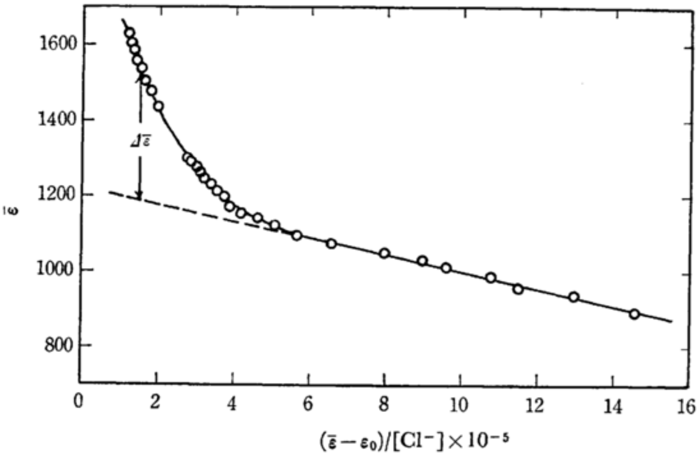

Fig. 4. The plot of $\bar{\varepsilon}$ *vs.* $(\bar{\varepsilon}-\varepsilon_0)/[Cl^-]$ at 400 m$\mu$. $[HClO_4]=0.02$ M, $\mu=0.10$, 25°C.

the purpose. Computation for the slope and the intercept of a straight line was performed by the method of least squares.

As results, $K_1=(4.2\pm0.1)\times10^3$ M$^{-1}$, and $\varepsilon_1{}^{400}=(1.24\pm0.01)\times10^3$ M$^{-1}$ cm$^{-1}$, both of which are in fairly good agreement with the values from Job's curves.

*Determination of* $K_2$. $K_2$ is defined as the stepwise formation constant of $FeCl_2{}^+$ in DMSO.

$$K_2 = [FeCl_2{}^+]/[FeCl^{2+}][Cl^-] \qquad (16)$$

Equations (3) and (14) can be extended to the following, by taking the presence of $FeCl_2{}^+$ into account,

$$[Fe(III)] = [Fe^{3+}] + [FeCl^{2+}] + [FeCl_2{}^+] \quad (17)$$

$$\bar{\varepsilon}[Fe(III)] = \varepsilon_0[Fe^{3+}] + \varepsilon_1[FeCl^{2+}] + \varepsilon_2[FeCl_2{}^+] \qquad (18)$$

in which $\varepsilon_2$ is the molar extinction coefficient of $FeCl_2{}^+$. Therefore, Eq. (15) is altered to

$$\varepsilon = \varepsilon_1 - \frac{1}{K_1}\frac{\bar{\varepsilon}-\varepsilon_0}{[Cl^-]} + (\varepsilon_2-\bar{\varepsilon})K_2[Cl^-] \qquad (19)$$

with the third term on the right-hand side of Eq. (19), which causes the plot to deviate from a straight line at higher concentrations of chloride ion in Fig. 4, because $\varepsilon_2$ is larger than $\bar{\varepsilon}$. Consequently, the deviation $\Delta\bar{\varepsilon}$ is defined as the difference between the observed $\bar{\varepsilon}$ and hypothetical $\bar{\varepsilon}$ which would have been obtained if no $FeCl_2{}^+$ formation had occurred, and Eq. (19) can be rearranged into another form in terms of $\Delta\bar{\varepsilon}$.

$$\bar{\varepsilon} = \varepsilon_2 - \frac{1}{K_2}\frac{\Delta\bar{\varepsilon}(1+K_1[Cl^-])}{K_1[Cl^-]^2} \qquad (20)$$

A plot of $\bar{\varepsilon}$ *vs.* $\Delta\bar{\varepsilon}(1+K_1[Cl^-])/K_1[Cl^-]^2$ will yield a straight line, whose slope and intercept indicate $-1/K_2$ and $\varepsilon_2$, respectively. In order to get the final correct values of $K_2$ and $\varepsilon_2$, a procedure similar to that in the case of $K_1$ has to be taken.

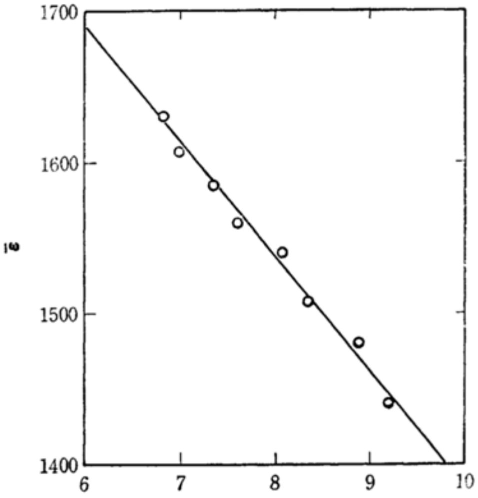

Fig. 5. The plot of $\bar{\varepsilon}$ *vs.* $\Delta\bar{\varepsilon}(1+K_1[Cl^-])/K_1[Cl^-]^2$ at 400 m$\mu$.
$[HClO_4]=0.02$ M, $\mu=0.10$, 25°C

The linearity is obvious in Fig. 5 when $[Fe(III)]=1.50\times10^{-4}$ M and $[Cl]=(3.0$—$6.5)\times10^{-3}$ M were used at $[HClO_4]=0.02$ M and $\mu=0.10$ M at 25°C and 400 m$\mu$. The results are $K_2=(1.33\pm0.05)\times10^2$ M$^{-1}$ and $\varepsilon_2{}^{400}=(2.14\pm0.03)\times10^3$ M$^{-1}$ cm$^{-1}$.

**Other Complementary Methods.** *Computer Method.* Collecting all the values of the optical density at many iron(III) and chloride ion concentrations as far as were measured, a high-speed digital computation yielded best fitted values of $K_1$ and $K_2$ along with the extinction coefficients as $K_1=(5.3\pm0.6)\times10^3$ M$^{-1}$ and $K_2=(1.1\pm0.3)\times10^2$ M$^{-1}$, $\varepsilon_1{}^{400}=1180\pm16$ and $\varepsilon_2{}^{400}=2350\pm130$ M$^{-1}$ cm$^{-1}$.[4,11]

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[11] Z. Z. Hugus, "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y. (1961), p. 379.

TABLE 2. SUMMARY OF THE VALUES OF $K_1$, $K_2$, $\varepsilon_1^{400}$ AND $\varepsilon_2^{400}$ MEASURED BY VARIOUS METHODS
$[HClO_4]=0.02$ M, $\mu=0.10$ M AT 25°C

| Method | $K_1\times10^{-3}$, M$^{-1}$ | $\varepsilon_1^{400}\times10^{-3}$, M$^{-1}$ cm$^{-1}$ | $K_2\times10^{-2}$ M$^{-1}$ | $\varepsilon_2^{400}\times10^{-3}$ M$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|
| Job's I | 3.7±1.2 | 1.30±0.05 | — | — |
| Job's I | 3.8±0.6* | 1.24±0.02* | — | — |
| Job's II | 3.1 | 1.30 | — | — |
| Job's III | 3.7±0.7 | 1.28±0.03 | — | — |
| Linearity | 4.2±0.1 | 1.24±0.01 | 1.33±0.05 | 2.14±0.03 |
| Computer | 5.3±0.6 | 1.18±0.02 | 1.1 ±0.3 | 2.35±0.13 |
| Kinetic | 5.4±1.0** | — | — | — |

* $[HClO_4]=0.07$ M   ** 20°C

TABLE 3. COMPARISON OF $K_1$, $K_2$, $\Delta H_1$ AND $\Delta S_1$ FOR THE FORMATION OF $FeCl^{2+}$ AND $FeCl_2^+$ IN WATER, NMA AND DMSO AT 25°C

| Solvent | log $K_1$ | log $K_2$ | $\Delta H_1$ kcal/mol | $\Delta S_1$ cal/deg·mol | Dielectric constant |
|---|---|---|---|---|---|
| Water | 1.48 | 0.65 | 8.5 | 35 | 80 |
| NMA | 2.88 | 1.11 | — | — | 178.9 (30°C)15) |
| DMSO | 3.62 | 2.10 | 7 | 40 | 46.7 (25°C)7) |

*Kinetic Method.* The electron transfer reaction between iron(II) and iron(III) in DMSO is accelerated by the presence of chloride ion. At very low concentrations of iron species, the apparent rate constant $\bar{k}$ is expressed by

$$\bar{k}[\mathrm{Fe(III)}] = k_0[\mathrm{Fe}^{3+}] + k_1[\mathrm{FeCl}^{2+}] \tag{21}$$

which is quite similar to Eq. (14) in appearance, except there are only $k$'s instead of $\varepsilon$'s. Accordingly a relationship corresponding to Eq. (15) is obtained as follows.12)

$$\bar{k} = k_1 - \frac{1}{K_1}\frac{\bar{k}-k_0}{[\mathrm{Cl}^-]} \tag{22}$$

By applying 36 pieces of data measured by Wada and Reynolds,4) $K_1$ and $k_1$ were found to be $K_1=(5.4\pm1.0)\times10^3$ M$^{-1}$ and $k_1=176$ M$^{-1}$ sec$^{-1}$ at $[HClO_4]=0.02$ M and $\mu=0.10$ M at 20°C. This is a convenient method to obtain $k_1$ without knowing $K_1$ separately measured in advance.

In Table 2, the values of $K_1$ and $K_2$ and $\varepsilon_1$ and $\varepsilon_2$ calculated by various methods are summarized together. In looking at the table, the agreement is good between the Job and the linearity methods with regard to $K_1$, although the computer and the kinetic methods give a little higher values. Besides this small discrepancy, $K_2$, $\varepsilon_1^{400}$ and $\varepsilon_2^{400}$ agree very well among their all measured values, respectively. Considering the accuracy and the reliability of the individual methods employed here, it seems safe to conclude that the most reasonable values are $\log K_1=3.62$ and $\log K_2=2.10$, and therefore $\log \beta_2=5.72$.

**Discussion.** The values of $K_1$, $K_2$, $\Delta H_1$ and $\Delta S_1$ in water13) and in *N*-methylacetamide (NMA)14) are listed in Table 3 together with those in DMSO. The decreasing dielectric constant of the solvent seems to favor increased formation of complex between iron(III) and chloride ion. This prevails in the cases of water and DMSO, where iron(III) ion is coordinated through oxygen atoms with the solvating molecules, as compared to nitrogen atoms in NMA. However, coordination through oxygen would favor increased dissociation of $FeCl^{2+}$ better than through nitrogen, considering the spectrochemical series of ligands. In fact, the larger values of $K_1$ and $K_2$ found in NMA than in water are really against expectation from the dielectric constant but due to the coordinating atom. The latter effect must be predominant over the former. The coincidence of $\Delta H_1$ and $\Delta S_1$ in water and DMSO seems to have come about rather by chance.

The electron transfer reaction between iron(II) and iron(III) in chloride ion-containing DMSO occurs through two paths.

$$\mathrm{Fe}^{2+} + {}^*\mathrm{Fe}^{3+} \rightarrow \mathrm{Fe}^{3+} + {}^*\mathrm{Fe}^{2+} \tag{23}$$

$$\mathrm{Fe}^{2+} + {}^*\mathrm{FeCl}^{2+} \rightarrow \mathrm{FeCl}^{2+} + {}^*\mathrm{Fe}^{2+} \tag{24}$$

The $K_1$ value obtained by the kinetic method means the formation constant of $FeCl^{2+}$ appearing in Reaction (24), which probably proceeds through the inner-sphere mechanism with an activated

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complex bridged by a chloride ion.4) Therefore, the approximate agreement between the $K_1$ values by the spectrophotometric and the kinetic methods, in other words, from independent sources of observation, will permit one to presume that the species of $FeCl^{2+}$ observed in the spectrophotometric method was the same as in the kinetic method, and accordingly, was not a mere association product between ions without liberating the solvating molecules to the ions, but a complex, in the true sense of the word, with a chloride ion, as a ligand, attached directly to the iron(III) ion.

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