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

Part II. Interfacial Transport

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In order to learn reasons of the slow formation/extraction rate of iron(III) with trifluoroacetylacetone in Triton X-100 micellar system, the rate of material transport of the extractable tris-complex from the bulk aqueous phase to the micellar pseudophase was investigated at 298 K. The rate was successfully measured using a micellar-concentration-jump stopped-flow technique; the rate was independent of the ligand, the hydrogen ion and the Triton X-100 concentrations of the starting solutions while it was first order with respect to the surfactant concentration of the resulting solutions. The rate of transport was slow enough to reduce the rates of the overall extraction reactions. The rate of formation/extraction in the micellar system was recalculated as if the extraction of the tris-complex was negligibly slow; the corrected rate constant agreed well with that obtained in the aqueous solution. The slow extraction rate observed in the trifluoroacetylacetone-Triton X-100 micellar system was concluded to be due to the slow interfacial transport of the tris-complex.

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As has been demonstrated in Part I,¹ the rate of formation/extraction of iron(III) with a kind of trifluoromethyl-substituted β -diketone (HA), trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione; Htfa) in aqueous Triton X-100 micellar solution system is sometimes slower than that estimated from the complex formation rate in the single aqueous solution, although the formation reaction proceeds only in the bulk aqueous phase. The difference in the rates observed and estimated are found to be larger when the ligand anion concentration in the bulk aqueous phase is higher and/or the surfactant concentration is higher. In such conditions, the molar fraction of the extracted tris-complex (FeA_3) to the whole complex species in the system (FeA^{2+} , FeA_2^+ , FeA_3 and FeA_{3m}) becomes higher. The formation reaction in the present micellar system is essentially controlled only by the formation of the mono-complex in the bulk aqueous phase and the equilibria among the three complex species in the bulk aqueous phase (FeA^{2+} , FeA_2^+ and FeA_3) are established while the reaction proceeds; hence, the deceleration phenomenon is assumed to be due to a slow material transport of the extractable tris-complex from the bulk aqueous phase to the micellar pseudophase.

In the present part of the series, the rate of material transport of the tris-complex from the bulk aqueous phase to the micellar pseudophase has been directly measured using a novel micellar-concentration-jump stopped-flow technique in order to learn the reason for the slow extraction of iron(III) with Htfa into Triton X-100 micellar pseudophase.

Experimental

All the reagents, instruments and experimental conditions are

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similar to those used in Part I.¹ The measurements for the material transport of the tris-complex were carried out as follows. An acidic metal solution containing 2×10^{-4} M iron(III), $4 \times 10^{-3} - 2 \times 10^{-2}$ M Htfa and 0.2, 0.5 or 1.0% Triton X-100, and an acidic ligand solution containing $4 \times 10^{-3} - 3 \times 10^{-2}$ M Htfa and 0.8 - 9.8% of the surfactant were mixed up and the change of absorbance at 435 nm was monitored by the stopped-flow spectrophotometer. The ligand anion concentration in the bulk aqueous phase of the resulting solution was controlled similar to that in the starting metal solution to avoid changes of total concentrations of complex species in the resulting solution just after the mixing with formation/decomposition due to some changes of the ligand anion concentration. The rate constants were taken as the average of results for a minimum of 5 kinetic runs. The absorbance and the pH of the resulting solutions were also monitored after the extraction equilibria were established.

Data Treatment

In the present paper, the chemical species in the micellar pseudophase are denoted by subscript "m", those in the bulk aqueous phase by lack of subscript, and those on the basis of total volume of the micellar solution by subscript "t". The subscript "(S)" denotes the species in the starting metal solution and "(R)" denotes a species in the resulting solution. The equilibrium and the rate constants defined in Part I¹ are utilized without any explanation.

If the rate of successive formation of $\text{FeA}_m^{(3-n)+}$ after the rate-determining-step (*i.e.*, formation of the mono-complex) is fast enough to establish the equilibria among the three complex species in the bulk aqueous phase and if the total concentrations of the complex species in the system do not change during the kinetic measurement, the molar fraction of the extracted tris-

complex among the whole complex species in the system becomes higher with increasing the volume fraction of the micellar pseudophase. By controlling the ligand anion concentration of the resulting solution similar to that of the starting metal solution, the sum of the fractions of the complex species in the bulk aqueous phase in the resulting solution just after the mixing can be kept similar to that in the starting metal solution. As estimated in Part I,¹ if the rate of tris-complex transport from the bulk aqueous phase to the micellar pseudophase is slower than that for successive formation in the bulk aqueous phase, the number of the tris-complex molecules which have already been extracted into the micelle at just after the mixing must be similar to that in the starting metal solution. Hence, the absorbance of the starting metal solution ($A_{(S)}$) and the resulting solution just after their mixing ($A_{(R)} T=0$) can be expressed as:

$$A_{(S)} = (\epsilon_1 F_{T1(S)} + \epsilon_2 F_{T2(S)} + \epsilon_3 F_{T3(S)} + \epsilon_{3m} F_{T3m(S)}) [Fe(III)_{(S)}]_t \\ = \{\epsilon_{av,CF(R)} (F_{T1(S)} + F_{T2(S)} + F_{T3(S)}) + \epsilon_{3m} F_{T3m(S)}\} [Fe(III)_{(S)}]_t \quad (1)$$

$$A_{(R)} T=0 = \left\{ \frac{\epsilon_1 F_{T1(R)} + \epsilon_2 F_{T2(R)} + \epsilon_3 F_{T3(R)}}{F_{T1(R)} + F_{T2(R)} + F_{T3(R)}} \times \right. \\ \left. (F_{T1(S)} + F_{T2(S)} + F_{T3(S)}) + \epsilon_{3m} F_{T3m(S)} \right\} [Fe(III)_{(R)}]_t \\ = \{\epsilon_{av,CF(R)} (F_{T1(S)} + F_{T2(S)} + F_{T3(S)}) + \epsilon_{3m} F_{T3m(S)}\} [Fe(III)_{(R)}]_t \quad (2)$$

Here, the components F_{Tn} give the molar fraction of the “ n -th” complex species among the total metal concentrations and $[Fe(III)]_t$ is the total metal concentration in the whole system. Because the starting metal solution is diluted twice with the same volume of the starting ligand solution, the concentration of iron(III) in the resulting solution, $[Fe(III)_{(R)}]_t$, must be the half of that in the starting metal solution, $[Fe(III)_{(S)}]_t$. After a long-time standing the absorbance of the resulting solution finally becomes

$$A_{(R)} T=\infty = \{\epsilon_1 F_{T1(R)} + \epsilon_2 F_{T2(R)} + \epsilon_3 F_{T3(R)} + \epsilon_{3m} F_{T3m(R)}\} [Fe(III)_{(R)}]_t \\ = \{\epsilon_{av,CF(R)} (F_{T1(R)} + F_{T2(R)} + F_{T3(R)}) + \epsilon_{3m} F_{T3m(R)}\} [Fe(III)_{(R)}]_t \quad (3)$$

The absorbance changes from $A_{(R)} T=0$ to $A_{(R)} T=\infty$ with the reaction time, and thus, the rate of transport of the tris-complex can be analyzed as the decrease in the total complex species in the bulk aqueous phase as:

$$R_{TR} = \frac{-dV([FeA_2^{2+}] + [FeA_2^+] + [FeA_3])}{dt} \\ = k_{TR \text{ obsd}} V([FeA_2^{2+}] + [FeA_2^+] + [FeA_3]) \quad (5)$$

Total concentrations of iron(III) complex species in the bulk aqueous phase of the resulting solution at a certain reaction time x , $C_{nAQ} T=x$, can be calculated as:

$$C_{nAQ} T=x = \frac{A_{(R)} T=x - \epsilon_{3m} (F_{T1(S)} + F_{T2(S)} + F_{T3(S)} + F_{T3m(S)}) [Fe(III)_{(R)}]_t}{\epsilon_{av,CF(R)} - \epsilon_{3m}} \quad (6)$$

The true rate for transport of FeA_3 from the bulk aqueous phase to the micellar pseudophase (k_{TR}) is calculated using the molar fraction of FeA_3 among the three complex species in the bulk aqueous phase:

$$k_{TR} = \frac{k_{TR \text{ obsd}} (F_{T1(R)} + F_{T2(R)} + F_{T3(R)})}{F_{T3(R)}} = k_{TR \text{ obsd}} / F_{T3(R)AQ} \quad (7)$$

Table 1 Rate of phase transport of $Fe(tfa)_3$ in Triton X-100 micellar solutions

(a) Conditions for starting metal solutions					
$\log[HA_T]/M$	pH	Triton X-100, %	$\Sigma F_{Tn(S)}$	$A_{(S)}/[Fe(III)_{(S)}]_t$ $M^{-1} \text{ cm}^{-1}$	Metal soln. No.
-2.33	2.95	0.2	0.830	6.60×10^2	A
-2.40	2.96	0.2	0.803	5.90×10^2	B
-2.00	2.58	0.5	0.853	7.30×10^2	C
-1.70	2.53	1.0	0.941	1.40×10^3	D
(b) Conditions for resulting solutions					
Soln. No.	$\log[HA_T]/M$	pH	Triton X-100, %	$\Sigma F_{Tn(R)}$	$\epsilon_{av,CF(R)}$ $M^{-1} \text{ cm}^{-1}$
A-1	-2.33	3.00	1.0	0.853	7.32×10^2
A-2	-2.33	3.00	2.0	0.858	7.12×10^2
B-1	-2.40	3.03	0.5	0.829	7.18×10^2
B-2	-2.30	3.00	1.0	0.869	7.57×10^2
B-3	-2.30	3.01	2.0	0.878	7.45×10^2
B-4	-2.40	3.09	5.0	0.863	6.80×10^2
C-1	-1.89	2.58	1.0	0.899	7.53×10^2
C-2	-1.89	2.58	2.0	0.904	7.33×10^2
D-1	-1.60	2.56	5.0	0.975	8.86×10^2
D-2	-1.30	2.52	5.0	0.995	1.12×10^3
(c) Results for kinetic measurements					
Soln. No.	$\log k_{TR \text{ obsd}}/s^{-1}$	$F_{C3(R)AQ}$	$\log k_{TR}/s^{-1}$	$\log \{M_{Triton X-100}/M_{(micelle)}\}$	$\log k_{TR}^*/M_{(micelle)}^{-1} s^{-1}$
A-1	-2.12	0.009	-0.07	-3.96	3.89
A-2	-1.89	0.008	0.21	-3.66	3.86
B-1	-2.64	0.008	-0.55	-4.27	3.71
B-2	-2.06	0.010	-0.06	-3.96	3.90
B-3	-1.86	0.009	0.17	-3.66	3.82
B-4	-1.65	0.007	0.52	-3.26	3.77
C-1	-2.21	0.010	-0.20	-3.96	3.76
C-2	-1.98	0.009	0.07	-3.66	3.73
D-1	-1.34	0.018	0.41	-3.26	3.67
D-2	-0.89	0.041	0.49	-3.26	3.75

The rate of transport of FeA_3 complex can be thus obtained by measuring the changes in absorbance introduced by mixing of aqueous $FeA_n^{(3-n)+}$ solution and Htfa-containing micellar solution.

Results and Discussion

Rate of $Fe(tfa)_3$ transport from bulk aqueous phase to Triton X-100 micellar pseudophase

The results on the rate of transport of the tris-complex measured by the micellar-concentration-jump stopped-flow technique are summarized in Table 1. The total fraction of the complex species in the system for the resulting solution at equilibria could not be kept very similar to that in the starting metal solution because the extraction capacity of the micellar pseudophase became high with the mixing, even though the ligand anion concentration in the resulting solution could be controlled similar to that in the starting metal solution. However, the total fraction of the complex species in the starting solution was higher than 80% and the additional formation was less than 6% (see Table 1); thus the effect would be small and no correction was made.

As seen in Table 1(c), the values of the transport rate for FeA_3 , k_{TR} , are independent of the starting conditions, such as Triton X-100 concentration, the resulting extractant concentration and pH, while they are first order with respect to the

concentrations of Triton X-100 micellar pseudophase in the resulting solution, $\{M_{\text{Triton X-100}}\}_t$. The concentration of the micelle is calculated as one micellar aggregate being formed with 143 molecules of the monomer.² More than 95% of the tris-complex formed in the system is extracted into the micellar pseudophase under the present experimental conditions; the obtained transport rate, k_{TR} , shows the rate of forward extraction. From the proportional relationship between k_{TR} and $\{M_{\text{Triton X-100}}\}_t$, the value of FeA_3 transport rate for one micelle, k_{TR}^* ($= k_{\text{TR}}/\{M_{\text{Triton X-100}}\}_t$) is calculated to be $10^{3.79 \pm 0.08} \text{ M}_{(\text{micelle})}^{-1} \text{ s}^{-1}$.

The author and coworkers³ have previously demonstrated that the intercept of the stopped-flow trace at time zero gives the chemical conditions of the resulting solution just after the mixing. In the present experiments, it is also noteworthy that the unusual slow transport of tris-complex may also be verified by the values of intercept in the kinetic trace with the stopped-flow measurements. The values of intercept obtained in the present experiments may be explained by the following three typical cases: (i) If the entire reactions are slow, the molar fractions of four complexes in the system do not change by the mixing. The absorbance of the resulting solution becomes half of that for the starting metal solution as in Eq. (1) ($A_{\text{CAL1}} = A_{\text{S}}/2$). (ii) If the additional formation of the complexes is negligible and the extraction of the tris-complex is slow, the total number of the complex species in the bulk aqueous phase as well as that of the tris-complex in the micellar pseudophase does not change, while the distributions of the complex species in the bulk aqueous phase can change due to changing the ligand anion concentration by mixing. The absorbance A_{CAL2} must be equal to $A_{\text{R}} \text{ } T=0$. (iii) If the additional complex formation is negligible but the reaction steps after the rate-determining-step are fast, the total number of the overall complex species in the system does not change, but the distributions of the complex species in the system can quickly change so as to fit the new ligand anion conditions of the system. The absorbance A_{CAL3} becomes $\{\epsilon_{\text{av,CF(R)}}(F_{\text{T1(R)}} + F_{\text{T2(R)}} + F_{\text{T3(R)}}) + \epsilon_{\text{3m}}F_{\text{T3m(R)}}\}[\text{Fe(III)}]_t$. Table 2 gives the observed and the calculated values of the absorbance of the resulting solution just after mixing for the kinetic experiments in Table 1. The experimentally obtained values for the intercept are the closest to A_{CAL2} for each kinetic run. The results also suggest that the tris-complex transport is slower than the successive reactions among the three complex species in the bulk aqueous phase, and thus, it may possibly decelerate the whole extraction reaction.

The overall extraction mechanism in Triton X-100 micellar system

As described above, the material transport of the tris-complex which is formed in the bulk aqueous phase to the micellar pseudophase is much slower than the reactions among the three complex species in the bulk aqueous phase.

The overall formation/extraction process includes two slow reactions, thus, the magnitude of the reaction rates in the two steps can be compared. The rate of material transport from the bulk aqueous phase to the micellar pseudophase ($k_{\text{TR calcd}}$) for each kinetic experiment for the formation/extraction in the micellar system (Table 4 in Part I¹) is calculated using the values of k_{TR}^* , $\{M_{\text{Triton X-100}}\}_t$ and $F_{\text{T3(R)}} \text{ AQ}$. The values are summarized in Table 3. The $k_{\text{TR calcd}}$ values are always slower than the estimated formation rate $k_{\text{EX,M calcd}}$ values; the whole reaction must be affected by the slow extraction of the tris-complex in the present Triton X-100 micellar system.

Table 2 Observed and calculated values of intercept of kinetic trace for phase transport of Fe(tfa)_3 in Triton X-100 micellar solutions

Soln. No.	$[\text{Fe(III)}_{(\text{R})}]/\text{M}$	$A_{T=0 \text{ obsd}}/\text{cm}^{-1}$	$A_{\text{CAL1}}/\text{cm}^{-1}$	$A_{\text{CAL2}}/\text{cm}^{-1}$	$A_{\text{CAL3}}/\text{cm}^{-1}$
A-1	1×10^{-4}	0.068	0.066	0.067	0.094
A-2	1×10^{-4}	0.068	0.066	0.066	0.115
B-1	1×10^{-4}	0.065	0.059	0.063	0.074
B-2	1×10^{-4}	0.067	0.059	0.066	0.097
B-3	1×10^{-4}	0.064	0.059	0.065	0.120
B-4	1×10^{-4}	0.061	0.059	0.060	0.148
C-1	1×10^{-4}	0.076	0.073	0.078	0.102
C-2	1×10^{-4}	0.077	0.073	0.077	0.124
D-1	1×10^{-4}	0.156	0.140	0.141	0.239
D-2	1×10^{-4}	0.168	0.140	0.157	0.279

Such effects of slow extraction rate on the overall extraction rate in the micellar system can be demonstrated as follows. The overall extraction rate can theoretically be defined as:

Here, $\{\text{FeA}^{2+} + \text{FeA}_2^+ + \text{FeA}_3\}$ indicates the equilibrium state for the three complex species, k_1 and k_{-1} are the forward and the backward reaction rates for the formation in the bulk aqueous phase, k_2 and k_{-2} are the forward and the backward rates for the interfacial transport. When the overall extraction equilibria are established, the following relationships between k_1 and k_{-1} as well as k_2 and k_{-2} can be deduced:

$$k_1 V[\text{Fe}^{3+}] = k_{-1} V\{\text{FeA}^{2+} + \text{FeA}_2^+ + \text{FeA}_3\} \quad (10)$$

$$k_2 V\{\text{FeA}^{2+} + \text{FeA}_2^+ + \text{FeA}_3\} = k_{-2} V_{\text{m}}[\text{FeA}_{3\text{m}}] \quad (11)$$

Since the values for k_1 and k_2 at a certain $[\text{A}^-]$ condition are known, the backward rate constants k_{-1} and k_{-2} can be obtained. By introducing the backward rates into Eq. (9), the concentrations at a certain time x , $[\text{Fe}^{3+}]_{T=x}$, $\{\text{FeA}^{2+}\}_{T=x} + [\text{FeA}_2^+]_{T=x} + [\text{FeA}_3]_{T=x}$ and $[\text{FeA}_{3\text{m}}]_{T=x}$, can be calculated and the changes in the absorbance and the averaged molar absorptivity can also be simulated as a function of reaction time:

$$A_{T=x} = \epsilon_{\text{av,CF}} V\{[\text{FeA}^{2+}]_{T=x} + [\text{FeA}_2^+]_{T=x} + [\text{FeA}_3]_{T=x}\} + \epsilon_{3\text{m}} V_{\text{m}}[\text{FeA}_{3\text{m}}]_{T=x} \quad (12)$$

$$\epsilon_{\text{av,EX } T=x} = A_{T=x} / \{V\{[\text{FeA}^{2+}]_{T=x} + [\text{FeA}_2^+]_{T=x} + [\text{FeA}_3]_{T=x}\} + V_{\text{m}}[\text{FeA}_{3\text{m}}]_{T=x}\} \quad (13)$$

Figures 1(a) and 1(b) show the changes in distributions of each metal species and those in the averaged molar absorptivity as a function of reaction time. As seen in Fig. 1(a), the decrease in Fe^{3+} (curve **a**) is rapid, while the total concentration of the three complex species in the bulk aqueous phase (curve **b**) shows a transient maximum at 14 s, and the percentage of extracted tris-complex (curve **c**) increases gradually to the final value (62.0%) at about 120 s. The averaged molar absorptivity in Fig. 1(b) is changed with the reaction time; it is similar to that for the aqueous three complexes ($\epsilon_{\text{av,CF}}$; see Eq. (17) in Part I¹) at initial stages, while it increases gradually and finally approaches to $\epsilon_{\text{av,EX}} (= 2.45 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})$. Figure 2 gives the results of the simulation for the change of absorbance. The original data in Fig. 2 (open circles) are similar to those in Fig. 2 in Part I.¹ The calculated trace obtained using Eq. (12) (closed circles) is well-

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

Exp. No. ^a	$\log k_{\text{EX,M calcd}}^*/\text{s}^{-1}$	$\log F_{\text{T3(R)AQ}}$	$\log k_{\text{TR calcd}}^*/\text{s}^{-1}$	$\varepsilon_{\text{av, CF}}/\text{M}^{-1}\text{cm}^{-1}$	$\log k_{\text{EX,M obsd}}^*/\text{s}^{-1}$	$\log k_{\text{EX,M}}^*/\text{s}^{-1}$
(a) Triton X-100 = 5.0%						
(a)-1	-1.95	-3.63	-3.14	3.41×10^2	-1.88	-1.63
(a)-2	-1.63	-3.01	-2.51	4.31×10^2	-1.59	-1.66
(a)-3	-1.40	-2.55	-2.06	5.43×10^2	-1.38	-1.68
(a)-4	-1.24	-2.26	-1.77	6.44×10^2	-1.24	-1.69
(a)-5	-1.15	-2.08	-1.58	7.20×10^2	-1.18	-1.73
(a)-6	-0.96	-1.81	-1.31	8.54×10^2	-0.98	-1.71
(a)-7	-0.82	-1.57	-1.08	9.90×10^2	-0.89	-1.76
(a)-8	-1.20	-2.14	-1.64	6.94×10^2	-1.17	-1.67
(a)-9	-1.35	-2.40	-1.91	5.92×10^2	-1.31	-1.66
(a)-10	-1.61	-2.87	-2.37	4.60×10^2	-1.59	-1.68
(b) Triton X-100 = 2.0%						
(b)-1	-2.17	-4.06	-3.96	3.06×10^2	-2.14	-1.67
(b)-2	-1.69	-3.10	-3.01	4.14×10^2	-1.72	-1.73
(b)-3	-1.46	-2.62	-2.53	5.22×10^2	-1.48	-1.72
(c) Triton X-100 = 1.0%						
(c)-1	-2.23	-4.18	-4.39	2.99×10^2	-2.17	-1.63
(c)-2	-1.98	-3.68	-3.89	3.37×10^2	-1.92	-1.64
(c)-3	-1.76	-3.25	-3.46	3.89×10^2	-1.78	-1.73
(d) Triton X-100 = 0.5%						
(d)-1	-2.53	-4.76	-5.28	2.75×10^2	-2.50	-1.67
(d)-2	-2.05	-3.78	-4.30	3.27×10^2	-2.10	-1.75
(d)-3	-1.82	-3.30	-3.82	3.81×10^2	-1.85	-1.73
(e) Triton X-100 = 0.2%						
(e)-1	-2.20	-4.11	-5.05	3.03×10^2	-2.16	-1.66
(e)-2	-1.95	-3.61	-4.54	3.44×10^2	-1.98	-1.73
(e)-3	-1.72	-3.15	-4.09	4.05×10^2	-1.76	-1.76
(e)-4	-1.45	-2.60	-3.54	5.28×10^2	-1.49	-1.74
(e)-5	-2.01	-3.71	-4.64	3.34×10^2	-1.96	-1.65

a. Taken from Table 4 in Ref. 1.

Fig. 1 (a) Changes in percentages of unreacted Fe^{3+} (curve **a**), the total of the three complexes in the bulk aqueous phase (curve **b**) and the extracted tris-complex (curve **c**) as a function of reaction time. (b) Changes in averaged molar absorptivity for the whole micellar solution system as a function of time. The parameters for the calculations are: $[\text{Fe(III)}]_i = 1 \times 10^{-4} \text{ M}$, $k_1 = 1.09 \times 10^{-1} \text{ s}^{-1}$, $k_{-1} = 7.36 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 4.63 \times 10^{-2} \text{ s}^{-1}$, $k_{-2} = 2.66 \times 10^{-2} \text{ s}^{-1}$, $\varepsilon_{\text{av,CF}} = 8.54 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{\text{3m}} = 3.35 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

fitted with the observed trace, and the formation/extraction mechanism estimated as in Eq. (9) seems to be correct.

Fig. 2 Changes in absorbance with the formation/extraction of iron (III) with Htfa in Triton X-100 micellar system as a function of time. The observed data (open circles) are taken from Fig. 2 in Part I. Closed circles show the estimated trace calculated on the basis of Eq. (12).

Correction for the rate of complex formation with Htfa in Triton X-100 micellar system

The deceleration phenomenon in the formation/extraction of iron(III) with Htfa in Triton X-100 micellar system is concluded to be due to the slow extraction rate of the tris-complex into the micellar pseudophase, compared to the rate of complex formation in the bulk aqueous phase. No obvious effect of the coexisting Triton X-100 monomer or the micelle was found

either on the rate of the mono-complex formation or on the equilibria among the three complex species in the bulk aqueous phase. Hence, the rate of the whole formation/extraction reaction can be recalculated using the averaged molar absorptivity of the three complex species in the bulk aqueous phase $\varepsilon_{av,CF}$ instead of $\varepsilon_{av,EX}$ for the formation/extraction kinetic data in the micellar system obtained in Part I.¹

The results of the recalculation of the kinetic data (Table 4 in Part I¹) are listed in Table 3. The pseudo-first-order plot for $[Fe_T]_t$ deviated gradually from a straight relationship with time by the change of true $\varepsilon_{av,EX}$ but gave a straight line for a short while. The rate was obtained using the slope of the plot in the early stage. After the corrections on the hydrolysis of the metal ions in the bulk aqueous phase (see Eq. (10) in Part I¹), the corrected rate of formation, $k_{EX,M \text{ obsd}}^*$, was found to be first order with respect to the ligand concentration and inverse first order with respect to the hydrogen-ion concentration, but no dependency was found on the surfactant concentration.

$$R_{EX,M \text{ correct}} = k_{EX,M \text{ obsd}}^* [Fe_T]_t = k_{EX,M}^* [Fe^{3+}] [HA] [H^+]^{-1} \quad (14)$$

The calculated values of $k_{EX,M}^*$ are also summarized in Table 3. From the limit of the calculation, the values obtained are somewhat erroneous, while the averaged value ($10^{-1.70 \pm 0.06} \text{ s}^{-1}$) agreed well with that for $k_{CF,M}$, $k_{CF,L}$ and $k_{EX,L}$ obtained separately in Part I.¹

When the other conditions such as pH and [HA] in the bulk aqueous phase are similar, the difference between the values of $\varepsilon_{av,CF}$ and $\varepsilon_{av,EX}$ becomes larger in the higher surfactant concentration region, because the value of F_{C3m} becomes higher with increasing the volume fraction of the micellar pseudophase. This increases the differences between the value of the rate observed and that corrected in the higher surfactant concentration region. However, the averaged distance between a tris-complex in the bulk aqueous phase to a micellar pseudophase becomes much closer and the surface area of the micelle becomes much larger with increasing the surfactant concentration. Thus the rate of transport of the tris-complex from the bulk aqueous phase to the micellar pseudophase becomes higher in higher surfactant concentration region. The deceleration effect is, thus, the result of a balance between the rate of material transport and the extractability of the tris-complex. The effective concentration of the micelle for which the appearance of the deceleration phenomenon varies for each extractant. For example, the phenomenon clearly appears in a lower Triton X-100 concentration region in benzoyltrifluoroacetone extraction system⁴ than in the present Htfa system.⁵

Previously,^{6,7} the author and coworkers concluded that the elemental reaction of a path for the complex formation of iron(III) and β -diketones in aqueous solutions which dependency of the rate on hydrogen ion is inverse first order, is the association of hydrolyzed iron(III), $Fe(OH)^{2+}$, and the enol form of the ligand, HA_{enol} , by comparing the rate constants obtained from the experiments with several β -diketones against those for the other ligands in the literature.⁸⁻¹¹

$$R_{CF} = k_{OH-enol} [FeOH^{2+}] [HA_{enol}] = \frac{k_{CF}(1 + K_{k-e})}{K_h K_{k-e}} [Fe^{3+}] [HA] [H^+]^{-1} \quad (15)$$

Here, K_{k-e} is the equilibrium constant for the keto-enol tautomerism of Htfa in the aqueous solution¹² ($= [HA_{enol}] [HA_{keto}]^{-1} = 10^{-1.96}$). By introducing the values for K_{k-e} and K_h ($= 10^{-3.1} \text{ M}$)¹³ and the value of $k_{CF,L}$, $k_{CF,M}$, $k_{EX,L}$ or $k_{EX,M}$ into Eq. (15), the rate constant $k_{OH-enol}$ can be obtained. The values are in the range of $10^{3.36} - 10^{3.38} \text{ M}^{-1} \text{ s}^{-1}$; they agree well with the values for

the elemental reaction for five β -diketones ($10^{3.4} - 10^{3.5} \text{ M}^{-1} \text{ s}^{-1}$) reported previously.⁷

The reasons for the slow material transport rate

There are some plausible reasons for the slow extraction of the tris-complex into the micelle: for example, slow transportation rate of the complex species in the bulk aqueous phase or slow penetration rate of the complex species at the aqueous-micellar interface. Both of these can reduce the rate of transport of the tris-complex, but the dependency on the Triton X-100 micellar concentration is different. If the transport of the tris-complex formed in the bulk aqueous phase to the water-micellar interface is the slow step, the rate has a relationship to the averaged distance between the spot where a tris-complex is formed and the surface of a micelle. Hence, the rate is dependent on the one-third power of the micellar concentration. If the collision and/or penetration of the tris-complex from the micellar surface to the "core" of the micelle is, on the other hand, the slow step, the rate must be proportional to the micellar concentration, namely the number of micelles or the areas of micellar surface. From these differences, the "true" slow step of the transport in the micellar system can theoretically be determined by comparing the dependencies of the rate on the concentration of micelle. In the present case, the rate-determining-step is thus concluded to be the part after collision of the complex and the micelle.

It is difficult to clarify the true part of the rate-determining-step in the physical reaction, however, the following discussions which have been presented previously by the author¹⁴ may be important. The partition constant of the tris-complexes of iron(III) with three kinds of trifluoromethyl substituted β -diketones in the micellar system is lower than that expected from the data obtained in the conventional hexane-water and diethyl ether-water systems. It has been suggested that an "oxyethylene-phobicity" of the complexes in the micellar "mantle" by their low wettability in the oxyethylene-water network yields the low extractability; the tris-complex species is most likely to locate in the "core" region. For the above characteristics of the tris-complex, the following two estimations of the reason for the slow extraction may be possible. One is that the adsorptivity of the complex onto the micellar surface may be low. To extract into the micelle, the complex must be trapped onto the micellar surface just after the collision. The surface of Triton X-100 micelle is surrounded by a "hydrophilic" hydroxyl group; the complex surrounded with trifluoromethyl group may have lower efficiency onto the surface than that with no trifluoromethyl group. The low efficiency in the adsorption may decrease the rate of transport, while the rate must be first order with respect to the micellar concentration. The other is that the "mantle" region of the micelle may be a high barrier to the penetration of the complex into the "core". The "mantle" region contains many water molecules^{2,15} and forms a network of hydrogen-bonds; thus, the "hydrophobic" complex may be repelled in the region and the repulsion force may decrease the rate of transport, while it must be first order with respect to the micellar concentration. However, clarifying the "true" reason of the slow transport is difficult only from the stopped-flow spectrophotometric data of the formation/extraction reaction in the present study; additional results obtained by other experimental technique are necessary.

Several works have been reported on the relationship between the rate of complex formation and the concentrations of micelles. Ito and coworkers successfully measured^{16,17} the partition constants of 8-quinolinol and 2-(2-thiazolylazo)-4-methylphenol between Triton X-100, Triton X-305 or Tween

#20 micelle and water using the relationship between the formation rate of their nickel(II) complexes and the concentration of the micelle. An inhibition effect of Triton X-100 micelle on the rate of formation of nickel(II) with pyridine-2-azo-*p*-dimethylaniline has been reported by Carbone *et al.*,¹⁸ and the phenomenon can be well explained only by the partitioning of the ligand between water and the pseudophase. In these studies, the deceleration effect found in the present study was not observed. However, as Szymanowski and Tondre¹⁹ mentioned in their review, the kinetics and mechanisms of metal extraction in micellar or microemulsion system generally do not mimic those in a conventional liquid-liquid extraction system. Differences in the characteristics between the two systems may affect the extraction behavior, as was found in the present study.

As discussed above, the extraction system is simple as the extractant has no large substituted group, the bulk aqueous phase contains no additional salt and the micellar surface has no cationic or anionic charge. Even so, the rate of extraction of iron(III) with Htfa can not be treated simply on the basis of a partition model similar to the conventional liquid-liquid system using a non-polar organic solvent. The present results reflect the most fundamental aspect of micellar extraction and will support not only on the investigation of mechanisms of interfacial-reaction-controlled extraction systems but also will support developing practical separation/analytical techniques. A thorough analysis of the deceleration effect is suggested in order to utilize the micellar and related biphasic systems in separation and analytical applications.

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