Kinetic Studies of the Solvent Extraction of Metal Complexes. II. The Rate of the Extraction of Iron(III) with Thenoyltrifluoroacetone into Carbon Tetrachloride

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The rate of the solvent extraction of iron(III) in 4.0 M perchlorate ionic media with 2-thenoyltrifluoroacetone (TTA) into carbon tetrachloride has been measured under various conditions. The rate was found to be first order with respect to the concentration of iron(III) in the aqueous phase, first-order with respect to TTA in the organic phase, but independent and inversely first-order with respect to the hydrogen-ion concentration. From these results, it was concluded that the rate-determining step in this extraction is the formation of the first complex between the undissociated form, TTA(HA), and Fe^{3+} in the higher acid concentration range, but that the reaction between the anionic form, TTA(A^-), and Fe^{3+} also becomes a rate-determining step as the acid concentration decreases. It was also found that chloride ions accelerate the extraction; this was interpreted by more rapid reactions between TTA (in the both forms, HA and A^-) and an iron(III) chloride complex. From these results, the rate constants for the rate-determining reactions were calculated to be $K_{HA}=10^{0.57}$ M^{-1} min^{-1} and $K_A=10^{6.84}$ M^{-1} min^{-1} in 4.0 M(H, Na)ClO_4 at 25 °C by means of these equations: $-d[Fe^{3+}]/dt=K_{HA}[Fe^{3+}][HA]$ (where [HA] is the total concentration of both enol and keto forms of uncharged TTA in the aqueous phase) and $-d[Fe^{3+}]/dt=K_A[Fe^{3+}]\cdot[A^-]$. The $FeCl^{2+}$ species reacts with both HA and A^- more rapidly than does the Fe^{3+} species, and the rate constants of the reactions of the former are in both cases higher than those of the latter by a factor of 28.

It has been pointed out that the rate of the reaction of metal ions in aqueous solutions is low when the charge is larger and/or when the radius is small; this has been explained as being due to the slow substitution of the hydrated water on such ions with the reactant. As examples of these metal ions, Be^{2+}, Al^{3+} and other strongly-hydrolysing metal ions were cited by Eigen.[1] In the previous paper of the present series,[2] it was reported that the solvent extraction of beryllium(II) with 2-thenoyltrifluoroacetone(TTA) in carbon tetrachloride is extremely slow because of the slow formation of the first complex of this metal ion in the aqueous phase with a TTA anion. In the course of another experiment of the present laboratory,[3] it was found that the extraction of iron(III) with TTA in chloroform was rather slow. The slow extraction of iron(III) with TTA has been reported by Bolomey and Wish[4] and by Adin and Newman.[5] It has been reported by Dyrssen[6] that the extraction of iron(III) with β-isopropyltropolone(IPT) is slow; the rate of this IPT extraction was studied more quantitatively by McClellan and Menis.[7] The extraction of iron(III) with alkylphosphoric acid has been studied kinetically by several workers, as Coleman and Roddy summarized in their review.[8]

The present study has been undertaken in order to make quantitative measurements of the rate of iron(III) extraction with TTA and in order to clarify the details of the mechanism of this slow extraction. The organic phase used is carbon tetrachloride, and the aqueous phase employed is perchlorate ionic media, 4.0 M(H, Na)ClO_4, except in a few cases. This aqueous phase was chosen in order to use the equilibrium data obtained for this aqueous solution in Ref. 3 for the analysis of the results. Since it has been found that the rate of extraction is accelerated by the addition of the chloride ion,[5,8] this effect was also measured.

Experimental

Reagents. The stock solution of iron(III) was prepared as follows. A weighed amount of analytical-grade metallic iron was dissolved in warm perchloric acid; the mixture was then stored as the stock solution. A working solution containing 1.0×10^{-2} M iron(III), 1.0 M perchloric acid, and 3.0 M sodium perchlorate was prepared from the above stock solution. The TTA was obtained from Dojindo & Co. The sodium perchlorate was prepared from sodium carbonate and perchloric acid, and it was recrystallized three times from water. All of the other reagents were of a reagent grade.

Procedures. The details of the procedures are essentially the same as those described in the previous paper[2] except that the amount of the metal ion was determined by colorimetry in the present study. The aqueous phase was prepared so as to contain 1.0×10^{-3} M of iron(III), 4.0 M of the perchlorate ion, and various amounts of sodium and hydrogen-ions. Some experiments were also carried out in order to ascertain the effect of coexisting salt on the rate of extraction by changing the sodium perchlorate concentration. The organic phase was carbon tetrachloride containing TTA. The initial volume of each phase was always 5.0 ml. The two phases were placed in stoppered glass tubes (volume, 20 ml) and vigorously agitated at 25±0.3 °C. The shaking speed was chosen so as to be high enough that no acceleration of the rate of extraction was observed upon a further increase in the agitation speed; thus, the effects due to the transport of materials and to any interfacial re-

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action could be eliminated from consideration, as has been described in the previous paper.[2)] After a certain interval, the two phases were centrifuged. A certain portion of the organic phase was pipetted out, and the content of the iron(III)-tris TTA chelate was determined by colorimetry. The absorption was determined at 500 nm; the molar extinction coefficient at this wavelength was found to be 3.7×10^3. It was found that Beer's law held, at least until a concentration of 2.0×10^{-4} M of the iron(III)-TTA chelate in carbon tetrachloride. The amount of aqueous iron(III) was estimated from the difference between the iron(III) concentration in the initial aqueous phase and that in the organic phase at equilibrium. The hydrogen-ion concentration was calculated from the amount of perchloric acid added.

Statistical

The rate of the extraction of Fe^{3+} ion with an acidic extractant, HA, may be written, in many cases, as follows:

$$-\frac{d[Fe^{3+}]}{dt}=k_0[Fe^{3+}]^a[HA]^b_{org}[H^+]^c \tag{1}$$

When the extractant and the hydrogen-ion are present in a large excess to iron(III), Eq. (1) can be written as follows:

$$-\frac{d[Fe^{3+}]}{dt}=q[Fe^{3+}]^a \tag{2}$$

Here, q is the multiplication of the rate constant, k_0, and the other two concentrations in Eq. (1), which are kept at certain values throughout a series of experiments. When the reaction order with respect to iron(III) is unity, as in the case of the present study, the following simplified statistical treatment is possible. Assuming that the value of a in Eq. (2) is unity, it can be written by integration as:

$$-\log[Fe^{3+}]=q't+C_0 \tag{3}$$

where C_0 is a constant and where q' is $q\times\log e$. Equation (3) shows that when a is unity, the $-\log[Fe^{3+}]$ *vs.* t plot should be a straight line with a slope of q'.

The reaction order with respect to the other two elements in Eq. (1) can be determined from the measurements when one of these two concentrations is kept at a certain value. For example, when the concentration of the hydrogen-ion is kept at h, the quantity, q_{HA}, can be written, in the first step, as follows:

$$\log q_{HA}=\log k_0h^c+b\log[HA]_{org} \tag{4}$$

As can be seen from Eq. (4), the reaction order with respect to the extractant, b, can be determined from the slope of the $\log q_{HA}$ *vs.* $\log[HA]_{org}$ plot.

Since the reaction order with respect to the hydrogen-ion, c, was found in the present study to change from minus one to zero upon an increase in the hydrogen-ion concentration, the following more general equation, containing a term in which the reaction order with respect to the hydrogen-ion concentration is zero, was employed:

$$-\frac{d[Fe^{3+}]}{dt}=k_0[Fe^{3+}][HA]^b_{org}(1+K_H[H^+]^{-1}) \tag{5}$$

On the other hand, when the concentration of the extractant is kept at a certain value, ha, the q_{H^+} quantity is obtained as:

$$\log q_{H^+}=\log k_0(ha)^b+\log(1+K_H[H^+]^{-1}) \tag{6}$$

Furthermore, since the addition of the chloride ion was found to accelerate the extraction, the following statistical treatment was made for this effect. Under the conditions where the concentrations of the extractant and hydrogen-ion are kept constant at h and ha, but where the aqueous phase contains a certain amount of the liquid, Cl^-, the rate may be represented by the following equation (the higher terms with respect to Cl^- are not given here and the b value is always unity in Eq. (6)):

$$-\frac{d[Fe^{3+}]}{dt}=q_L[Fe^{3+}] \tag{7}$$

where q_L is

$$\log q_L=\log k_0(ha)(1+K_Hh^{-1})+\log(1+K_{Cl}[Cl^-]) \tag{8}$$

The constants in Eqs. (6) and (8) can be determined by a curve-fitting method.[2,9-11)]

When the initial concentration of the extractant in the organic phase is denoted by $C_{HA(org)}$, the following equations are obtained if the volumes of the two phases are the same and if $[A^-]\ll C_{HA(org)}$:

$$K_a=[H^+][A^-][HA]^{-1} \tag{9}$$

$$K_d=[HA]_{org}[HA]^{-1} \tag{10}$$

$$C_{HA(org)}=[HA]_{org}+[HA]+[A^-] \tag{11}$$

$$[A^-]=C_{HA(org)}K_a(K_d+1)^{-1}[H^+]^{-1} \tag{12}$$

The values of these constants in the carbon tetrachloride–4.0 M (H, Na)ClO_4 system have been reported to be $\log K_a=-6.57$ and $\log K_d=1.93$.[2)] Since $K_d\gg1$, and since, thus, $C_{HA}\simeq[HA]_{org}$, Eq. (12) can be written as:

$$[A^-]=[HA]_{org}K_aK_d^{-1}[H^+]^{-1} \tag{13}$$

Results

Iron(III) was always added initially to the aqueous phase. Since the data used for the analysis were only those obtained from the experiments in the early stage of extraction, the effect of the back extraction may be negligible.

Reaction Order with Respect to Fe^{3+}. In all the experiments, each of the $-\log[Fe^{3+}]$ *vs.* t plots always gave a staright line. Thus, as can be seen from Eq. (3), the reaction order with respect to iron(III) is always unity.

Reaction Order with Respect to TTA(HA). The rate of extraction was determined in the TTA concentration range between 0.05 M and 0.3 M and at the hydrogen-ion concentration of 1.0 M. The $\log q_{HA}$ *vs.* $\log[HA]_{org}$ plot is given in Fig. 1. As may be seen from the figure, the plot obtained is a straight ling with a slope of +1; thus, the rate of extraction was concluded to be proportional to the TTA concentration under these conditions.

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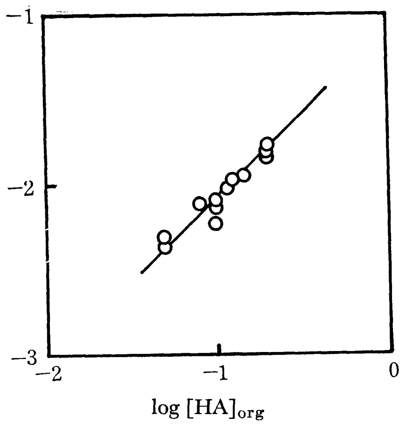

Fig. 1. Dependence of the rate of Fe(III) extraction on the TTA concentration in the organic phase (q_{HA} *cf.* Eq. (4)).

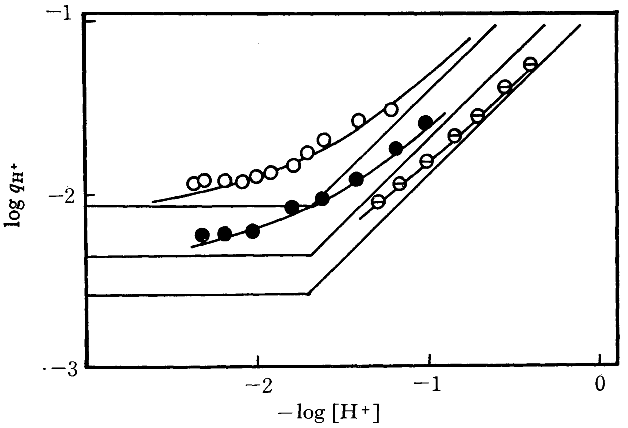

Fig. 2. Dependence of the rate of Fe(III) extraction on the hydrogen-ion concentration (q_{H^+} *cf.* Eq. (6)). ○: CCl_4 containing 0.2 M TTA, ●: CCl_4 containing 0.1 M TTA and ⊖: CCl_4 containing 0.05 M TTA. The two straight lines for each plot are the two asymptotes; $Y=\log k_0(ha)$ and $Y=\log k_0K_H(ha)\ -\log[H^+]$, and the solid curve is calculated by introducing the rate constants in Table 1 into Eq. (6).

Table 1. Summary of constants

(a) Constants for the equation:

$$-d[Fe^{3+}]/dt$$
$$=k_0[Fe^{3+}][HA]_{org}(1+K_H[H^+]^{-1})(1+K_{Cl}[Cl^-])$$

$\log k_0 = -1.36\ (M^{-1}\,min^{-1})$

$\log K_H = -0.30\ (M)$

$\log K_{Cl} = 2.32\ (M^{-1})$

(b) Reaction constants($M^{-1}\,min^{-1}$) defined by Eqs. (14) and (15).[a]

$\log K_{HA} = 0.57$

$\log K_A = 6.84$

$\log K_{HA-Cl} = 2.01$

$\log K_{A-Cl} = 8.28$

[a] Rate constant for the reaction between Fe^{3+} and HA (K_{HA}) which has been computed by using the total concentration of HA in the aqueous phase, Fe^{3+} and $A^-(K_A)$, $FeCl^{2+}$ and $HA(K_{HA-Cl})$, and $FeCl^{2+}$ and $A^-(K_{A-Cl})$.

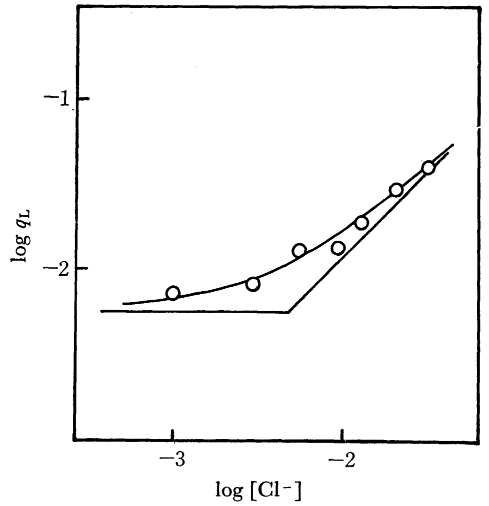

Fig. 3. Dependence of the rate of Fe(III) extraction on the chloride ion concentration. The straight lines are two asymptotes; $Y=\log C$ and $Y=\log CK_{Cl}+\log[Cl^-]$ where C is equal to $\log k_0(ha)(1+K_Hh^{-1})$ in which ha is 0.1 M and h is 1.0 M. The solid curve was obtained by introducing the constants in Table 1 into Eq. (8).

Reaction Order with Respect to H^+. The rate of extraction was determined in the range of hydrogen-ion concentrations from 2.0 M to 0.04 M and at the TTA concentrations of 0.05 M, 0.1 M, and 0.2 M. Figure 2 gives the log q_{H^+} *vs.* $-\log[H^+]$ plot. As may be seen from Fig. 2, the slope for the plot approaches zero in the lowest $-\log[H^+]$ region, but it increases with the increase in $-\log[H^+]$ until it approaches unity. From this fact, it was concluded that there are two mechanisms for the extraction and that they can be represented by Eq. (6).

The rate constants in the absence of chloride ions were determined from these results by the curve-fitting method; they are listed in Table 1(a).

Effect of the Chloride Ions. The rate was determined as a function of the chloride-ion concentration in the aqueous phase when the TTA concentration was 0.1 M and when the hydrogen-ion concentration was 1.0 M. Figure 3 gives the log q_L plot where L is Cl^-; the rate is accelerated by the chloride ion, and it becomes almost proportional to the chloride concentration in the higher range. The constant, K_{Cl}, in Eq. (8) was determined from this plot by the curve-fitting method; it is listed in Table 1.

In order to consider the effect of the chloride ion on the rate of extraction further, the rate was determined with 0.1 M TTA in the organic phase in the presence of the chloride-ion at a certain concentration, 5×10^{-3} M, but in the presence of the hydrogen-ion at various concentrations. Figure 4 shows these results. As may be seen from Fig. 4, the addition of chloride always increases the rate by a factor of $10^{0.24}$. Thus, it can be concluded that both mechanisms, one independent of, and the other inversely first-order dependent on the hydrogen-ion, are affected by the chloride-ion in the same manner. From the amounts of the chloride complexes, $FeCl^{2+}$ and $FeCl_2^+$, in the aqueous phase, which were computed by using the stability constants in 4.0 M (H, Na)ClO_4,[3] that is, log $\beta_1=0.88$ and $\beta_2=0.80$, the rate constants for the extraction in the presence of chloride-ion were determined to be

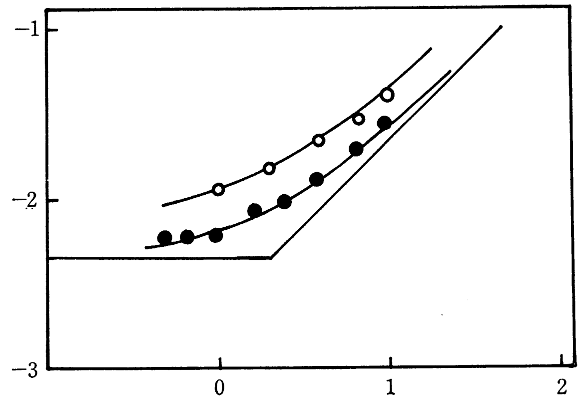

Fig. 4. Dependence of the rate of Fe(III) extraction on the hydrogen ion concentration in the presence of 5×10^{-3} M chloride-ion (○) and its absence (●) in the aqueous phase when the TTA concentration in the organic phase is 0.1 M. The two straight lines are the same as those given in Fig. 2. The curve for the full circle is $Y=\log k_0(ha)\,(1+K_H[H^+]^{-1})$ and that for the open circles is $Y=\log k_0(ha)(1+K_{Cl}[Cl^-]_a)(1+K_H[H^+]^{-1})$ in which ha is 0.1 M and $[Cl^-]_a$ is 5.0×10^{-3} M.

as listed in Table 1 (b).

Since the rate of the extraction of iron(III) with IPT has been reported to be dependent on the concentration of the coexisting sodium perchlorate,[7] the dependence of the rate on the sodium perchlorate concentration was also determined. The results are given in Table 2. As may be seen from the table, the rate is not very much affected by the change in the salt concentration.

Discussion

Since the rate of extraction is always first-order with respect to TTA, and zero and inversely first-order with respect to the hydrogen-ion, and since the effect of interfacial reaction is negligible in the present study, Eq. 5 may, by introducing Eq. (13), be written as:

$$-\frac{d[Fe^{3+}]}{dt}=K_{HA}[Fe^{3+}][HA]+K_A[Fe^{3+}][A^-] \qquad (14)$$

where $K_{HA}=k_0K_d$ and where $K_A=k_0K_HK_dK_a^{-1}$. Equation (14) shows that the rate of extraction is controlled by two reactions, one between Fe^{3+} and HA and the other between Fe^{3+} and A^- in the aqueous phase.

Table 2. The effect of ionic strength adjusted by sodium perchlorate on the rate of extraction at two hydrogen ion concentrations (q_{H^+} *cf.* Eq. (6))

Ionic strength	log q_{H^+}	
	at $[H^+]=1.0$ M	at $[H^+]=0.05$ M
4.0 M	−2.18	−1.32
3.0 M	−2.17	−1.28
1.0 M	−2.20	−1.22
0.1 M		−1.09

The effect of the chloride-ion can, then, be treated from Eqs. (8) and (14) and the stability constant of the $FeCl^{2+}$ species as follows:

$$-\frac{d[Fe^{3+}]}{dt}=K_{HA}[Fe^{3+}][HA]+K_A[Fe^{3+}][A^-]$$
$$+K_{HA-Cl}[FeCl^{2+}][HA]+K_{A-Cl}[FeCl^{2+}][A^-] \qquad (15)$$

where $K_{HA-Cl}=K_{HA}K_{Cl}\beta_1^{-1}$ and where $K_{A-Cl}=K_AK_{Cl}\beta_1^{-1}$.

By using the constants in Table 1(a) and these relations, the values of these constants were calculated to be as given in Table 1(b).

Adin and Newman[5] determined the rate of the extraction of iron(III) with TTA and reported that the TTA extraction of iron(III) takes place by way of two mechanisms; one is independent of, and the other is dependent on, $[H^+]^{-1}$. They also reported an acceleration of the extraction by the chloride-ion. These results are summarized in Table 3. Their results are similar to those obtained in the present study, although the solvent is different and the electrolyte concentration and the background cation are different. These authors, however, explained the inversely first-order dependence of the rate on the hydrogen-ion in terms of the hydrolysis of iron(III); in other words, they assumed that the $FeOH^{2+}$ species reacted with the HA-form TTA much faster than did the Fe^{3+} species, and they assumed that the $FeOH^{2+}$ species reacted much faster than the $FeCl^{2+}$ species. According to these authors, the $FeOH^{2+}$ species reacts with the HA-form TTA faster than does the Fe^{3+} species by a factor of 10^4.

Statistically, it is impossible to distinguish whether this inversely first-order dependence on the hydrogen-ion which has been observed in both the previous and the present studies is due to a $Fe^{3+}+A^-\rightarrow FeA^{2+}$ re-

Table 3. Previous work on the rate of iron(III) extraction with chelating extractants

Chelate	Organic phase	Aqueous phase	k ($M^{-1}\,min^{-1}$)	Ref.	Remarks
TTA (room temparature)	C_6H_6	—	—	4	Slow extraction at pH 4.5 but rapid back extraction
TTA (25 °C)	C_6H_6	1.0 M(H, Li)ClO_4	30 2.6×10^4 1.2×10^3	5	$Fe^{3+}+(HTTA)_{enol}\rightarrow FeTTA^{2+}+H^+$ $FeOH^{2+}+(HTTA)_{enol}\rightarrow FeTTA^{2+}$ $FeCl^{2+}+(HTTA)_{enol}\rightarrow FeTTA^{2+}+H^++Cl^-$
IPT (21±1 °C)	$CHCl_3$	1.0 M(H, Na)ClO_4 $[H^+]=1.0$	1.5×10^{10}	7	$Fe^{3+}+IPT^-\rightarrow Fe(IPT)^{2+}$ First-order dependence on $NaClO_4$ when its concentration is 1—4 M and zeroth-order dependence on H^+ in the range $[H^+]$ 1—5 M were also observed.

action or to a $FeOH^{2+}+HA \rightarrow FeA^{2+}+H_2O$ reaction. The present authors, however, believe that the former mechanism is dominant in the system studied in this paper, because, as may be seen from Fig. 4, the rate of extraction is always increased by the chloride-ion by a factor of $10^{0.24}$ at 5×10^{-3} M; that is, the increase is the same for lower $-\log[H^+]$ region, where the reactions between HA and the Fe^{3+} and $FeCl^{2+}$ species are dominant, and for the higher region, where the reactions between A^- and the Fe^{3+} and $FeCl^{2+}$ species are also dominant.

According to the viewpoint of previous authors,[5] the rate of extraction can be represented by:

$$-\frac{d[Fe^{3+}]}{dt}=k[HA]([Fe^{3+}]+K'[FeCl^{2+}]+K''[FeOH^{2+}])$$

$$=k[Fe^{3+}][HA](1+K'\beta_1[Cl^-]+K''K_h[H^+]^{-1}) \qquad (16)$$

where $K_h=[FeOH^{2+}][H^+][Fe^{3+}]^{-1}$. Thus, when the chloride concentration is zero and a certain value, L_1, and when the concentration of the extractant in the aqueous phase was a certain value of ha_1, the rates may be represented by:

$$-\frac{d[Fe^{3+}]}{dt}=k(ha_1)[Fe^{3+}](1+K''K_h[H^+]^{-1}) \qquad (17)$$

$$-\frac{d[Fe^{3+}]}{dt}=k(ha_1)[Fe^{3+}](1+K'\beta_1L_1+K''K_h[H^+]^{-1}) \qquad (18)$$

From these equations, it is obvious that the ratio of the two rates, which can be obtained by dividing Eq. (18) by Eq. (17), changes with the change in the hydrogen-ion concentration; this is not observed in the results in Fig. 4.

Although the hydrolysis does not seem to be the reason for the inversely first-order dependence of the rate on the hydrogen-ion shown in Figs. 3 and 4, hydrolysis seems to accelerate the rate of extraction. Unfortunately, since the rate in the higher $-\log[H^+]$ region, where the effect can be expected, is too high to be measured accurately by the experimental method employed here, the quantitative relation between the rate and the degree of hydrolysis could not be determined.

The conclusion drawn in the present study is somewhat similar to that reported by McCllelan and Menis for the extraction of Fe^{3+} with IPT.[7] They described that the extraction is proportional to $[HIPT]_{org}$ and $[H^+]^{-1}$, and they explained these dependences in terms of the $Fe^{3+}+IPT^- \rightarrow FeIPT^{2+}$ reaction. At the same time, they described that the rate is independent of $[H^+]$ when it is from 1.0 M to 5.0 M, although they did not give any rate constant for this latter reaction. They also reported that the rate at 0.1 M $[H^+]$ shown a first-order dependence on the concentration of the coexisting sodium perchlorate. In the present study, however, the effect of the change in the sodium perchlorate concentration on the rate of TTA extraction was found to be only slight, as may be seen from Table 2.

The results in Table 1 can be compared with those obtained with regard to beryllium(II) TTA extraction from a 4.0 M sodium perchlorate solution into carbon tetrachloride.[2] The rate constant of the formation of the first beryllium(II)–TTA complex in 4.0 M sodium perchlorate, $-d[Be^{2+}]/dt=k[Be^{2+}][A^-]$, was obtained as $10^{4.3}$ M^{-1} min^{-1}, which is about one three-hundredth of the rate constant of the first iron(III)–TTA complex under the same conditions. It is remarkable that the rate of the TTA extraction of beryllium(II) is only slightly affected by the formation of $BeCl^+$ species. For example, when the chloride concentration in a 4.0 M Na(Cl, ClO_4) medium is 1.0 M, about 25% of the total beryllium(II) is assumed to be in the $BeCl^+$ and $BeCl_2$ forms ($\beta_1=10^{-0.85}$ and $\beta_2=10^{-0.70}$)[12], but the difference in the rate of the TTA complex formation in the presence of the 1.0 M chloride-ion from that in its absence is small (Fig. 4 in Ref. 2).

It is remarkable that the TTA anion reacts with the hydrated Fe^{3+} ion much faster than does the undissociated TTA. Since it is known that the enol-form TTA in the aqueous phase reacts with a metal ion much faster than does the keto-form, and since the concentration of the enol-form is only one-sixtieth of the keto-form,[13] we may reasonably assume that the rate constant for the reaction which actually takes place, $Fe^{3+}+HA(enol) \rightarrow FeA^{2+}+H^+$, is about $10^{2.4}$ (M^{-1} min^{-1}) (60 times the K_{HA} value in Table 1(b) and that the $Fe^{3+}A^- \rightarrow FeA^{2+}$ reaction is thus $10^{4.5}$ times faster than the reaction with the enol-form undissociated TTA.

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