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Kinetic Studies of Solvent Extraction of Metal Complexes. VIII. Rate of Complex Formation and Solvent Extraction of Iron(III) in Aqueous Perchlorate Solutions with 1,1,1-Trifluoro-2,4-pentanedione

Tatsuya Sekine* and Kazuho Inaba
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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The rate of the extraction of iron(III) in aqueous 4 mol dm^{-3} sodium perchlorate solutions with 1,1,1-trifluoro-2,4-pentanedione (Htfa) into carbon tetrachloride was measured, and the rate constants for the controlling reactions in the aqueous phase:

$$Fe^{3+} + Htfa \longrightarrow Fe(tfa)^{2+} + H^+ \text{ and } Fe(OH)^{2+} + Htfa \longrightarrow Fe(tfa)^{2+} + H_2O,$$

were calculated. These constants were also determined from spectrophotometric measurements of the aqueous solutions in the absence of the organic phase. The two series of rate constants obtained by the independent experiments agreed well. It was pointed out that equilibrium constants among the complexes in the aqueous and organic phases are indispensable in order to make a precise discussion of the solvent extraction of metal ions when aqueous-complex formation controls the whole process.

In this series, the rate of the solvent extraction of beryllium(II),[1] iron(III),[2,3] and gallium(III)[4] with β-diketones into nonpolar solvents was measured, and it was concluded that the formation of metal complexes took place in the aqueous phase first, and then the uncharged one among them was extracted into the organic phase. Thus, the whole process in these extractions was controlled by the formation of the first complex in the aqueous phase. In these previous studies, the effects of mass transport and interfacial reactions were neglected because the experiments were carried out at such an agitation speed that no increase in the rate was found on its further increase. This type of extraction mechanism seems to be very common among the extractions done under similar experimental conditions.[5] In the present study, the rate of the solvent extraction of iron(III) in aqueous 4 mol dm^{-3} perchlorate solutions with 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone, Htfa) into carbon tetrachloride was determined at 298 K. At the same time, the rate of the complex formation of iron(III) with this ligand in these aqueous solutions was determined in separate experiments in the absence of the organic phase by a spectrophotometric method. From the results of these two series of experiments, two kinds of reaction routes were found for the complex formation; the two sets of rate constants, one of them obtained from the spectrophotometric data, and the other calculated from the extraction data, agreed well each other.

Experimental

The rate was always determined at 298 K. The aqueous solutions were constant ionic media, 4 mol dm^{-3} (H, Na)ClO$_4$. The hydrogen-ion concentration of the sample solutions was measured potentiometrically. By measuring a series of standard solutions, the acid concentrations of which had been determined by titration with a standard sodium hydroxide solution, a calibration curve of the emf *vs.* the hydrogen-ion concentration was prepared. The hydrogen-ion concentration in the sample solutions was calculated from the potentiometric data by using this curve. Thus the stoichiometric units are used in this study. The experiments by the spectrophotometric method was made with Htfa in a large excess to iron(III). The spectrophotometric experiments were made in a manner similar to that described previously except that the absorptions at 450 nm were measured at certain time intervals after the metal ion and the ligand solutions had been mixed.[6] The experiments of the solvent extraction were made in a manner similar to that previously described.[2,3,6] A carbon tetrachloride solution containing Htfa and a perchlorate solution containing iron(III) perchlorate at 5×10^{-4} mol dm^{-3} were agitated so vigorously that no increase in the rate was found on a further increase in the agitation speed. The amount of iron(III) extracted after a certain time interval was determined by an atomic-absorption method.

Statistical

Any chemical species in the organic phase will be denoted by the subscript "org" and those in the aqueous phase, by the lack of any subscript. The initial concentration will be denoted by the subscript "init."

The acid-dissociation and two-phase distribution constants of the ligand and the stability constant of the "*n*-th" complex are defined as:

$$K_a = [H^+][tfa^-][Htfa]^{-1} \tag{1}$$

$$K_d = [Htfa]_{org}[Htfa]^{-1} \tag{2}$$

$$\beta_n = [Fe(tfa)_n{}^{3-n}][Fe^{3+}]^{-1}[tfa^-]^{-n}. \tag{3}$$

As will be seen later, the two-phase distribution constant of the uncharged complex is necessary to correlate the rate constants for the solvent extraction and for the complex formation. It is defined as:

$$K_{dm} = [Fe(tfa)_3]_{org}[Fe(tfa)_3]^{-1}. \tag{4}$$

When the rate of the complex formation of Fe^{3+} in aqueous solutions is first-order with respect to Fe^{3+}, and when several reaction routes are present, it can generally be written as:

$$V = -d[Fe^{3+}]/dt = \sum K_{CF(a,b\cdots)}[Fe^{3+}][Htfa]^a[H^+]^b\cdots, \tag{5}$$

where a,b$\cdots$ are certain integers. From Eq. 5, the following equation is obtained when a certain component, for example, H$^+$, is changed, but the others are kept constant:

$$-\log[\mathrm{Fe}^{3+}] = q_{\mathrm{H}^+} \times t + \log[\mathrm{Fe}^{3+}]_{\mathrm{init}} \tag{6}$$

$$q_{\mathrm{H}^+} = \sum K^*_{\mathrm{CF(a,b\cdots)}} \times \mathrm{C_{Htfa}}^{\mathrm{a}} \times [\mathrm{H}^+]^{\mathrm{b}}\cdots, \tag{7}$$

where $K^*_{\mathrm{CF(a,b\cdots)}} = K_{\mathrm{CF(a,b\cdots)}}/\ln(10)$ and where C_{Htfa} is the concentration of Htfa kept at a certain value. Similar equations may be written with respect to the other components.

Treatment of Optical Absorption Data. When the rate of complex formation is first-order with respect to Fe^{3+}, and when an equilibrium is established for all practical purposes among the complexes, the following treatments of the optical-absorption data are possible.

When the absorption due to the Fe^{3+} species is negligible, the over-all absorbance experimentally measured can be written as:[6]

$$\begin{aligned}\varepsilon_{\mathrm{T}} &= (\varepsilon_1[\mathrm{Fe(tfa)}^{2+}] + \varepsilon_2[\mathrm{Fe(tfa)_2}^+] + \varepsilon_3[\mathrm{Fe(tfa)_3}])\\ &\quad([\mathrm{Fe(tfa)}^{2+}] + [\mathrm{Fe(tfa)_2}^+] + [\mathrm{Fe(tfa)_3}])^{-1}\\ &= (\varepsilon_1\beta_1[\mathrm{tfa}^-] + \varepsilon_2\beta_2[\mathrm{tfa}^-]^2 + \varepsilon_3\beta_3[\mathrm{tfa}^-]^3)(\beta_1[\mathrm{tfa}^-]\\ &\quad + \beta_2[\mathrm{tfa}^-]^2 + \beta_3[\mathrm{tfa}^-]^3)^{-1},\end{aligned} \tag{8}$$

where ε_n is the molar absorption coefficient of the "n-th" complex. The value of ε_{T} can be calculated from ε_n and β_n for a certain [tfa$^-$], and by using this parameter and the absorbance experimentally measured, the total amount of complexes or the decrease in [Fe^{3+}] by the complex formation can be obtained as:

$$\begin{aligned}E/\varepsilon_{\mathrm{T}} &= [\mathrm{Fe(tfa)}^{2+}] + [\mathrm{Fe(tfa)_2}^+] + [\mathrm{Fe(tfa)_3}]\\ &= [\mathrm{Fe}^{3+}]_{\mathrm{init}} - [\mathrm{Fe}^{3+}].\end{aligned} \tag{9}$$

By introducing [Fe^{3+}] into Eq. 6, the value of q_{H^+} (or q with respect to the other components) under certain conditions can be obtained, and from the slope of the plot of log q *versus* the logarithmic concentration of the component, the dependences, a, b···, can be obtained.

Treatment of Solvent-extraction Data. When several roues are present in the solvent extraction of Fe^{3+} in the aqueous phase with Htfa, the rate may be written in a way similar to Eqs. 5 to 7:

$$\begin{aligned}V &= -\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t\\ &= \sum K_{\mathrm{SE(a,b\cdots)}}[\mathrm{Fe(III)}][\mathrm{Htfa}]^{\mathrm{a}}[\mathrm{H}^+]^{\mathrm{b}}\cdots.\end{aligned} \tag{10}$$

Here, the total concentration of iron(III) species in the aqueous phase is considered instead of the Fe^{3+} concentration in Eq. 5. For example, with respect to H^+, the following equation can be written:

$$-\log[\mathrm{Fe(III)}] = q_{\mathrm{H}^+} \times t + \log[\mathrm{Fe(III)}]_{\mathrm{init}} \tag{11}$$

$$q_{\mathrm{H}^+} = \sum K^*_{\mathrm{SE(a,b)}} \times C_{\mathrm{Htfa}}{}^{\mathrm{a}} \times [\mathrm{H}^+]^{\mathrm{b}}\cdots. \tag{12}$$

Results

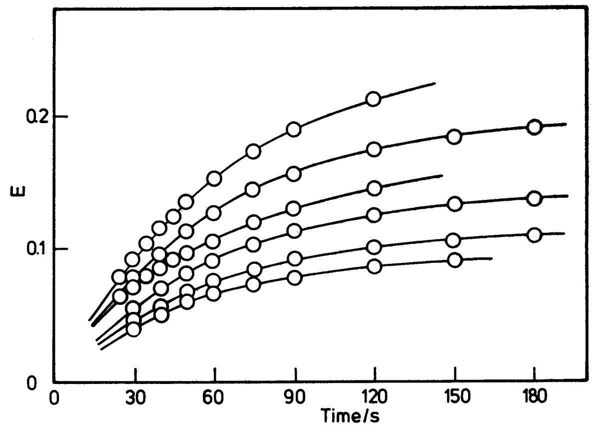

Fig. 1. Example of the change in the absorption at 450 nm as a function of time by formation of iron(III)–tfa complexes in the aqueous 4 mol dm^{-3} (H, Na)ClO$_4$ ionic media.
[Htfa] is 5.0×10^{-2} mol dm^{-3}, [H$^+$] is 0.33, 0.43, 0.6, 0.63, 0.85, and 1.0 mol dm^{-3} from the top to the bottom.

TABLE 1. EQUILIBRIUM CONSTANTS FOR HTFA AND IRON-(III) IN 4 mol dm^{-3} (H,Na)ClO$_4$ SOLUTIONS AT 298 K

$K_{\mathrm{a}}=10^{-6.59}$	
$K_{\mathrm{d}}=10^{0.39}$	
$K_{\mathrm{e}}^{\mathrm{a)}}=10^{-1.96}$	
$\beta_1=10^{7.7}$	$\varepsilon_1=170$
$\beta_2=10^{14.4}$	$\varepsilon_2=1050$
$\beta_3=10^{19.8}$	$\varepsilon_3=2560$
$K_{\mathrm{dm}}=10^{4.2}$	
$K_{\mathrm{h}}^{\mathrm{b)}}=10^{-3.1}$	

a) $K_{\mathrm{e}}=[\mathrm{Htfa}]_{\mathrm{enol}}[\mathrm{Htfa}]^{-1}_{\mathrm{keto}}$. b) $K_{\mathrm{h}}=[\mathrm{Fe(OH)}^{2+}][\mathrm{H}^+][\mathrm{Fe}^{3+}]^{-1}$ (in 3 mol dm^{-3} (H, Na)ClO$_4$ Ref. 9).

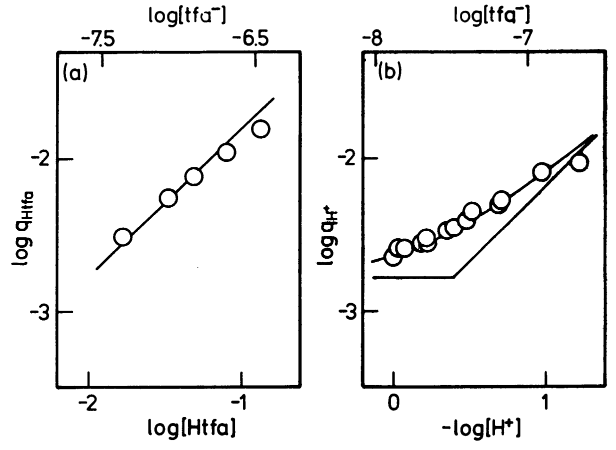

Fig. 2. Dependence of the rate of complex formation of iron(III): (a) on the Htfa concentration when [H$^+$] is 1.0×10^{-1} mol dm^{-3} and (b) on the hydrogen-ion concentration when [Htfa] is 5.0×10^{-2} mol dm^{-3}.
The straight line in (a) and the curve in (b) are calculated by introducing the constants in Table 2 into Eq. 13. The two lines in (b) are the asymptotes for the curve.

Rate of Change in Optical Absorption. The absorption in the range from 400 to 600 nm of aqueous perchlorate solutions containing Fe^{3+} and Htfa was only slight at first but it gradually increased until a maximum absorption was observed at about 450 nm. The absorbance at this wavelength was measured at certain time intervals. Figure 1 gives an example of such results. In order to treat these absorption data, it was assumed that the formation of the first complex, $\mathrm{Fe(tfa)}^{2+}$, from Fe^{3+} was the controlling step and that the formation of the higher complexes proceeded much more rapidly than this, in other words, the three complexes, $\mathrm{Fe(tfa)}^{2+}$, $\mathrm{Fe(tfa)_2}^+$, and $\mathrm{Fe(tfa)_3}$, were in an equilibrium with each other. From the absorbance and the concentrations of Htfa and hydrogen ions, the total amount of complexes formed, that is, the decrease in the Fe^{3+} concentration, was calculated on the basis of Eq. 8 by introducing the molar-absorption coefficients and stability constants in Table 1, which had been determined in a previous study.[6] From this calculated decrease in the Fe^{3+} concentration, the parameters, q, were obtained. Figure 2 gives the dependence of q on the Htfa and hydrogen-ion concentrations. As may be seen, the rate was first-order with respect to Htfa. However, the dependence of the rate on the hydrogen ions approached to zero-order in the higher acidity range, while it approached to inverse-first-order in the lower acidity range. From these data, the rate of complex formation was concluded to be given by:

$$V = K_{CF(1,0)}[Fe^{3+}][Htfa] + K_{CF(1,-1)}[Fe^{3+}][Htfa][H^+]^{-1}$$
$$= K_{CF(1,0)}[Fe^{3+}][Htfa](1 + K_{CF(1,-1)}/K_{CF(1,0)}[H^+]^{-1}). \quad (13)$$

The values of $K_{CF(1,0)}$ and $K_{CF(1,-1)}/K_{CF(1,0)}$ were determined graphically. The plot in Fig. 2(b) was fitted with a standard curve:

$$y = \log(1 + w) : x = \log w \quad (14)$$

and the values were obtained from the parameters of the fitted curve (*cf.* pp. 85 to 96 in Ref. 7). The rate constants obtained are listed in Table 2.

Table 2. Summary of rate constants

The aqueous media are 4 mol dm^{-3} $(H,Na)ClO_4$ at 298 K.

$K_{SE(1,-1)} = 10^{-1.6}$ (s^{-1})

$K_{CF(1,0)}{}^{a)} = 10^{-1.1}$ $(mol^{-1}\ dm^3\ s^{-1})$

$K_{CF(1,-1)}{}^{a)} = 10^{-1.5}$ (s^{-1})

$K_{CF(1,0)}{}^{b)} = 10^{-1.2}$ $(mol^{-1}\ dm^3\ s^{-1})$

$K_{CF(1,-1)}{}^{b)} = 10^{-1.6}$ (s^{-1})

a) Spectrophotometric method. b) Solvent-extraction method.

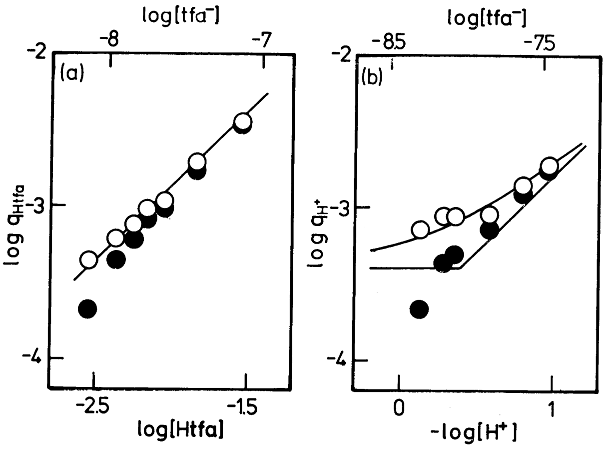

Fig. 3. Dependence of the rate of extraction of iron(III) (closed circles) and the rate of complex formation calculated from the extraction data using Eq. 21 and the constants in Table 1 (open circles): (a) on [Htfa] when $[H^+]$ is 1.0×10^{-1} mol dm^{-3} and (b) on $[H^+]$ when [Htfa] is 1.4×10^{-2} mol dm^{-3}.
The straight line in (a) and the curve in (b) are calculated by introducing the constants in Table 2 into Eq. 13. The two lines in (b) are the asymptotes for the curve.

Rate of Solvent Extraction. The amount of iron(III) extracted into the organic phase was measured as a function of the time; the parameters given by Eqs. 11 and 12 were also calculated as has been described previously.[1-4,7] The closed-circle in Fig. 3 give the dependence of the rate on the Htfa and hydrogen-ion concentrations in the aqueous phase. The rates are apparently first-order and inverse-first-order with respect to [Htfa] and $[H^+]$ respectively. From these data, the rate was concluded to be given (*cf.* Eqs. 10 and 11) by:

$$V = K_{SE(1,-1)}[Fe(III)][Htfa][H^+]^{-1}. \quad (15)$$

The rate constant for the solvent extraction, $K_{SE(1,-1)}$, was obtained from the data in Fig. 3 (*cf.* Table 2).

Discussion

In aqueous solutions, β-diketones are mainly in the keto hydrate form.[8] However, the complex formation in the aqueous phase should take place between hydrated metal ions and the β-diketone in the enol form. The controlling step for a reaction route whose rate is dependent only on the Htfa concentration in Eq. 13 should be:

$$Fe^{3+} + Htfa \longrightarrow Fe(tfa)^{2+} + H^+. \quad (16)$$

However, that for the reaction which is first-order with respect to Htfa and inverse-first-order with respect to hydrogen ions can be both:

$$Fe^{3+} + tfa^- \longrightarrow Fe(tfa)^{2+} \quad (17)$$

$$Fe(OH)^{2+} + Htfa \longrightarrow Fe(tfa)^{2+} + H_2O. \quad (18)$$

Since the reaction in Eq. 18 explains the rate of complex formation of Fe^{3+} with several β-diketones more reasonably,[3] this will also be adopted in the present study. The rate constant assuming the reaction in Eqs. 16 and 18 with the enol form of Htfa is calculated using the hydrolysis constant of Fe^{3+} given in Table 1.[9] (This was given for the equilibrium in 3 mol dm^{-3} $NaClO_4$ media, but the difference of the value in 4 mol dm^{-3} $NaClO_4$ media in the present study should not be large.) Using the constant for the keto-enol equilibrium of Htfa in aqueous solutions in Table 1,[8] the rate constant for the following reactions can be calculated:

$$Fe^{3+} + Htfa_{(enol)} \longrightarrow Fe(tfa)^{2+} + H^+$$
$$K_{CF(1,0)enol} = K_{CF(1,0)} \times (K_e + 1)K_e^{-1} \quad (19)$$
$$Fe(OH)^{2+} + Htfa_{(enol)} \longrightarrow Fe(tfa)^{2+} + H_2O$$
$$K_{CF(1,-1)enol} = K_{CF(1,-1)} \times K_h^{-1}(K_e + 1)K_e^{-1}. \quad (20)$$

The calculated values are listed in Table 3.

The kinetics of the complex formation of iron(III) has been studied with several ligands. These data with β-diketones and 4-isopropyltropolone are summarized in Table 3.[10-14] The rate constants with other types of ligands are also in nearly the same order (10^0 to 10^2 for the type of reaction in Eq. 16 and 10^2 to 10^5 for the type of reaction in Eq. 18. For example, Refs. 15 to 29 and also those cited in Ref. 15).

The rate of extraction is determined from the amount of extracted iron(III) and is treated by Eq. 15. This was first-order with respect to the total aqueous concentration of iron(III). When the whole extraction is controlled by the formation of the first complex in the

TABLE 3. RATE CONSTANTS FOR FORMATION OF IRON(III) COMPLEXES IN AQUEOUS PERCHLORATE IONIC MEDIA AT 298 K

Ligand (HL)	$Fe^{3+}+HL$ ($mol^{-1}\,dm^3\,s^{-1}$)	$Fe(OH)^{2+}+HL$ ($mol^{-1}\,dm^3\,s^{-1}$)	Ionic strength / $mol\,dm^{-3}$	Ref.
Acetylacetone[a)]	$10^{0.7}$	$10^{3.6}$	1.0	10
2-Thenoyltrifluoroacetone	$10^{-0.3}$	$10^{2.6}$	1.0	11
2-Thenoyltrifluoroacetone	$10^{0.1}$	$10^{3.1}$	1.0	12
4-Isopropyltropolone	$10^{1.4}$	$10^{3.7}$	1.0	13
Trifluoroacetylacetone	$10^{0.9}$	$10^{3.6}$	4.0	b)
Triouoroacetylacetone	$10^{0.8}$	$10^{3.5}$	4.0	c)

a) Another study was also made of the rate of the complex formation of Fe^{3+} and acetylacetone by assuming a somewhat different mechanism.[14] b) Spectrophotometric method in the present work. c) Solvent-extraction method in the present work.

aqueous phase, and when, consequently, the three aqueous complexes and the tris complex in the organic phase are in an equilibrium to each other, the decrease in the Fe^{3+} concentration should give the rate of this controlling reaction. The $[Fe^{3+}]$ concentration can be written as:

$$\begin{aligned}[Fe^{3+}] &= [Fe(III)]_{init} - ([Fe(tfa)^{2+}] + [Fe(tfa)_2{}^{+}] \\ &\quad + [Fe(tfa)_3] + [Fe(tfa)_3]_{org}) \\ &= [Fe(III)]_{init} - ((\beta_1\beta_3{}^{-1}[tfa^-]^{-2} + \beta_2\beta_3{}^{-1} \\ &\quad [tfa^-]^{-1} + 1) \times K_{dm}{}^{-1} + 1) \times [Fe(tfa)_3]_{org}. \qquad (21)\end{aligned}$$

Thus, if the rate constant for the formation of the first complex in the aqueous phase is calculated from the extraction data, the decrease in the Fe^{3+} concentration, which can be obtained from the $Fe(tfa)_3$ concentration in the organic phase means of Eq. 21, should be employed instead of the decrease in the total aqueous iron(III) concentration. The open symbols in Fig. 3 were calculated in this way. As may be seen, the open symbols in Fig. 3 should correspond with the plot in Fig. 2, and by treating these data in a similar manner, the rate constants for the complex formation listed in Table 2 were obtained; they agreed well with those obtained from the spectrophotometric data. The rate constants for the complex formation with the enol form of Htfa in Eqs. 19 and 20 can also be obtained from the rate constant for the extraction. These values are also listed in Table 3.

Figure 3 shows that when no consideration is given to the reaction given by Eq. 21, no final conclusion as to the reaction mechanism of the solvent extraction in such systems can be drawn. Moreover, in general, it is not possible to determine the dependence of the rate of extraction on the extractant and the hydrogen ion; in other words, it is not always possible to know the controlling reaction only from a plot such as given by Eq. 10. In this series, we have often observed that the slope of such a plot as Fig. 3 deviates from that to be expected from the assumed controlling reaction; the above is presumably the reason for such deviations. This kind of deviation should be great when the proportion of the extracted complex to the total amount of the complexes produced after the controlling step is small. From Eq. 21, it may be seen that such a deviation occurs when the concentration of the ligand ($[tfa^-]$ in the present study) is low and/or when K_{dm} is low. Figure 4 gives the calculated percentage distributions of the complexes in the two phases when their volumes are the same. As may be seen, in the region where $[tfa^-] > 10^{-7}$ mol dm^{-3} the molar ratio of the extracted complex to the total amount of the aqueous complexes is very high, and thus the deviation should be negligible. As may be seen from Fig. 3, a deviation occured in our experiments, and since $[tfa^-]$ in these experiments was lower than 10^{-7} mol dm^{-3}, this deviation can be explained reasonably by Fig. 4 and Eq. 21. In some kinetic studies of the extraction of iron(III) with chelating reagents, it was possible to conclude only from the extraction data, that the mechanism was that given by Eq. 16, making no consideration of such an effect.[2,30] It was also possible in another study to conclude, though no consideration of the equilibrium was made, that the formation of the first complex controlled the complex formation of iron(III) in aqueous solutions with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, Htta, and also the solvent extraction of the metal ion.[11] This was possible because the experiments were made under conditions where the ligand concentration was high and/or the K_{dm} in Eq. 4 was large.

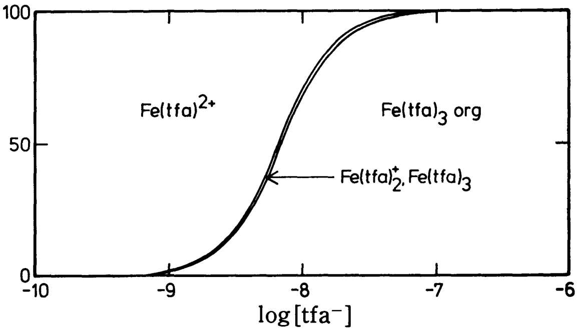

Fig. 4. Percentage distribution of complexes as a function of the ligand concentration when the volumes of the two phases are the same. The percentage gives the ratio of the concentration of each complex to the total concentration of the complexes, $([Fe(tfa)^{2+}] + [Fe(tfa)_2{}^{+}] + [Fe(tfa)_3] + [Fe(tfa)_3]_{org})$.

From the good agreement of the rate constant for the formation of the iron(III) complex in the aqueous phase determined from the spectrophotometric and solvent-extraction data, it may finally be concluded that the extraction mechanism proposed above is reasonable and that the reaction on the interface is negligible.

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