The Solvent Extraction of Iron(III) in Perchlorate Solutions Containing Chloride or Bromide Ions with 2-Thenoyltrifluoroacetone and Trioctylphosphine Oxide

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(Received July 29, 1971)

Iron(III) in aqueous solutions, in which $[H^+]=1.0\text{M}$, $[Na^+]=3.0\text{M}$, and $[L^-]+[ClO_4^-]=4.0\text{M}$, where L^- is a chloride or bromide ion, was extracted with thenoyltrifluoroacetone (TTA) in carbon tetrachloride or with trioctylphosphine oxide (TOPO) in hexane. From the TTA extraction, it was concluded that iron(III) formed the first and the second complexes with both chloride ($\beta_1=10^{0.88}$ and $\beta_2=10^{0.80}$) and bromide ($\beta_1=10^{-0.10}$ and $\beta_2=10^{0.00}$) ions in the aqueous phase. The distribution data of iron(III) with TOPO were then explained in terms of the extraction of the ion-pairs, $Fe(ClO_4)_3$, $FeL(ClO_4)_2$, and $FeL_2(ClO_4)$, by using these stability constants. When the aqueous phase contained only chloride or bromide ions, and no perchlorate ion, the increase in the extraction with the increase in the halide ion concentration was much larger than that observed when the aqueous phase contained both halide and perchlorate ions. From the determination of the extraction of hydrogen ions and halide ions with TOPO, the extracted species in the absence of a perchlorate ion were identified as FeL_3 and/or $HFeL_4$. It was concluded that the difference in the extraction of iron(III) when a perchlorate ion was present and when it was absent is mainly caused by (i) the extraction of perchloric acid, which combines with TOPO in the organic phase and interferes with the extraction of the iron(III) halide complexes, and (ii) the extraction of iron(III) species containing one or more perchlorate ions which are large enough to be extractable with TOPO in the organic phase.

The solvent extraction of iron(III) in hydrochloric acid with diethylether was one of the earliest examples of the application of this experimental technique.[1,2] However, the chemical equilibria involved in such solvent extraction systems containing strong acids in the aqueous phase, and a polar solvent, such as an ether or a ketone, in the organic phase have not been analyzed very clearly, although Diamond and Tuck[3] and Marcus and Kertes[4] made comprehensive discussions of this problem.

The difficulties in the analysis of the thermodynamic equilibria involved in such systems are mainly due to the changes in the chemical properties of the organic phase caused by the extraction of the strong acid.

It has also been reported that iron(III) in hydrochloric acid is extractable with tributylphosphate (TBP)[5-9] or trioctylphosphine oxide (TOPO).[10,11] The chemical equilibria in these extraction systems, especially when the organic phase is a nonpolar solvent containing a small amount of one of these extractants, are assumed to be much simpler than those in extraction systems containing a polar solvent, because the extraction behavior of strong acids is much simpler when the organic solvent is nonpolar than when it is polar.

In the present investigation, the authors studied the chemical equilibria of iron(III) in aqueous sodium perchlorate solutions containing chloride or bromide ions and the extraction of iron(III) from these aqueous solutions into carbon tetrachloride containing TTA or into hexane containing TOPO. They determined the stability constants of these halide complexes in the aqueous phase and the chemical form of the extracted species in the organic phase. From these results, they discussed the role of perchlorate ions in the extraction of iron(III) in such systems.

Experimental

Tracer and Reagents. The iron-59 tracer was obtained from the Union Carbide Corporation, USA. It was purified as follows: a 6N hydrochloric acid solution of the tracer was shaken with the same volume of methylisobutylketone (MIBK), and then the tracer was extracted into the organic phase. The organic phase was washed with an equal volume of 4N hydrochloric acid, and then the tracer was back-extracted into the same volume of water. The solution thus prepared was diluted with 0.01N nitric acid and used as the stock solution. The concentration of chloride ions back-extracted together with the tracer into the final aqueous solutions was assumed to be very small[12] ($[Cl^-]$ is $4\times10^{-4}\text{M}$ in the stock tracer solution and, consequently it is $7\times10^{-6}\text{M}$ in the final solution). Furthermore, since only 0.1 m*l* of this tracer solution was added to 5 m*l* of the aqueous phase, the nitrate concentration in the latter solution was also very low ($2\times10^{-4}\text{M}$). The effect of these ions was checked by changing the amount of the tracer solution added to the aqueous phase, but no change in the distribution ratio of iron(III) was thus observed. The TTA and the TOPO were obtained from the Dojin-Do & Co. The MIBK was

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[1] M. Hanroit, *Bull. Soc. Chim. Fr.*, (3) **7**, 171 (1892).

[2] J. W. Rothe, *Chem. News*, **66**, 182 (1892).

[3] R. M. Diamond and D. G. Tuck, *Progr. Inorg. Chem.*, **2**, 109 (1960).

[4] Y. Marcus and A. S. Kertes, "Ion exchange and solvent extraction of metal complexes," Willy-Interscience, London 1969, p. 575.

[5] S. K. Majumdar and A. K. De, *Talanta*, **7**, 1 (1960).

[6] G. Weidmann, *Can. J. Chem.*, **38**, 459 (1960).

[7] H. Specker and M. Cremer, *Z. Anal. Chem.*, **167**, 110 (1959).

[8] A. Alian and R. Shabana, *Microchem. J.*, **12**, 427 (1967).

[9] O. D. Lyakh, I. A. Sheka, and A. I. Porfil'ev, *Zh. Prikl. Khim.*, **39**, 1799 (1966).

[10] W. J. Ross and J. C. White, U. S. At. Energy Comm. Rept. ORNL-2382 (1957).

[11] J. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, **4**, 101 (1960).

[12] T. Sekine, T. Fukushima, and Y. Hasegawa, This Bulletin, **43**, 2638 (1970).

obtained from the Tokyo Kasei Co. The MIBK was washed with 0.1 N perchloric acid, water, and a 0.1 N sodium hydroxide solution successively, and then several times with water. The sodium perchlorate was prepared from sodium carbonate and perchloric acid and recrystallized three times from water. The other reagents were of an analytical-grade and were used without further purification.

Procedures. All of the procedures were carried out in a thermostated room at 25°C. Stoppered glass tubes (volume, 20 m*l*) were used to equilibrate the two phases. A five-milliliter portion of an aqueous solution containing iron(III) (carrier-free iron-59 or a small amount of an iron(III) carrier prepared from an analytical-grade reagent and labelled by iron-59) and various amounts of the ligand and sodium perchlorate, and a 5-m*l* portion of carbon tetrachloride containing TTA or hexane containing TOPO were placed in the tubes. The aqueous phase contained 4 M electrolytes, unless noted. The initial concentration of iron(III) ions in the aqueous phase was 2×10^{-4} M to 1×10^{-5} M in the TTA extraction system and about 10^{-8} M in the TOPO extraction system. The tubes containing the aqueous and organic phases were placed on a rotating framework, and the two phases were agitated mechanically (20 rpm) for 24 hr and then centrifuged. A four-milliliter portion was pipetted from each phase and transferred into a small test tube. The γ-radioactivity in the sample solutions was measured with a well-type (NaI) scintillation counter, and the distribution ratio of iron(III) was calculated as follows:

$$D=\frac{[\text{Fe(III)}]_{org,\,total}}{[\text{Fe(III)}]_{total}}=\frac{\gamma\text{-count-rate per m}l\text{ of the organic phase}}{\gamma\text{-count-rate per m}l\text{ of the aqueous phase}}$$

The titration of the hydrogen ion in the organic phase was made by using a standard barium hydroxide solution, with phenolphthalein as the indicator.

Statistical

The stability constants of iron(III) complexes with L^- in the aqueous phase may be described as follows;

$$\text{Fe}^{3+}+n\text{L}^- \rightleftarrows \text{FeL}_n{}^{3-n}$$

$$\beta_n=\frac{[\text{FeL}_n{}^{3-n}]}{[\text{Fe}^{3+}][\text{L}^-]^n} \qquad (1)$$

The total iron(III) concentration in the aqueous solution may then be described as;

$$\begin{aligned}[\text{Fe(III)}]_{total}&=[\text{Fe}^{3+}]+[\text{FeL}^{2+}]+[\text{FeL}_2{}^+]+\cdots\\&\quad+[\text{FeL}_n{}^{3-n}]\\&=[\text{Fe}^{3+}](1+\sum\beta_n[\text{L}^-]^n)\end{aligned} \qquad (2)$$

When iron(III) is extracted into the organic phase with an organophilic chelating acid, the distribution equilibrium may be described as;

$$\text{Fe}^{3+}+3\text{HA(org)} \rightleftarrows \text{FeA}_3\text{(org)}+3\text{H}^+$$

$$K_{ex}=\frac{[\text{FeA}_3]_{org}[\text{H}^+]^3}{[\text{Fe}^{3+}][\text{HA}]^3_{org}} \qquad (3)$$

If no complex formation or no hydrolysis of iron(III) in the aqueous phase is assumed, the distribution ratio is given by (here the subscript "0" denotes no complex formation in the aqueous phase);

$$D_0=\frac{[\text{FeA}_3]_{org}}{[\text{Fe}^{3+}]}=K_{ex}[\text{HA}]^3{}_{org}[\text{H}^+]^{-3} \qquad (4)$$

However, when iron(III) forms complexes with L^-, in the aqueous phase, the distribution ratio is given from Eqs. (2) and (4) as;

$$\begin{aligned}D&=\frac{[\text{FeA}_3]_{org}}{[\text{Fe}^{3+}]+[\text{FeL}^{2+}]+[\text{FeL}_2{}^+]+\cdots}\\&=\frac{K_{ex}[\text{HA}]^3{}_{org}[\text{H}^+]^{-3}}{1+\beta_1[\text{L}^-]+\beta_2[\text{L}^-]^2+\cdots}\end{aligned} \qquad (5)$$

From Eq. (5), the following relation is obtained;

$$\log D[\text{H}^+]^3[\text{HA}]_{org}{}^{-3}K_{ex}{}^{-1}=-\log(1+\sum\beta_n[\text{L}^-]^n) \qquad (6)$$

As may be seen (*cf.* Fig. 1, Table 1(a)), the formation of only the first and the second complexes in the aqueous phase was assumed, and the data were found to be represented by the following equation;[13,14]

$$Y=-\log(1+\beta_1[\text{L}^-]+\beta_2[\text{L}^-]^2) \qquad (7)$$

The plot may be fitted with a family of standard curves;

$$Y=-\log(1+pv+v^2),\quad X=\log v \qquad (8)$$

and the constants, β_1 and β_2, can be determined from the parameters of the "best-fit" standard curve.

It is possible that iron(III) in the aqueous phase is extracted with a neutral extractant, E, as various uncharged species containing the ligand anions, L^-, and/or perchlorate ions. The extraction equilibria can be described as follows;

$$\text{Fe}^{3+}+a\text{L}^-+(3-a)\text{ClO}_4{}^-+e\text{E}(org) \rightleftarrows \text{FeL}_a(\text{ClO}_4)_{3-a}\text{E}_e(org)$$

$$K_{ex'3-a,a}=\frac{[\text{FeL}_a(\text{ClO}_4)_{3-a}\text{E}_e]_{org}}{[\text{Fe}^{3+}][\text{L}^-]^a[\text{ClO}_4{}^-]^{3-a}[\text{E}]^e_{org}} \qquad (9)$$

However, when the concentration of the extractant is kept constant throughout a series of experiments, the $[\text{E}]^e{}_{org}$ term can be eliminated from the equation and the following equation can be used instead of Eq. (9);

$$K_{ex3-a,a}=\frac{[\text{FeL}_a(\text{ClO}_4)_{3-a}]_{org}}{[\text{Fe}^{3+}][\text{L}^-]^a[\text{ClO}_4{}^-]^{3-a}} \qquad (10)$$

It is also possible that ion-pairs of anionic iron(III) complexes with sodium in the background salt such as $\text{Na}^+\text{Fe(ClO}_4)_4{}^-$ are extracted. However, as will be seen later, this type of extraction is negligible in the present study, and so it will not be considered here.

The distribution ratio under these conditions may, then, be described as;

$$D=\frac{[\text{Fe(ClO}_4)_3]_{org}+[\text{FeL(ClO}_4)_2]_{org}+[\text{FeL}_2(\text{ClO}_4)]_{org}+[\text{FeL}_3]_{org}}{[\text{Fe}^{3+}]+[\text{FeL}^{2+}]+[\text{FeL}_2{}^+]+\cdots} \qquad (11)$$

As will be seen, the data were found to be represented well if the formation of the first and the second complexes in the aqueous phase and the extraction of the ion-pairs with perchlorate ions, $\text{Fe(ClO}_4)_3$, $\text{FeL(ClO}_4)_2$, and $\text{FeL}_2(\text{ClO}_4)$, were assumed (*cf.* Figs. 1, 3, and 4, Table 1); thus, by introducing the equilibrium constants, Eq. (11) can be rewritten as;

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[13] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

[14] T. Sekine and Y. Hasegawa, *ibid.*, **39**, 240 (1966).

$$D=\frac{K_{ex_{3,0}}[\mathrm{ClO_4^-}]^3+K_{ex_{2,1}}[\mathrm{ClO_4^-}]^2[\mathrm{L^-}]+K_{ex_{1,2}}[\mathrm{ClO_4^-}][\mathrm{L^-}]^2}{1+\beta_1[\mathrm{L^-}]+\beta_2[\mathrm{L^-}]^2} \tag{12}$$

From Eq. (12), the following relation is obtained;

$$\log\frac{D(1+\beta_1[\mathrm{L^-}]+\beta_2[\mathrm{L^-}]^2)}{[\mathrm{ClO_4^-}]^3} = \log K_{ex_{3,0}} + \log\left\{1+\frac{K_{ex_{2,1}}}{K_{ex_{3,0}}}\left(\frac{[\mathrm{L^-}]}{[\mathrm{ClO_4^-}]}\right) + \frac{K_{ex_{1,2}}}{K_{ex_{3,0}}}\left(\frac{[\mathrm{L^-}]}{[\mathrm{ClO_4^-}]}\right)^2\right\} \tag{13}$$

The plot may also be fitted with the following family of standard curves;[13,14]

$$Y=\log(1+pv+v^2),\ X=\log v \tag{14}$$

and the constants, $K_{ex_{3,0}}$, $K_{ex_{2,1}}$, and $K_{ex_{1,2}}$, can be determined from the curve-fitting.

Results

Rate of Extraction. In the present study, it was found that the extraction of iron(III) with TTA is a slow reaction, as had previously been reported.[15,16] It took almost 20 hr until the distribution equilibrium was reached under the conditions employed. The rate of the extraction of the uncharged species of iron(III) with TOPO was also small, especially when the ligand concentration in the 4M sodium perchlorate medium was very low (where only the $Fe(ClO_4)_3$ species is extracted). Thus, the mechanical agitation of the two phases was always carried out for 24 hr before they separated.

TTA Extraction from an Aqueous Phase Containing no Ligand. Since the hydrogen-ion concentration in most of the experiments in this work was 1.0M, the extraction of iron(III) from an aqueous solution containing 1.0M perchloric acid and 3.0M sodium perchlorate with TTA in carbon tetrachloride was determined as a function of the TTA concentration. It was found from these determinations that the $D_0[H^+]^3[HA]_{org}^{-3}$ values obtained are nearly constant (log K_{ex} is 3.99). Thus, as can be seen from Eq. (4), the TTA complexes in the aqueous phase are practically negligible in the aqueous phase. Since the hydrogen-ion concentration was kept constant, no information about the hydrolysis of iron(III) was obtained from these distribution data alone. However, as the previously reported values of the hydrolysis constants of iron(III) in 3M sodium perchlorate solutions[17] are $*K_1=[FeOH^{2+}][H^+]/[Fe^{3+}]=10^{-3.05}$, $*\beta_2=[Fe(OH)_2^+][H^+]^2/[Fe^{3+}]=10^{-6.31}$, and $*\beta_{22}=[Fe_2(OH)_2^{4+}][H^+]^2/[Fe^{3+}]^2=10^{-2.96}$, the hydrolysis in 4M sodium perchlorate media at hydrogen-ion concentrations higher than 1M can be regarded as negligible.

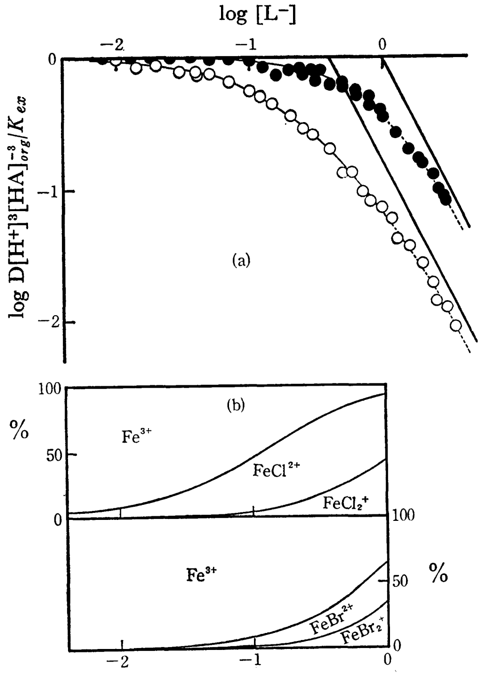

Fig. 1(a). Decrease in the TTA extraction of iron (III) as a function of the chloride (○) or bromide (●) concentration. Org. phase: carbon tetrachloride containing 0.1M TTA, Aq. phase: 4M perchlorate inoic medium in which $[H^+]=1.0M$, $[Na^+]=3.0M$, and $[L^-]+[ClO_4]=4.0M$. The solid cruves ($[L^-]<1.0M$) and the dotted lines ($[L^-]>1.0M$) are calculated by using the following equation and the stability constants in Table I(a):

$$\log D[\mathrm{H^+}]^3[\mathrm{HA}]_{org}^{-3}\ K_{ex}^{-1}=-\log(1+\beta_1[\mathrm{L^-}]+\beta_2[\mathrm{L^-}]^2)$$

1(b). The distribution of the chemical species in the aqueous phase as a function of the ligand concentration calculated by using the stability constants in Table 1(a).

TTA Extraction from an Aqueous Phase Containing Chloride or Bromide Ions. Figure 1(a) gives the log $D[H^+]^3[HA]_{org}^{-3}K_{ex}^{-1}$ *vs.* log$[L^-]$ plot (*cf.* Eq. (6)) when the aqueous phase contained chloride (open circles) or bromide (closed circles) ions in a 4M sodium perchlorate medium at the hydrogen-ion concentration of 1.0M. The stability constants were determined by

TABLE 1. EQUILIBRIUM CONSTANTS FOR IRON(III) AT 25°C

(a) Stability constants for iron (III) complexes in a 4M perchlorate ionic medium in which $[H^+]=1.0M$, $[Na^+]=3.0M$, and $[L^-]+[ClO^-]=4.0M$.

Ligand	Cl^-	Br^-
log β_1	0.88	−0.10
log β_2	0.80	0.00

(b) Extraction constants for iron (III) species with TOPO. Org. phase: hexane containing 0.03M TOPO, Aq. phase: aqueous solutions in which $[H^+]=1.0M$, $[Na^+]=3.0M$, and $[L^-]+[ClO^-_3{}^-]=4.0M$.

$K_{ex_{3,0}}=[Fe(ClO_4)_3]_{org}/[Fe^{3+}][ClO^-_4]^3$
$K_{ex_{2,1}}=[FeL(ClO_4)_2]_{org}/[Fe^{3+}][L^-][ClO_4^-]^2$
$K_{ex_{1,2}}=[FeL_2(ClO_4)]_{org}/[Fe^{3+}][L^-]^2[ClO_4^-]$

Ligand	Cl^-	Br^-
log $K_{ex_{3,0}}$	−1.31	
log $K_{ex_{2,1}}$	0.39	−0.01
log $K_{ex_{1,2}}$	0.53	0.21

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[15] R. A. Bolomey and L. Wish, *J. Amer. Chem. Soc.*, **72**, 4483 (1950).

[16] A. Adin and L. Newman, *J. Inorg. Nucl. Chem.*, **32**, 3321 (1970).

[17] A. Martell and L. G. Sillén, "Stability constants," the Chemical Society, London, spec. pub. No. 17 (1964).

using the data in the ligand-concentration region below 1.0M. By the curve-fitting, the stability constants for the first and the second complexes were determined to be as are listed in Table 1(a). The solid curves in Fig. 1(a) are the curves calculated from these constants. The dotted lines in Fig. 1(a) are calculated by using these constants for the ligand-concentration region above 1.0M.

Figure 1(b) gives the distribution of iron(III) complex species in the aqueous phase as a function of the ligand concentration.

TOPO Extraction from Aqueous Solutions Containing Chloride or Bromide Ions. The extraction of iron(III) with TOPO in hexane was reproducible only when the iron(III) concentration was very low; the distribution ratio was constant when the iron(III) concentration was changed between 10^{-8}M to 10^{-6}M, but it became lower than this value when the initial iron(III) concentration in the aqueous phase was above 10^{-5}M, the extraction being almost negligible when the iron(III) concentration was higher than 10^{-4}M. Thus, the initial iron(III) concentration in the aqueous phase was settled to be about 10^{-8}M.

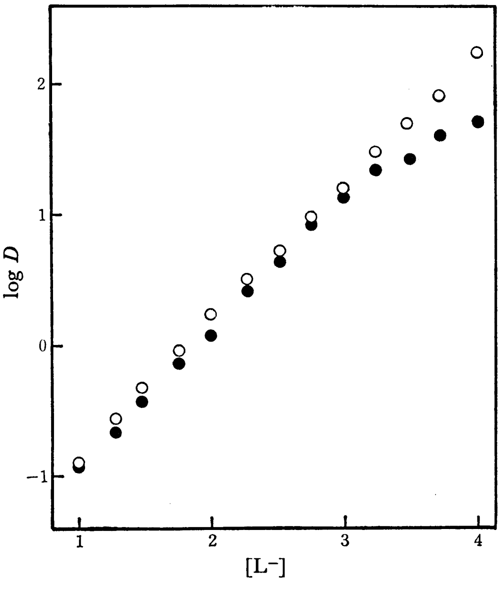

Fig. 2. TOPO extraction of iron (III) in the absence of perchlorate ions as a function of the chloride (○) or bromide (●) concentration in the aqueous phase. Org. phase: hexane containing 0.03 M TOPO, Aq. phase: aqueous solutions containing 1.0 M hydrohalic acid and various amounts of sodium halide but no perchlorate.

Figure 2 gives the extraction of iron(III) when the organic phase is hexane containing 0.03M TOPO and when the aqueous phase contains 1.0M hydrochloric acid and various amounts of sodium chloride, or when it contains 1.0M hydrobromic acid and various amounts of sodium bromide. The distribution ratio always increases with an increase in the halide concentration.

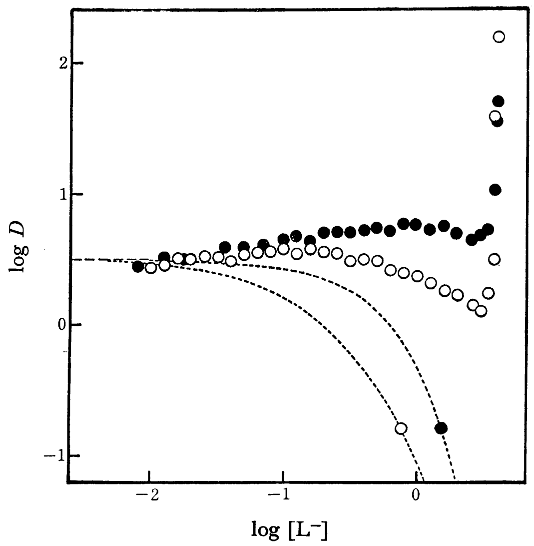

Fig. 3. TOPO extraction of iron(III) in the presence of p.rchlorate ions as a function of the chloride (○) or bromide (●) concentration. Org. phase: hexane containing 0.03M TOPO, Aq. phase: aqueous solutions in which $[H^+]=1.0$M, $[Na^+]=3.0$M, and $[L^-]+[ClO_4]=4.0$M. The broken line indicates the extraction in the absence of halide ions ($D=10^{0.50}$). The dotted lindes are the calculated curves (○: chloride system and ●: bromide system) assuming only the extraction of iron(III) perchlorate by using the equation, $\log D=\log K_{ex3.0}[ClO_4^-]^3-\log(1+\beta_1[L^-]+\beta_2[L^-]^2)$ where β_1 and β_2 were taken from Table 1(a).

Figure 3 gives the extraction of iron(III) when the organic phase is also hexane containing 0.03M TOPO, but when the aqueous phase contains 1.0M hydrogen ions, 3.0M sodium ions and various amounts of perchlorate and chloride or bromide ions (prepared by mixing a solution containing 1.0M perchloric acid and 3.0M sodium perchlorate and a solution containing 1.0M hydrohalic acid and 3.0M sodium halide at various mixing ratios). The distribution ratio was $10^{0.50}$ (indicated by a broken line) when the aqueous phase was a perchlorate solution containing no halide ions.

As may be seen from Fig. 3, the distribution ratio is not changed very much by the halide ions when the

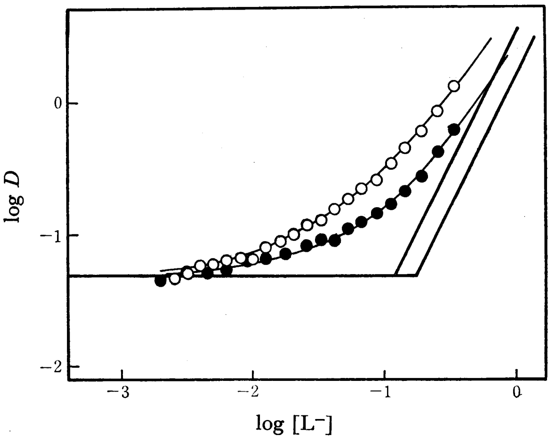

Fig. 4. Determination of the extraction constants (○: chloride and ●: bromide).

$K_{ex_{3,0}}=[Fe(ClO_4)_3]_{org}/[Fe^{3+}][ClO_4^-]^3$

$K_{ex_{2,1}}=[FeL(ClO_4)_2]_{org}/[Fe^{3+}][L^-][ClO_4^-]^2$

$K_{ex_{1,2}}=[FeL_2(ClO_4)]_{org}/[Fe^3][L^-]^2[ClO_4^-]$

Org. phase: hexane containing 0.03M TOPO, Aq. phase: aqueous solutions in which $[H^+]=1.0$M, $[Na^+]=3.0$M, and $[L^-]+[ClO_4^-]=4.0$M. The solid curves are calculated by using the following equation and the constants in Table 1.

$$\log D(1+\beta_1[L^-]+\beta_2[L^-]^2)/[ClO_4^-]^3=\log\{K_{ex_{3,0}}+K_{ex_{2,1}}[L^-]/[ClO_4^-]+K_{ex_{1,2}}([L^-]/[ClO_4^-])^2\}$$

concentration is lower than 3M, but it increases drastically in the region between 3M and 4M.

In order to determine the equilibrium constants in these extractions, the data were analyzed on the basis of Eq. (12). Figure 4 gives the log$D(1+\beta_1[L^-]+\beta_2[L^-]^2)[ClO_4^-]^{-3}$ *vs.* log$[L^-][ClO_4^-]^{-1}$ plot. Since the limitting slope for the plot in Fig. 4 is 0 or +2, it was concluded from Eq. (13) that the extracted species were $Fe(ClO_4)_3$, $FeL(ClO_4)_2$, and $FeL_2(ClO_4)$ in the ligand-concentration region below 1.0M and when the TOPO concentration was 0.03M. The extraction constants were determined by the curve-fitting of the plot in Fig. 4: they are listed in Table 1(b). The extraction of ion-pairs of the iron(III) ion, $Fe(ClO_4)_3$, and the first and the second complexes, $FeL(ClO_4)_2$ and $FeL_2(ClO_4)$, seems to explain the results in Fig. 3 reasonably, for if only the extraction of the $Fe(ClO_4)_3$ ion-pair occurs, the distribution ratio should decrease due to the complex formation in the aqueous phase and due to the decrease in the perchlorate concentration as the halide concentration increases. The dotted lines in Fig. 3 give the calculated curves assuming only the extraction of the $Fe(ClO_4)_3$ species, that is, assuming $D=K_{ex3,0}[ClO_4^-]^3/(1+\beta_1[L^-]+\beta_2[L^-]^2)$. However, as may be seen from Fig. 3, the data experimentally observed are higher than these except in the very low ligand-concentration region. This is probably due to the extraction of halide complexes as ion-pairs, as was pointed out above. The solid curves in Fig. 4 are the curves calculated by using the constants listed in Table 1.

It was observed that the extraction from a solution containing 4.0M perchlorate ions ($[H^+]=1.0$M) or one containing 3.0M perchlorate and 1.0M bromide ions ($[H^+]=1.0$M) is proportional to the 1.5th order of the TOPO concentration in the 2×10^{-3}M to 3×10^{-2}M range. It was also found that the extraction from the 4.0M perchlorate ionic medium containing halide ions is practically independent of the hydrogen-ion concentration between 0.1M and 1.0M. Thus, the extracted species from these solutions should not contain protons. On the other hand, the extraction from 4.0M chloride or bromide solutions containing no perchlorate ions is dependent on the hydrogen-ion concentration, the distribution ratio when the hydrogen-ion concentration is 1.0M is about ten times larger than the distribution ratio when it is 0.1M; thus the iron(III) extracted from these solutions should, at least some part of it, contain protons.

In order to obtain further information, the extraction of hydrogen ions into the organic phase was determined.

Extraction of Acids into the Organic Phase. Table 2 gives the hydrogen-ion concentration determined by titration with barium hydroxide. It may be seen from Table 2(a) that the extraction of perchloric acid into hexane containing 0.03M TOPO is practically independent of the acid concentration, whereas that of hydrohalic acid increases as the acid concentration increases. It may be seen from Table 2(b) that the extraction of hydrogen ion from the aqueous phase containing perchlorate and halide ions is also independent of the composition of the aqueous phase. Its extraction in the absence of perchlorate ions is also dependent on the salt concentration. It was also found in the organic phase that precipitates of silver halide were always formed by the addition of a silver nitrate solution if no perchlorate was present in the aqueous phase, but no precipitate was formed if perchlorate ions were present in the aqueous phase together with the halide ions.

This fact indicates that all of the acid extracted from the aqueous halide solutions is perchloric acid as long as the solution contains perchlorate ions, and that the organic phase is saturated with perchloric acid by the following extraction:

$$H^+ + ClO_4^- + 2TOPO(org) \rightleftharpoons (HClO_4)(TOPO)_2(org) \qquad (15)$$

Since extraction from an aqueous phase containing no sodium salt gives the same results (Table 2(a)), the extraction of sodium perchlorate under these conditions is negligible.

TABLE 2. EXTRACTION OF ACIDS WITH 0.03M TOPO IN HEXANE

(a) Extraction from an aqueous phase containing only an acid and no sodium salt

$[HClO_4]$	$[H^+]_{org}$	[HCl]	$[H^+]_{org}$	[HBr]	$[H^+]_{org}$
1.0M	1.4×10^{-2}M	1.0M	3.1×10^{-4}M	1.0M	1.4×10^{-3}M
2.0	1.5×10^{-2}	2.0	1.3×10^{-3}	2.0	5.6×10^{-3}
3.0	1.6×10^{-2}	3.0	3.7×10^{-3}	3.0	1.1×10^{-2}
4.0	1.5×10^{-2}	4.0	8.9×10^{-3}	4.0	1.6×10^{-2}

(b) Extraction from an aqueous phase at $[H^+]=1.00$M containing various amounts of sodium salt

$[HClO_4]$	$[NaClO_4]$	[NaCl]	$[H^+]_{org}$	$[HClO_4]$	$[NaClO_4]$	[NaBr]	$[H^+]_{org}$
1.0M	3.0M	0.0M	1.5×10^{-2}M	1.0M	3.0M	0.0M	1.5×10^{-2}M
1.0	2.0	1.0	1.5×10^{-2}	1.0	2.0	1.0	1.6×10^{-2}
1.0	1.0	2.0	1.5×10^{-2}	1.0	1.0	2.0	1.6×10^{-2}
1.0	0.0	3.0	1.5×10^{-2}	1.0	0.0	3.0	1.5×10^{-2}

[HCl]	$[NaClO_4]$	[NaCl]	$[H^+]_{org}$	[HBr]	$[NaClO_4]$	[NaBr]	$[H^+]_{org}$
1.0M	—	0.0M	3.1×10^{-4}M	1.0M	—	0.0M	1.4×10^{-3}M
1.0	—	1.0	1.1×10^{-3}	1.0	—	1.0	3.6×10^{-3}
1.0	—	2.0	1.6×10^{-3}	1.0	—	2.0	6.0×10^{-3}
1.0	—	3.0	2.3×10^{-3}	1.0	—	3.0	9.9×10^{-3}

Discussion

There have been several reports on the stability constants for iron(III) complexes with chloride or bromide ions.[17] The values reported for the chloride complexes ($\beta_1=10^{0.5}$ to $10^{1.0}$, $K_2\simeq10^{0.0}$) and for the bromide complex ($\beta_1\simeq10^{0.0}$) nearly agree with the present results. The higher complex, FeL_3 or FeL_4^-, may be very unstable, and the stability constants may be negligible even when the halide concentration is high.

The role of perchlorate ions and perchloric acid in the TOPO extraction system is remarkable. In the absence of perchlorate ions, the FeL_3 and the $HFeL_4$ (or $NaFeL_4$) species are possibly extracted into the organic phase, but these extractions are not remarkable when the halide concentration is lower than 2M (*cf.* Fig. 2). In the perchlorate ionic medium, the distribution of iron(III) is practically constant over a wide range of ligand concentration due to the extraction of ion-pairs, Fe^{3+}, FeL^{2+}, and FeL_2^+, with perchlorate ions.

Perchlorate solutions have often been used in order to control the activity of solutes in the aqueous phase. When such an aqueous phase is equilibrated with an organic phase, and when some portion of the anions is extracted together with hydrogen ion into the organic phase, the effect of the extracted acid should also be taken into account, because the extraction of the iron(III) species with TOPO combined with perchloric acid can be different from that with TOPO combined with hydrochloric or hydrobromic acid. However, under the conditions employed in the present study, the organic phase at equilibrium with the aqueous phase always contains 0.015M perchloric acid, even when 75% of the perchlorate ions is replaced by halide ions (*cf.* Table 2(b) and the fact that no halide ions were detected in these organic phases). Thus, the organic phase can be regarded as constant, even when the ligand ions are added to the aqueous phase. On the other hand, the extraction of the acid from the aqueous phase containing no perchlorate changes very much as the hydrogen ion or the salt concentration increases. Such changes in the composition in the aqueous phase should change not only the activity coefficients of the solutes in the aqueous phase, but also those in the organic phase.

The determination of the chemical form of the extracted species from chloride or bromide solutions containing no perchlorate seems to be difficult for the above reasons. However, from the observation described, the extracted species are assumed to be FeL_3 and/or $HFeL_4$. The extraction of these iron(III) halides seems to compete with the extraction of perchloric acid. Since the extraction of perchloric acid is effective, the addition of a small amount of perchlorate into the aqueous phase turns all the TOPO into the $(HClO_4)(TOPO)_2$ form. It is likely that the extraction of the FeL_3 and/or $HFeL_4$ species with this $(HClO_4)(TOPO)_2$ is much poorer than with free TOPO. This explains why the replacement of a small fraction of halide ions in the 4M halide solution by perchlorate ions causes a drastic decrease in the extraction of iron(III) (in the highest ligand-concentration range), as may be seen from Fig. 3.

The extraction of perchloric acid with TOPO in carbon tetrachloride was reported by Conocchioli, Tocher, and Diamond.[18] They described that the predominant species in the organic phase is the ion-pair $H_3O^+3TOPO\cdot ClO_4^-$ when the acid concentration is low enough, but for high concentrations of acid, the predominant species is $H^+TOPO\cdot ClO_4^-$. This does not agree with the present observation, which was made by using hexane as the diluent.

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[18] T. J. Conocchioli, M. I. Tocher, and R. M. Diamond, *J. Phys. Chem.*, **69**, 1106 (1965).