Unusually Slow Extraction Rate and Mechanism of Iron(III) with Trifluoroacetylacetone in Triton X-100 Micellar System.

Part I. Extraction Routes

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The rate of formation/extraction of iron(III) with trifluoroacetylacetone in Triton X-100 micellar solution at 298 K was measured by stopped-flow spectrophotometry to identify the route and mechanism of the extraction process. The rate was first order with respect to the metal ion and the extractant in the bulk aqueous phase and inverse first order to the hydrogen ion when the formation of extractable tris-complex was small. The rate obtained under such conditions agreed well with that of complex formation in the single aqueous solution; this suggests that the whole reactions is controlled only by the formation of the mono-complex in the bulk aqueous phase. On the other hand, the rate did not show clear dependencies on the ligand and the hydrogen ion, and was slower than the one expected from the complex formation in the aqueous solution when the formation of the extractable tris-complex was dominant. A slow material transport of the tris-complex from the bulk aqueous phase to the micellar pseudophase was estimated.

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Micellar and related biphasic solution systems have been used in many fields of chemistry instead of liquid-liquid systems,¹⁻⁵ because of the unique characteristics that the solutions can be handled safely and are environmentally-friendly while each system seems to have two phases without the use of toxic and/or flammable organic solvent. Many studies on the extraction of metals with water-insoluble chelating reagents using this useful medium have been reported, not only for applications in separation and preconcentration⁶⁻⁹ but also for fundamental research on the equilibria and kinetics of the extraction.¹⁰⁻¹⁶ The author has been interested in differences of extraction efficiencies in both equilibria and kinetics between micellar and conventional liquid-liquid systems and has studied to determine the effectiveness and possibility of the pseudophase system being applied for a practical separation/determination medium as to be an analogy of droplets of organic solvents.^{17,18} During the kinetic study of the extraction of iron(III) with benzoylacetone (Hbza) and benzoyltrifluoroacetone (Hbfa) into Triton X-100 micelle, the extraction mechanism with the latter extractant was found to be somewhat different from that in a conventional non-polar organic solvent-water system such as hexane-water, although the whole extraction equilibria in the micellar system can be analyzed by a manner similar to that in the liquid-liquid system.¹⁷ The ligands had no long alkyl chains and no additional salt was dissolved in the bulk aqueous phase during the study; thus the whole formation/extraction reaction in the system should be controlled by formation of the mono-complex in the bulk aqueous phase. All the overall reactions with Hbza were controlled only by the formation of the mono-complex in the bulk aqueous phase; however, the rate for Hbfa extraction was slower than that for the complex formation in the bulk aqueous phase as estimated from the partition constant of the extractant. The effect found in the Hbfa extraction system

has been observed also in the other trifluoromethyl substituted β -diketone system.¹⁹ Such differences may affect the efficiencies of analysis *i.e.*, separation factor or determination time, and thus, thorough considerations are necessary to utilize the medium for practical analytical processes.

In the present study, the rate of formation/extraction of iron(III) with trifluoroacetylacetone in the Triton X-100 micellar system has been investigated and compared with the rate of complex formation measured separately in aqueous solutions in order to clarify the change of the extraction rate. The ligand is much simpler and more water soluble than Hbfa; thus the rate of complex formation in the aqueous phase can be measured easily and the difference in the mechanism of complex formation in these solutions can be discussed precisely.

Experimental

All the reagents were of analytical grade and were used without purification. The trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione; Htfa) was supplied by Dojin Chemicals (Kumamoto, Japan). A nonionic surfactant Triton X-100 (polyethylene glycol *t*-octylphenyl ether; Fluka, more than 99% pure) was used as the micelle-forming reagent.

All the experiments were carried out in a thermostated room at 298 ± 0.5 K. In order to avoid ion-pair extraction of charged metal species into the micellar pseudophase, no additional salt was dissolved and the hydrogen-ion concentration was controlled by sulfuric acid.

The metal solution was prepared by dissolving a weighed amount of iron(III) perchlorate hexahydrate (Nacalai Tesque, Kyoto, Japan) into aqueous 0.01 M sulfuric acid and was stocked as 0.01 M solution. The measurements in the micellar system were carried out as follows. A certain volume of an

acidic micellar solution containing $2 \times 10^{-5} - 4 \times 10^{-3}$ M iron(III) and an equal volume of an acidic micellar solution containing $2 \times 10^{-4} - 0.1$ M of the extractant were mixed. To determine the rate of formation/extraction, changes in the absorbance of the resulting solution due to the formation/extraction of iron(III) complexes with the ligand were measured as a function of time, while the absorbance after a long-time standing was measured to determine the equilibria. The absorbance was monitored at 435 nm. The measurements were performed using an Otsuka Electronics RA-401 stopped-flow spectrophotometer using 1-cm light path or a Shimadzu UV-160 spectrophotometer using 1- or 5-cm light path. In the kinetic measurements with the stopped-flow instrument, the temperature was controlled at 298 ± 0.2 K by using a thermostated bath in the thermostated room. The concentrations of Triton X-100 in the micellar experiments were within the range $3.2 \times 10^{-3} - 0.08$ M (0.2 – 5.0%). The rate constants were taken as the average of a minimum of 5 kinetic runs. The hydrogen-ion concentration of the solutions was measured potentiometrically by a Toa IM-40S potentiometer using a glass electrode.

Data Treatment

In the present paper, all the chemical species in the micellar pseudophase are denoted by subscript “m”, those in the bulk aqueous phase by lack of any subscript, and those on the basis of total volume of the micellar solution by subscript “t”.

If the overall distribution reactions in the micellar system can be assumed to be similar to those in the conventional liquid-liquid systems, the following data treatment can be performed. The acid dissociation and partition constants of the β -diketone (HA) are expressed as:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] \quad (1)$$

$$K_d = [\text{HA}]_m/[\text{HA}] \quad (2)$$

The volume fractions of the micellar and bulk aqueous phases, V_m and V , can be defined as:

$$V_m = \phi(C_{\text{Triton X-100}} - C_{\text{CMC}}) \quad (3)$$

$$V = 1 - V_m \quad (4)$$

Here, ϕ is the molar volume of the micelle (1.29 M^{-1}),⁷ and $C_{\text{Triton X-100}}$ and C_{CMC} are the total concentration of Triton X-100 and the critical micelle concentration of the surfactant ($2.4 \times 10^{-4} \text{ M}$),²⁰ respectively. Using the above equilibrium constants, the mass balance of the extractant in the whole micellar solution can be written as:

$$[\text{HA}]_t = [\text{HA}]_m V_m + [\text{HA}]V + [\text{A}^-]V = \left\{ \frac{(K_d V_m + V)[\text{H}^+]}{K_a} + V \right\} [\text{A}^-] \quad (5)$$

where $[\text{HA}]_t$ gives the total amount of Htfa in the system based on the total volume of the micellar solution. The K_a value has been reported previously¹⁸ as $10^{-6.44 \pm 0.03}$ M by the author.

Under the present experimental conditions a trace amount (*i.e.*, three times of the total iron(III) concentration) of perchlorate anion exists in the solutions; however, the concentration is very low and no extraction of the charged species can be detected.¹⁸ Thus, only the tris-complex is extractable and the distribution ratio of the iron(III) in the

micellar solution can be defined by the ratio of the concentrations of the metal in the micellar and in the bulk aqueous phase as

$$D = \frac{[\text{Fe(III)}]_m}{[\text{Fe(III)}]} = \frac{[\text{FeA}_3]_m}{[\text{Fe}^{3+}] + [\text{FeA}^{2+}] + [\text{FeA}_2^{+}] + [\text{FeA}_3]} \\ = \frac{\beta_3 K_{dm} [\text{A}^-]^3}{1 + \sum \beta_n [\text{A}^-]^n} \quad (6)$$

Here, K_{dm} is the partition constant of the tris-complex and β_n is the stability constant of the “ n -th” complex in the bulk aqueous phase:

$$K_{dm} = [\text{FeA}_3]_m/[\text{FeA}_3] \quad (7)$$

$$\beta_n = [\text{FeA}_n^{(3-n)+}]/[\text{Fe}^{3+}][\text{A}^-]^n \quad (8)$$

As Berezin *et al.*²¹ have pointed out, it is possible to consider that the formation/extraction of metal ions with chelating reagent into micellar pseudophase takes two different routes; one is that the formation reaction proceeds only in the bulk aqueous phase and then the extractable tris-complex is extracted into the micellar pseudophase, and the other is that the whole complex formation reaction occurs in the micellar pseudophase.

$$R_{EX} = R_{AQ} + R_{MI} = k_{AQ}[\text{Fe}_T]V + k_{MI}[\text{Fe}_{T,m}]V_m \\ = \frac{k_{AQ}V + k_{MI}K_{Fe}V_m}{V + K_{Fe}V_m} [\text{Fe}_T^*]_t \quad (9)$$

Here, R_{AQ} and R_{MI} indicate the rate through the routes which are controlled by the formation reactions in the bulk aqueous and in the micellar phase, $[\text{Fe}_T]$, $[\text{Fe}_{T,m}]$ and $[\text{Fe}_T^*]_t$ are the uncomplex-formed iron(III) concentrations in the bulk aqueous and micellar phases, and the overall solution, and K_{Fe} is the partition constant for the uncomplex-formed metal ions. The values of the rates for the two paths R_{AQ} and R_{MI} is dependent on the parameters k_{AQ} , k_{MI} , K_{Fe} , V and V_m ; however, the value of K_{Fe} seems to be negligible in the present study because no additional salt was dissolved in the system. This means $[\text{Fe}_T^*]_t$ is similar to $[\text{Fe}_T]V$ ($= [\text{Fe}_T]_t$), and hence the whole formation/extraction seems to proceed only in the bulk aqueous phase.

The rate of formation/extraction of iron(III) complexes, R , is defined as the decrease of uncomplex-formed iron(III) in the aqueous phase (Fe_T) for the experiments which are carried out under the condition that the ligand concentration is far higher than that of the metal. On the other hand, the rate is defined as the decrease of unreacted extractant for determination of the rate of the mono-complex formation. The rate is analyzed by changes in the absorbance at the appropriate wavelength on the basis of the pseudo-first-order treatment. Under the experimental conditions of $[\text{Fe}_T]$ and pH, the iron(III) in the starting aqueous solutions may distribute to Fe^{3+} , Fe(OH)^{2+} and $\text{Fe}_2(\text{OH})_2^{4+}$. However, the concentration of $\text{Fe}_2(\text{OH})_2^{4+}$ among the total iron(III) becomes less than a few %, so only Fe^{3+} and Fe(OH)^{2+} are considered in the present study. The concentrations of Fe^{3+} and Fe(OH)^{2+} are calculated from the uncomplex-formed iron(III) using the hydrolysis constant ($K_h = 10^{-3.1} \text{ M}$)²² written as

$$[\text{Fe}_T] = [\text{Fe}^{3+}] + [\text{Fe(OH)}^{2+}] = ([\text{H}^+] + K_h)[\text{Fe}^{3+}]/[\text{H}^+] \quad (10)$$

$$K_h = [\text{Fe(OH)}^{2+}][\text{H}^+]/[\text{Fe}^{3+}] \quad (11)$$

Fig. 1 Relationship between $[\text{Fe(III)}]/A$ and $1/[\text{A}^-]$ for Htfa. Open symbols show the data obtained in the absence of Triton X-100, while closed ones give those in the presence of 2×10^{-4} M Triton X-100 monomer. The straight line gives the result obtained by a least square calculation on the basis of Eq. (13).

Results and Discussion

Equilibrium constants of iron(III) complexes with Htfa

The values of the stability constants as well as the molar absorptivity of the complex species, $\text{FeA}_n^{(3-n)+}$, formed in the aqueous phase were reexamined and recalculated to obtain a more precise set of these data to analyze the distribution of the complex species and the molar absorptivity in the kinetic measurements. When the metal ion and the ligand anion in aqueous solution can form colored 1:1 to 1:3 complex species, but no other species is formed, the absorbance of the solution normalized to the total metal concentration can be expressed as:

$$\frac{A}{[\text{Fe(III)}]} = \frac{\varepsilon_1[\text{FeA}^{2+}] + \varepsilon_2[\text{FeA}_2^+] + \varepsilon_3[\text{FeA}_3]}{[\text{Fe}^{3+}] + [\text{FeA}^{2+}] + [\text{FeA}_2^+] + [\text{FeA}_3]} \\ = \frac{\varepsilon_1\beta_1[\text{A}^-] + \varepsilon_2\beta_2[\text{A}^-]^2 + \varepsilon_3\beta_3[\text{A}^-]^3}{1 + \beta_1[\text{A}^-] + \beta_2[\text{A}^-]^2 + \beta_3[\text{A}^-]^3} \quad (12)$$

Here, ε_n is the molar absorptivity of the “ n -th” complex. When the ligand anion concentration is low enough, only the unreacted metal ion and the mono-complex species, FeA^{2+} , can exist in the aqueous solution and the reciprocal plot gives a set of β_1 and ε_1 values.

$$\frac{[\text{Fe(III)}]}{A} = \frac{1}{\varepsilon_1\beta_1[\text{A}^-]} + \frac{1}{\varepsilon_1} \quad (13)$$

Figure 1 shows the results. The plot gave a straight line when the ligand anion concentration was low but no difference was observed between the data in the absence and presence of 2×10^{-4} M Triton X-100 monomer. From the values of the slope and the intercept, a set of β_1 and ε_1 was calculated, as listed in Table 1.

Using the values of β_1 and ε_1 thus obtained and a that of ε_3 measured directly by dissolving tris(trifluoroacetylacetonato)iron(III) salt ($\varepsilon_3 = 3030 \text{ M}^{-1} \text{ cm}^{-1}$ at 435 nm),¹⁸ the other factors in Eq. (12), β_2 , β_3 and ε_2 , were recalculated by introducing the spectrophotometric data for all the experimental conditions of $[\text{A}^-]$ (see Fig. 2 in Ref. 18). The recalculated

Table 1 Summary of equilibrium constants for Htfa and its iron(III) complexes

Fe-Htfa (435 nm)	
$\log K_a (\text{M})$	-6.44 ± 0.03^a
$\log K_d$	0.63 ± 0.10
$\log K_{dm}$	3.00 ± 0.09
$\log \beta_1 (\text{M}^{-1})$	6.54 ± 0.10
$\log \beta_2 (\text{M}^{-2})$	12.11 ± 0.18
$\log \beta_3 (\text{M}^{-3})$	16.30 ± 0.46
$\varepsilon_1 (\text{M}^{-1} \text{ cm}^{-1})$	250 ± 20
$\varepsilon_2 (\text{M}^{-1} \text{ cm}^{-1})$	1500 ± 150
$\varepsilon_3 (\text{M}^{-1} \text{ cm}^{-1})$	3030 ± 20^a
$\varepsilon_{3m} (\text{M}^{-1} \text{ cm}^{-1})$	3350 ± 130^a

a. Ref. 18.

values are listed in Table 1.

Values of the partition constants of the ligand and the uncharged tris-complex, K_d and K_{dm} , were also recalculated from the spectrophotometric data (see Figs. 4(a) – 4(c) in Ref. 18) using the following equation:

$$\frac{A_t}{[\text{Fe(III)}]_t} = \frac{\varepsilon_1\beta_1V[\text{A}^-] + \varepsilon_2\beta_2V[\text{A}^-]^2 + \varepsilon_3\beta_3V[\text{A}^-]^3 + \varepsilon_{3m}\beta_3K_{dm}V_m[\text{A}^-]^3}{V + \beta_1V[\text{A}^-] + \beta_2V[\text{A}^-]^2 + \beta_3V[\text{A}^-]^3 + \beta_3K_{dm}V_m[\text{A}^-]^3} \quad (14)$$

Here, ε_n and ε_{3m} are the molar absorptivities of “ n -th” complexes in the bulk aqueous phase and of FeA_3 in the micellar pseudophase, which are based on the total volume of the micellar solution. The value of $[\text{A}^-]$ for each experiment can be calculated on the basis of Eq. (5). The results are also listed in Table 1.

Rate of formation of iron(III) complexes with Htfa in aqueous solutions

The rate of complex formation in the single aqueous solution was first measured to learn the whole formation/extraction rate and mechanism in the micellar system. Two different types of experiments were performed in the present study. To measure the true rate of the controlling step, the formation of the mono(trifluoroacetylacetonato)iron(III) complex species in the aqueous solution was determined under the condition that the initial iron(III) concentration was higher than the ligand concentration. The other type of experiment was carried out under the condition that Htfa concentration was far higher than that of the metal, so the metal was able to form higher complex species (*i.e.*, FeA_2^+ and FeA_3). The rates were measured in the absence and the presence of 2×10^{-4} M Triton X-100 to check effects of coexisting surfactant monomers on the rates.

The rate of formation of the mono-complex FeA^{2+} in the aqueous solution, $R_{\text{CF,L}}$, was measured by the decrease in the ligand concentration under several metal-ion and hydrogen-ion concentrations using the value of ε_1 ($= 250 \text{ M}^{-1} \text{ cm}^{-1}$). The results are listed in Table 2(a). After the correction of the formation of Fe(OH)^{2+} species for the unreacted metal concentration using Eq. (10), the rate was concluded to be first order with respect to the metal ion and inverse first order with respect to the hydrogen ion. From these, the rate equation can be written as

$$R_{\text{CF,L}} = k_{\text{CF,L,obsd}}[\text{HA}] = k_{\text{CF,L}}[\text{Fe}^{3+}][\text{HA}][\text{H}^+]^{-1} \quad (15)$$

The values of $k_{\text{CF,L}}$ are also listed in Table 2(a). The rate of formation of the mono-complex species in the aqueous solution

Table 2 Rate of complex formation of iron(III) with Htfa in aqueous solutions

(a) Rate of decrease in Htfa					
log[Fe _T]/M	pH	C _{Triton X-100} /M	log <i>k</i> _{CF,L obsd} /s ⁻¹	log <i>k</i> _{CF,L} /s ⁻¹	
-3.00	1.52	0	-3.12	-1.63	
-3.00	1.75	0	-2.98	-1.71	
-3.00	1.94	0	-2.78	-1.69	
-3.30	2.04	0	-3.02	-1.72	
-3.00	1.64	2 × 10 ⁻⁴	-3.00	-1.62	
-3.00	1.96	2 × 10 ⁻⁴	-2.76	-1.69	

(b) Rate of decrease in Fe _T					
log[HA _T]/M	pH	C _{Triton X-100} /M	ε _{av,CF} /M ⁻¹ cm ⁻¹	log <i>k</i> _{CF,M obsd} /s ⁻¹	log <i>k</i> _{CF,M} /s ⁻¹
-2.00	1.27	0	2.81 × 10 ²	-2.40	-1.66
-2.00	1.53	0	3.05 × 10 ²	-2.15	-1.67
-2.00	1.78	0	3.45 × 10 ²	-1.90	-1.66
-2.00	2.02	0	4.07 × 10 ²	-1.76	-1.74
-2.12	2.02	0	3.71 × 10 ²	-1.90	-1.76
-2.43	2.02	0	3.13 × 10 ²	-2.18	-1.74
-2.60	2.02	0	2.93 × 10 ²	-2.35	-1.73
-2.00	1.53	2 × 10 ⁻⁴	3.05 × 10 ²	-2.13	-1.65
-2.00	2.03	2 × 10 ⁻⁴	4.10 × 10 ²	-1.74	-1.73
-2.43	2.02	2 × 10 ⁻⁴	3.13 × 10 ²	-2.13	-1.69

is not affected by the addition of 2 × 10⁻⁴ M Triton X-100.

The rate of formation was also determined under the condition that the ligand concentration was far higher than that of the metal ion. In the experiments, the following assumption can be made.²³⁻²⁵ The formation of mono-complex is the rate-determining-step among all the formation reactions and that of the higher complex species is established rapidly. Hence, the complex species in the solution are in equilibria and the distribution of the three species does not change as the formation reaction progresses:

The increase in the absorbance during the reaction can be analyzed using an averaged molar absorptivity which can be calculated from the stability constants and the molar absorptivities of the complexes in Table 1. The averaged value, ε_{av,CF}, can be defined as:

$$\begin{aligned} \varepsilon_{\text{av,CF}} &= \frac{\varepsilon_1[\text{FeA}^{2+}] + \varepsilon_2[\text{FeA}_2^+] + \varepsilon_3[\text{FeA}_3]}{[\text{FeA}^{2+}] + [\text{FeA}_2^+] + [\text{FeA}_3]} \\ &= \frac{\varepsilon_1\beta_1[\text{A}^-] + \varepsilon_2\beta_2[\text{A}^-]^2 + \varepsilon_3\beta_3[\text{A}^-]^3}{\beta_1[\text{A}^-] + \beta_2[\text{A}^-]^2 + \beta_3[\text{A}^-]^3} \end{aligned} \quad (17)$$

Using this averaged molar absorptivity, we analyzed the rate of complex formation of iron(III) with Htfa. The values of observed rate constant, *k*_{CF,M obsd}, under several ligand and hydrogen-ion concentrations are summarized in Table 2(b). The rate was found to be first order with respect to the ligand concentration and inverse first order with respect to the hydrogen-ion concentration after the correction for the hydrolyzed species of the metal ions. From these, the rate equation for the formation of the whole complex species in the aqueous solution can be written as

$$R_{\text{CF,M}} = k_{\text{CF,M obsd}}[\text{Fe}_T] = k_{\text{CF,M}}[\text{Fe}^{3+}][\text{HA}][\text{H}^+]^{-1} \quad (18)$$

Table 3 Rate of mono-complex formation of iron(III) with Htfa in Triton X-100 micellar solutions

log[Fe _T]/M	pH	Triton X-100, %	log <i>k</i> _{EX,L obsd} /s ⁻¹	log <i>k</i> _{EX,L} /s ⁻¹
-3.00	1.74	5.0	-3.01	-1.65
-3.00	1.82	5.0	-2.96	-1.68
-3.00	2.17	5.0	-2.60	-1.64
-2.70	1.80	5.0	-2.69	-1.69
-3.00	1.75	1.0	-3.01	-1.72
-3.00	2.06	1.0	-2.74	-1.74
-3.00	2.17	1.0	-2.57	-1.67

The values of rate constant *k*_{CF,M} obtained are also listed in Table 2(b). As seen in Table 2(b), no obvious effect of the coexisting surfactant monomer is found.

The good agreement of the values of *k*_{CF,L} and *k*_{CF,M} (the averaged values of *k*_{CF,L} and *k*_{CF,M} are 10^{-1.68±0.04} s⁻¹ and 10^{-1.70±0.04} s⁻¹, respectively) indicates that the rate-determining-step of the formation reaction of iron(III) complexes with Htfa in the aqueous solution is the formation of mono-complex and the equilibria among the three complex species are established during the reaction.

Rate of formation/extraction of iron(III) with Htfa in Triton X-100 micellar solution

Two different types of experiments were performed in the present micellar system; one is the formation of the mono-complex, while the other is the formation/extraction of the four complexes (*i.e.*, FeA²⁺, FeA₂⁺, FeA₃ and FeA_{3m}).

The rate of mono-complex formation of iron(III) with Htfa in Triton X-100 micellar solutions was measured under the conditions that the iron(III) is excess to the extractant concentration. When the partition equilibrium of the extractant between the micellar pseudophase and the bulk aqueous phase is established during the formation reaction progress, the rate can be defined as the decrease in the total concentration of the extractant. The observed rate constant, *k*_{EX,L obsd}, in the several iron(III), hydrogen-ion and Triton X-100 concentrations calculated by the change of absorbance with formation of the mono-complex in the bulk aqueous phase using the value of ε₁, is summarized in Table 3. The rate was first order with respect to the metal, extractant and pH in each Triton X-100 concentration.

If the formation reaction proceeds only in the bulk aqueous phase, the rate equation can be written using the partition constant of the extractant and the volume fractions as:

$$\begin{aligned} R_{\text{EX}} &= \frac{-d(V[\text{HA}] + V_m[\text{HA}]_m)}{dt} = k_{\text{EX,L obsd}}(V[\text{HA}] + V_m[\text{HA}]_m) \\ &= k_{\text{EX,L obsd}}(V + K_d V_m)[\text{HA}] = k_{\text{EX,L}}[\text{Fe}^{3+}][\text{HA}][\text{H}^+]^{-1} \end{aligned} \quad (20)$$

The values of the rate constant, *k*_{EX,L}, obtained are summarized in Table 3, agreed well with each other even though the micellar concentration is varied. The averaged value (10^{-1.68±0.04} M⁻¹ s⁻¹) well agreed with that for *k*_{CF,M} or *k*_{CF,L}; such similarity in the results indicates that the formation reaction in the micellar system proceeds only in the bulk aqueous phase and that the extraction of uncomplex-formed iron(III) into the micellar pseudophase (*K*_{Fe}) is negligible.

The rate for the higher complex formation/extraction was measured under the conditions that the extractant concentration

Fig. 2 Typical stopped-flow trace of the formation/extraction of iron(III) with Htfa in Triton X-100 micellar system (open circles). Experimental conditions are: $C_{\text{Triton X-100}} = 5.0\%$, $[\text{Fe(III)}]_t = 1 \times 10^{-4} \text{ M}$, $[\text{HA-T}]_t = 5 \times 10^{-2} \text{ M}$ and $\text{pH} = 2.22$, (a)-6 in Table 4. The molar fraction of the extracted complex to the total complexes at equilibria (F_{C3m}) is 0.639, and 97.6% of the initially contained metal ions convert to the complex species at equilibria. Closed circles with numbers indicate the “ n -th” half-life calculated from the first half-life of the observed trace (14.7 s) using the difference in absorbance at just after mixing ($A_0 = 0$) and that at equilibrium ($A_\infty = 0.240$) on the basis of a mono-exponential reaction. Broken lines give estimated mono-exponential traces calculated using $k_{\text{EX,M calcd}} (= 1.09 \times 10^{-1} \text{ s}^{-1})$ and the averaged molar absorptivity for the appropriate condition: **a**, for the formation/extraction reactions in the whole extraction system ($\epsilon_{\text{av,EX}} = 2.45 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$); **b**, for the formation reactions only in the bulk aqueous phase and no extraction occurring ($\epsilon_{\text{av,CF}} = 8.54 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$). The concentration ratios of complex formed iron(III) to the total metals at equilibria are 97.6% (trace **a**) and 93.5% (trace **b**).

is largely in excess of the concentrations of metals. Because the partition constant of the uncharged FeA_3 complex, K_{dm} , is rather low (see Eq. (6)) and the volume ratio of the micellar pseudophase to the bulk aqueous phase is less than 1, the amount of iron(III) extracted is not similar to that of total complex species formed in the whole system. Therefore, the change in the optical absorbance of the micellar solution during the reaction does not directly reflect the increase in the extracted iron(III) into the micellar pseudophase, but the increase in all the complex species formed in the whole micellar solution. As was demonstrated in the previous papers,²³⁻²⁵ if all chemical reactions are controlled by the formation of the mono-complex and the reactions after the rate-determining-step proceed rapidly, the four complexes which are formed after the rate-determining-step can be assumed to be in equilibria:

The change in the absorbance can be analyzed using the averaged molar absorptivity, $\epsilon_{\text{av,EX}}$.

$$\begin{aligned} \epsilon_{\text{av,EX}} &= \frac{\epsilon_1 V[\text{FeA}^{2+}] + \epsilon_2 V[\text{FeA}_2^+] + \epsilon_3 V[\text{FeA}_3] + \epsilon_{3\text{m}} V_{\text{m}}[\text{FeA}_{3\text{m}}]}{V[\text{FeA}^{2+}] + V[\text{FeA}_2^+] + V[\text{FeA}_3] + V_{\text{m}}[\text{FeA}_{3\text{m}}]} \\ &= \frac{\epsilon_1 \beta_1 V[\text{A}^-] + \epsilon_2 \beta_2 V[\text{A}^-]^2 + \epsilon_3 \beta_3 V[\text{A}^-]^3 + \epsilon_{3\text{m}} \beta_3 K_{\text{dm}} V_{\text{m}}[\text{A}^-]^3}{\beta_1 V[\text{A}^-] + \beta_2 V[\text{A}^-]^2 + \beta_3 V[\text{A}^-]^3 + \beta_3 K_{\text{dm}} V_{\text{m}}[\text{A}^-]^3} \quad (22) \end{aligned}$$

During the measurements, it was found that the kinetic trace of the formation/extraction sometimes did not fit a typical mono-exponential curve on the unreacted metal concentration; the rate of the change in the absorbance in the early stage was slower than that after the first half-life. Figure 2 shows an example of the kinetic trace of the formation/extraction of iron(III) with Htfa in the micellar solution. The curvature for the observed trace (open circles) was somewhat different from the estimated mono-exponential curve (closed circles); the observed values became higher after the first half-life was past. Hence, the rate in the present measurement was calculated using the data obtained in the early stage.

The values of the observed rate constant for the formation/extraction of iron(III) with Htfa in the micellar system and the values of $\epsilon_{\text{av,EX}}$ calculated under several Triton X-100, Htfa and hydrogen-ion concentrations are listed in Table 4. The values of the first order rate constant for the R_{AQ} route $k_{\text{EX,M calcd}} (= k_{\text{CF,M}}[\text{HA}][\text{H}^+]^{-1} = k_{\text{CF,L}}[\text{HA}][\text{H}^+]^{-1})$, which are calculated as if the whole formation/extraction reaction proceeds only in the bulk aqueous phase, for each set of experimental conditions on $[\text{HA}]$ and $[\text{H}^+]$ are also given in Table 4. The observed rate constant $k_{\text{EX,M obsd}}$ showed first order dependency on the Htfa in the bulk aqueous phase and pH when the Triton X-100 concentration was lower and/or the ligand anion concentration in the bulk aqueous phase was lower ($[\text{HA}]$ was lower and/or $[\text{H}^+]$ was higher). In such cases, the values of $k_{\text{EX,M obsd}}$ were found to be similar to those of $k_{\text{EX,M calcd}}$. The facts indicate that the rate-determining-step of the formation/extraction reaction under such conditions is the formation of the mono-complex in the bulk aqueous phase and the extraction of the unreacted iron(III) and/or the formation reaction in the micellar pseudophase does not contribute to the whole extraction reaction. Hence, the following rate equation for the formation/extraction in the micellar system can be defined only for the results obtained under such conditions.

$$R_{\text{EX,M}} = k_{\text{EX,M obsd}}[\text{Fe-T}]_t = k_{\text{EX,M}}[\text{Fe}^{3+}][\text{HA}][\text{H}^+]^{-1} \quad (23)$$

On the other hand, no clear dependency of the rate of complex formation on the extractant and hydrogen-ion concentrations was found under the conditions that the surfactant concentration was higher and/or the ligand anion concentration in the bulk aqueous phase was higher ($[\text{HA}]$ was higher and/or $[\text{H}^+]$ was lower). In these cases, the values of $k_{\text{EX,M obsd}}$ became smaller than those of $k_{\text{EX,M calcd}}$, namely the rate of the formation/extraction was decelerated by some unknown reasons. Such differences in the two rates were observed only when the surfactant concentration was above 2.0%. The observed rate constant, however, approached to the calculated one with decreasing the ligand anion concentration, even though the surfactant concentration was high (5.0%). These facts suggest that the distribution of unreacted iron(III) into the micellar pseudophase is still small ($K_{\text{Fe}} \approx 0$), namely, the R_{MI} route is negligible in such higher surfactant concentration regions. The kinetic results for the higher $[\text{A}^-]$ region in the high surfactant concentration are, thus, analyzed tentatively as if the rate is first order with respect to the extractant in the bulk aqueous phase and the pH; the values of $k_{\text{EX,M}}$ are listed in Table 4. Because the dependencies on the components are unclear for some data, the values are not similar to each other.

Conditions for appearance of deceleration phenomenon in the micellar system

By considering the experimental conditions and the results described above, we can conclude that (i) the coexisting

Table 4 Rate of formation/extraction of iron(III) with Htfa in Triton X-100 micellar solutions

Exp. No.	$\log[\text{HA}_T]/\text{M}$	pH	$\epsilon_{\text{av,EX}}/\text{M}^{-1}\text{cm}^{-1}$	$\log k_{\text{EX,M obsd}}/\text{s}^{-1}$	$\log k_{\text{EX,M calcd}}/\text{s}^{-1}$	F_{C3m}	$\log k_{\text{EX,M}}/\text{s}^{-1}$
(a) Triton X-100 = 5.0%							
(a)-1	-1.60	1.49	4.19×10^2	-1.99	-1.95	0.026	-1.74
(a)-2	-1.60	1.82	7.25×10^2	-1.84	-1.63	0.101	-1.91
(a)-3	-1.60	2.07	1.22×10^3	-1.76	-1.40	0.242	-2.06
(a)-4	-1.60	2.24	1.69×10^3	-1.69	-1.24	0.385	-2.14
(a)-5	-1.60	2.35	2.00×10^3	-1.66	-1.15	0.488	-2.21
(a)-6	-1.30	2.22	2.45×10^3	-1.37	-0.96	0.639	-2.11
(a)-7	-1.30	2.38	2.77×10^3	-1.36	-0.82	0.753	-2.23
(a)-8	-1.70	2.41	1.90×10^3	-1.61	-1.20	0.453	-2.11
(a)-9	-1.82	2.38	1.45×10^3	-1.74	-1.35	0.312	-2.09
(a)-10	-2.10	2.39	8.46×10^2	-1.85	-1.61	0.134	-1.94
(b) Triton X-100 = 2.0%							
(b)-1	-1.90	1.50	3.18×10^2	-2.15	-2.17	0.004	-1.68
(b)-2	-1.90	2.00	5.10×10^2	-1.83	-1.69	0.033	-1.84
(b)-3	-1.90	2.26	7.81×10^2	-1.71	-1.46	0.092	-1.95
(c) Triton X-100 = 1.0%							
(c)-1	-1.90	1.41	3.03×10^2	-2.18	-2.23	0.001	-1.65
(c)-2	-1.90	1.67	3.50×10^2	-1.94	-1.98	0.004	-1.66
(c)-3	-1.90	1.90	4.24×10^2	-1.80	-1.76	0.012	-1.74
(d) Triton X-100 = 0.5%							
(d)-1	-2.30	1.50	2.76×10^2	-2.50	-2.53	< 0.001	-1.67
(d)-2	-2.30	2.00	3.32×10^2	-2.10	-2.05	0.002	-1.75
(d)-3	-2.30	2.25	3.96×10^2	-1.86	-1.82	0.005	-1.74
(e) Triton X-100 = 0.2%							
(e)-1	-2.00	1.52	3.04×10^2	-2.16	-2.20	< 0.001	-1.66
(e)-2	-2.00	1.78	3.46×10^2	-1.98	-1.95	0.001	-1.73
(e)-3	-2.00	2.02	4.13×10^2	-1.76	-1.72	0.003	-1.74
(e)-4	-2.00	2.32	5.55×10^2	-1.49	-1.45	0.009	-1.74
(e)-5	-2.30	2.03	3.36×10^2	-1.98	-2.01	0.001	-1.67

surfactant monomer does not affect the formation equilibria of the complex species, (ii) the partition of the extractant between the micellar pseudophase and the bulk aqueous phase is rapid and is in the equilibrium, (iii) the extraction of the uncomplexed iron(III) into the micellar pseudophase is negligibly small, (iv) the formation of iron(III) complexes with Htfa in Triton X-100 micellar system proceeds only in the bulk aqueous phase, and (v) the reaction in the bulk aqueous phase is essentially controlled by the formation of the mono-complex. Hence, the deceleration phenomenon on the formation/extraction observed in the present study is due to a change of reaction rate or equilibria after the rate-determining-step by a blocking reaction.

As seen from Table 4, the deceleration phenomenon was found when the ligand anion concentration in the bulk aqueous phase was higher. Moreover, the difference varied with the change of the concentration of Triton X-100 micelle; being higher in higher surfactant concentration. On the other hand, the effect was not found when the surfactant concentration was less than 1.0%. These facts indicate that the changes in the distribution of four complex species in the system may affect the deceleration phenomenon. In the higher $[\text{A}^-]$ and/or the higher surfactant concentration regions, the higher complex species becomes dominant in the equilibria among the successively formed four complex species. It is possible to conclude that the equilibria among the three complex species in the bulk aqueous phase are established during the reaction; so the deceleration phenomenon may be due to the slow extraction process of the tris-complex FeA_3 formed in the bulk aqueous phase into the micellar pseudophase. The fraction of the extracted tris-complex among the whole complex species at

equilibria, F_{C3m} , can be calculated as

$$F_{\text{C3m}} = \frac{V_{\text{m}}[\text{FeA}_3]_{\text{m}}}{V[\text{FeA}^{2+}] + V[\text{FeA}_2^+] + V[\text{FeA}_3] + V_{\text{m}}[\text{FeA}_3]_{\text{m}}} \\ = \frac{\beta_3 K_{\text{dm}} V_{\text{m}} [\text{A}^-]^3}{\beta_1 V [\text{A}^-] + \beta_2 V [\text{A}^-]^2 + \beta_3 V [\text{A}^-]^3 + \beta_3 K_{\text{dm}} V_{\text{m}} [\text{A}^-]^3} \quad (24)$$

The values of F_{C3m} are also listed in Table 4. The difference between the values of $k_{\text{EX,M obsd}}$ and $k_{\text{EX,M calcd}}$ is larger when the value of F_{C3m} is larger than 0.03, while these two values are almost similar when the value is lower than 0.01.

The above estimation can be explained in Fig. 2. Broken line **a** shows the estimated curve for which the rate of mono-complex formation in the bulk aqueous phase controls the whole extraction system, on the other hand, broken line **b** gives the trace for which the complex species exists only in the bulk aqueous phase. If the extraction rate of the tris-complex into the micellar pseudophase is much smaller than that of the formation, the complex species exists only in the bulk aqueous phase in the early stage of the reaction and the averaged molar absorptivity for the whole system ($\epsilon_{\text{av,EX}}$) must become similar to the value of $\epsilon_{\text{av,CF}}$. Hence, the observed absorbance (open circles) becomes lower than that estimated for the whole extraction (trace **a**) but fits with that for complex formation (trace **b**) in the early stage, even though the formation reaction is controlled only by the mono-complex formation in the bulk aqueous phase. The value of $\epsilon_{\text{av,EX}}$ is variable during each kinetic measurement; it gives the $\epsilon_{\text{av,CF}}$ value initially but increases gradually with the slow extraction of FeA_3 and finally approaches to the value of $\epsilon_{\text{av,EX}}$. This may be a reason for the

deceleration in the change of absorbance (open circles) by comparing to the “chemically-driven” curvature (trace **a**) and also for the deviation of the shape of the trace from a mono-exponential curvature.

The above observations strongly suggest that the unusually slow extraction rate found in the present micellar extraction system is due to the slow extraction process of tris-complex formed in the bulk aqueous phase to the micellar pseudophase. The effect of the interfacial transport of the tris-complex on the whole extraction rate will be investigated and discussed precisely in the Part II of the present series.²⁶

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