Interfacial Phenomena in Ion-Association Extraction Kinetics of Iron(II) with 1,10-Phenanthrolines

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The role of the interface in ion-association extraction kinetics of iron(II) with 1,10-phenanthroline(phen), 4,7-dimethyl-1,10-phenanthroline(DMP) or 4,7-diphenyl-1,10-phenanthroline(DPP) from sodium salt solutions was investigated by means of a high-speed stirring technique and a stopped-flow method. The initial extraction rates of the ion pairs were proportional to the first order of both iron(II) and the ligand concentrations in all cases studied; it was therefore suggested that the rate-controlling step is the formation of mono-complexes. From analyses using the adsorption constants and the distribution constants of the ligands and the formation-rate constants of the mono-complexes in the aqueous phase it was concluded that the location where the rate-controlling reaction takes place depends on the ligands: a bulk aqueous phase in phen, an interface in DPP, and both of a bulk aqueous phase and an interface in the case of DMP. The extraction rates were apparently reduced by an interfacial adsorption of the ion pairs, which was governed by the hydrophobicity of the ligands and the hydrophilicity of the counter anions.

Interfacial phenomena in the solvent extraction processes of metal ions have become of interest in recent years regarding fundamental solvent extraction chemistry[1] as well as solvent extraction technology.[2,3] Especially, the role of the interface in extraction kinetics is a most attractive subject for the purposes of evaluating the participation of an interfacial reaction to the rate-controlling process and for elucidating a real extraction mechanism.[4,5]

In our previous studies concerning the role of the interface in chelate extraction kinetics, some attractive results were found by means of a high-speed stirring method which allowed simultaneous measurements of both the extraction rate and the interfacial amount of extractant under the same conditions. For example, the extraction rates of Zn(II) and Ni(II) with *n*-alkyl-substituted dithizones[6] and those of Ni(II) with 2′-hydroxy-5′-nonylacetophenone oxime[7] in vigorously stirred systems were governed by the formation rate of a 1:1 complex at the liquid-liquid interface. In these systems, the low solubility of the extractants into the aqueous phase, the high interfacial adsorptivity of their dissociated form, and the low interfacial adsorptivity of the complexes favored an interfacial rate-controlling mechanism, under the conditions of vigorous stirring, which produced a large interfacial area.

As for ion-association extraction systems, on the other hand, kinetic studies concerning the extraction mechanisms have been very limited, since the extraction of an ion pair is generally a fast process.[8] It has been reported, however, that the rate of ion-association extraction of some divalent metal ions with 1,10-phenanthrolines is quite slow, reflecting the slow formation rate of metal ions with 1,10-phenanthrolines.[9]

We have recently found a strong adsorptivity of $[Fe(phen)_3]^{2+}$ (where phen denotes 1,10-phenanthroline) at the interface of chloroform/0.1 M (1 M=1 mol dm^{-3}) NaCl by means of interfacial tension measurements,[10] in contrast to the fact that no adsorption of the complex ion was observed at the air/water interface.[11] Interfacial adsorption of the protonated species of 1,10-phenanthrolines in highly stirred chloroform/dilute hydrochloric acid was found by means of a high-speed stirring apparatus.[12] Tris(4,7-diphenyl-1,10-phenanthroline)iron(II) also showed the characteristic adsorptivity at the interface of agitated liquid-liquid systems, depending on the nature of the counter anions, as reported in a preceding paper.[13] These findings strongly suggested a significant role of the interface in the extraction kinetics of iron(II) with 1,10-phenanthrolines.

In the present study we intended to clarify the role of the interface in the ion-association extraction of iron(II) with 1,10-phenanthrolines(abbreviated by L) from the kinetic approach employing the high-speed stirring apparatus and a stopped-flow method.

Experimental

Chemicals. Phen, DMP, and DPP, which were of all Wako reagent grade, were used without further purification. The stock solution of Fe(II) was prepared by dissolving purified $FeCl_2 \cdot 2H_2O$ or $FeSO_4 \cdot 7H_2O$, both Wako G.R., into dilute acid containing hydroxylamine or ascorbic acid in order to depress the oxidation of Fe(II). Chloroform, Wako G.R., was washed three times with water to remove ethanol dissolved as a stabilizer just prior to use. Water was purified by means of a Yamato Auto Still WAG 28, and then by a Millipore MilliQ-II system. Sodium perchlorate was synthesized by the neutralization of concentrated $HClO_4$ by Na_2CO_3, and purified by recrystallization from concentrated aqueous solution as its dehydrated form. Other sodium salts were all of reagent grade and were used as purchased. Acetate buffer (0.002M) and hydrochloric acid, perchloric acid or sodium hydroxide were used to control the pH of the aqueous phase.

Extraction Experiments. The extraction rates of iron(II) with 1,10-phenanthrolines were measured by means of a high-speed stirring apparatus which was essentially the same as the one reported previously.[7] Fifty ml of phen, DMP, or DPP in chloroform and 45 ml of aqueous salt solution were stirred at a speed of 4700 rpm in an extraction vessel thermostated at 25±0.1 °C. Injection of 5 ml of the iron(II) solution initiated the extraction. The organic phase was continuously separated by a Teflon phase separator and circulated by Lab Pump Jr. RHSY (Fluid Metering, Inc. U.S.A.) at a flow rate of 13 ml min^{-1} through a flow cell (2.5 mm in optical length and 8 μl in volume) attached to the Jasco UVIDEC 430 A Spectrophotometer. The absorbance values of the organic phase, A', at the absorption-maximum wavelength of the ion pair $[\text{FeL}_3]\text{X}_2$ (X denotes an extractable anion) was stored in an NEC microcomputer system at an acquisition rate of 1 Hz.

The initial extraction rates, defined as $r^\circ_{\text{obs}}=(\text{d}A'/\text{d}t)_{t=0}$, were calculated as follows: the observed absorbance values in the initial stage of extraction were represented as a second-order equation with respect to time, $A'=pt^2+qt+r$, where p, q and r are constants determined by a least-square regression method. It was then differenciated by time at the starting time of extraction. The reproducibility of r°_{obs} for repeated runs was within 5%.

The interfacial adsorption of ion pairs in the agitated system was measured from the stirring effect after equilibration in the kinetic runs; the organic phase absorbance was raised to some constant value when the vigorous stirring was stopped; it decreased when the stirring was started again. From the absorbance change caused by stopping the stirring, the interfacial amount of the ion pair was estimated.

Stopped-Flow Measurements. The formation rates of tris-complexes of iron(II) with phen, DMP, or DPP were measured by means of a stopped-flow spectrophotometer (Photal RA414) at 25±0.1 °C. In phen and DMP systems kinetic measurements were carried out in aqueous solutions of 0.1 M sodium perchlorate; in the DPP system, however, mixed solvents of water and ethanol were used in order to completely dissolve the Fe(II)-DPP complex which was produced. Quasi-first-order conditions were provided in all cases by using an excess amount of the ligand, so that the rate constants corresponding to the formation of a 1 : 1 complex, k_1, were calculated from the linear correlation between the observed first-order rate constants and the ligand concentrations.

Distribution of Ligands. The distribution constants, K_{D}, of phen and DMP in chloroform/0.1 M NaClO_4 were determined by an ordinary batch method and spectrophotometry. The distribution constants of DPP in Cl^- and SO_4^{2-} systems were determined from the distribution ratio in chloroform/hydrochloric acid and chloroform/sulfuric acid systems, employing $\text{p}K_{\text{a}}=4.84$ for DPP.[14] In the chloroform/perchloric acid system, the ion pair extraction of $\text{HDPP}^+\cdot\text{ClO}_4^-$ prevented any direct determination of K_{D}. Consequently, K_{D} in the perchlorate system was calculated from the solubilities of DPP in 0.1 M NaClO_4 and 0.0333M Na_2SO_4, while assuming a proportionality between the solubility and the distribution constant; $K_{\text{D}}(\text{ClO}_4^-)=K_{\text{D}}(\text{SO}_4^{2-})\text{S}(\text{SO}_4^{2-})/\text{S}(\text{ClO}_4^-)$ where $K_{\text{D}}(\text{ClO}_4^-)$ and $K_{\text{D}}(\text{SO}_4^{2-})$ refer to the distribution constants in ClO_4^- and SO_4^{2-} systems, and $\text{S}(\text{ClO}_4^-)$ and $\text{S}(\text{SO}_4^{2-})$ to the solubilities in the corresponding systems, respectively. The values of K_{D} obtained in the present study at 25±1 °C are listed in Table 1.

Results

Extraction Rate. Typical examples of the extraction profiles of tris-phen, DMP, and DPP complexes of iron(II) as ion pairs with perchlorate ion are shown in Fig. 1. The initial extraction rate, r°_{obs}, was obtained from the initial stage of extraction with various concentrations of iron(II) and ligands. As shown in Fig. 2, r°_{obs} is proportional to the product of the initial concentrations, $[\text{Fe}^{2+}]_{\text{init}}[\text{L}]_{\text{o,init}}$, in three ligand systems. The effect of anions on the extraction rate was examined in the Fe(II)-DPP system employing ClO_4^-, CCl_3COO^-, Br^-, Cl^-, and SO_4^{2-} as

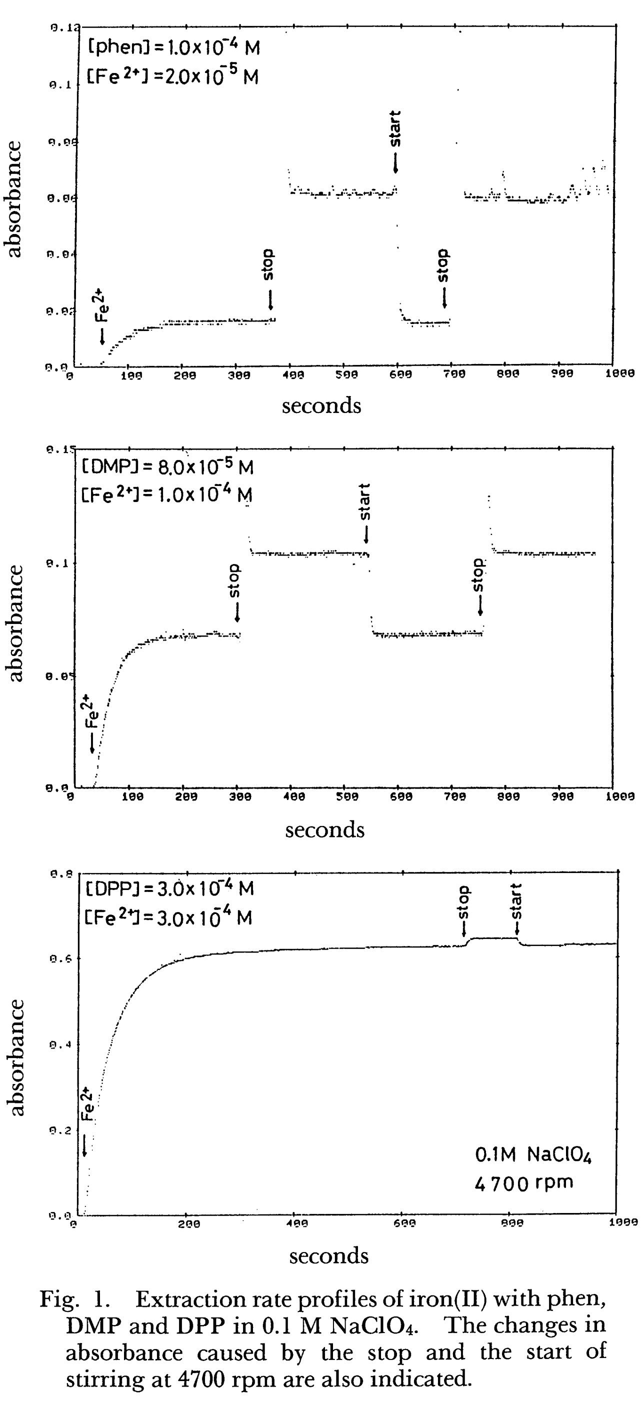

Fig. 1. Extraction rate profiles of iron(II) with phen, DMP and DPP in 0.1 M NaClO_4. The changes in absorbance caused by the stop and the start of stirring at 4700 rpm are also indicated.

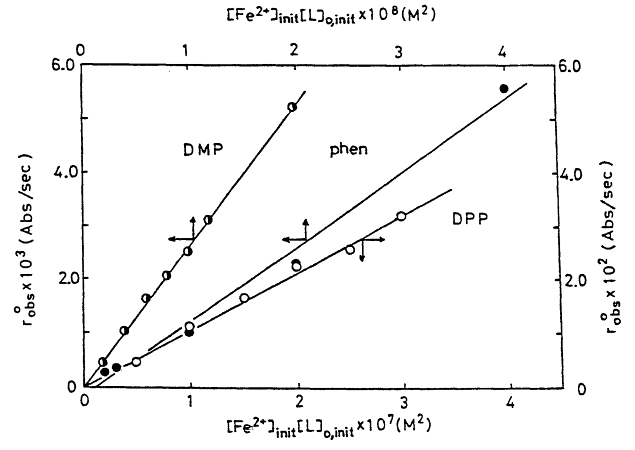

Fig. 2. Linear correlations between the observed initial extraction rates and the products of the initial concentrations of iron(II) and the ligands in 0.1 M $NaClO_4$.

counter anions. Figure 3 shows obviously different effects of Cl^- and ClO_4^- on the extraction rates: slower in 0.1 M NaCl and faster in 0.1 M $NaClO_4$. In Fig. 4, the linear correlations between r^0_{obs} and the iron(II) concentration and those between r^0_{obs} and the DPP concentration are shown for four anion systems. In the SO_4^{2-} system, although there was no significant extraction of an ion pair into the organic phase, the formation rate of $[Fe(DPP)_3]^{2+}$ at the interface could be measured from the decreasing rate of the DPP concentration in the organic phase, and a linear correlation between the formation rate and the DPP concentration was observed. The influence of the pH on the initial extraction rate of $[Fe(DPP)_3]X_2$ was also

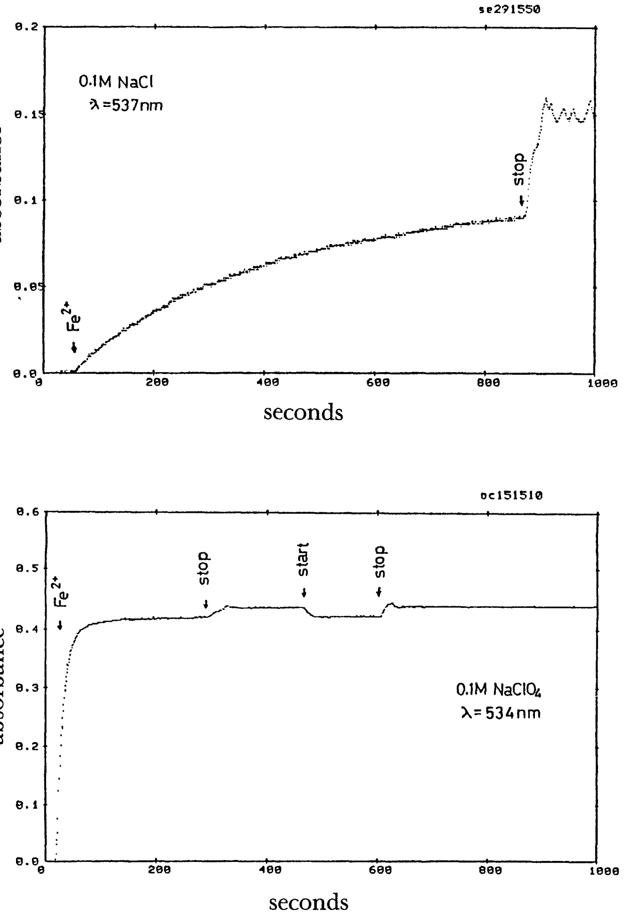

Fig. 3. Effects of Cl^- and ClO_4^- on the extraction rate profiles of $[Fe(DPP)_3]^{2+}$; $[Fe^{2+}]_{init}=1.0\times10^{-3}$ M and $[DPP]_{init}=2.0\times10^{-4}$ M. The effect of stirring is also indicated.

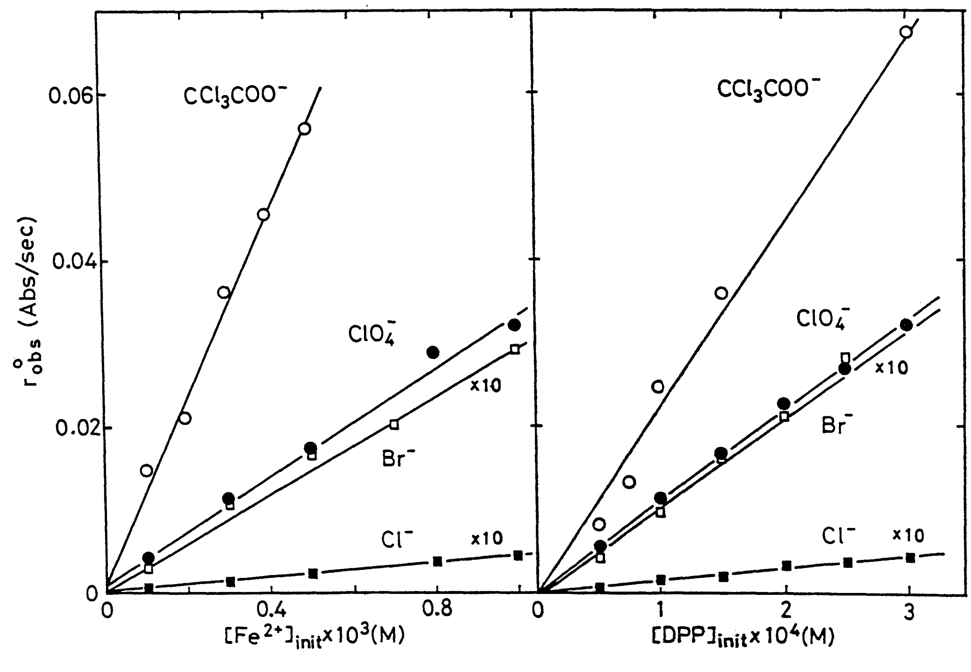

Fig. 4. Dependences of the observed initial extraction rates on the initial concentration of iron(II) with $[DPP]_{init}=3.0\times10^{-4}$ M and on the initial concentration of DPP with $[Fe^{2+}]_{init}=1.0\times10^{-3}$ M in the four 0.1 M anion systems.

examined employing ClO_4^-, CCl_3COO^- and Br^- as counter anions. As a result, there was no appreciable change in r°_{obs} in the region pH=4—6. Under acidic conditions, where pH<4, r°_{obs} decreased with a decrease in the pH because of a protonation of DPP.

From the results of the extraction rate measurements, the rate law regarding the present extraction systems was determined:

$$\frac{r^{\circ}_{obs}}{\varepsilon l}=\left(\frac{d[FeL_3X_2]_o}{dt}\right)_{t=0}=k_{obs}[Fe^{2+}]_{init}[L]_{o,init}, \qquad (1)$$

where ε and l refer to the molar absorptivity of the ion pair, $[FeL_3]X_2$, and the length of the flow cell, k_{obs} to the observed extraction rate constant. The values of k_{obs} are listed in Table 1.

Interfacial Adsorption. As noticed in kinetic runs (Fig. 1), the absorbance of ion pairs in the organic phase was strongly affected by stopping or starting of the stirring. Similar stirring effects were also observed in the distribution of 1,10-phenanthrolines in chloroform/hydrochloric acid[12] and in other systems;[15,16] they are attributed to interfacial adsorption of the organic phase species. These stirring effects are essentially responsible for the interfacial area under stirring, A_i, which became as larger as 2.3×10^4 cm^2 [13] under the present conditions. The absorbance change, ΔA, caused by stopping or starting of stirring (after extraction equilibrium is established) was increased with an increase in the organic phase absorbance under stirring at equilibrium, A' (Fig. 5), for systems of phen, DMP, and DPP. These results were analysed by assuming a Langmuir isotherm,

$$[FeL_3X_2]_i=\frac{aK'[FeL_3X_2]_o}{a+K'[FeL_3X_2]_o}, \qquad (2)$$

where subscripts i and o refer to an interface and an organic phase; a and K' refer to the saturated interfacial concentration (mol cm^{-2}) and the adsorption constant (dm^3) defined by $K'=[FeL_3X_2]_i/[FeL_3X_2]_o$ at infinite dilution. From Eq. 2, the relation between ΔA and A' was derived as

$$\frac{1}{\Delta A}=\left(\frac{1}{a}+\frac{\varepsilon}{K'A'}\right)\frac{V_o}{\varepsilon A_i}, \qquad (3)$$

where V_o refers to the volume of the organic phase.

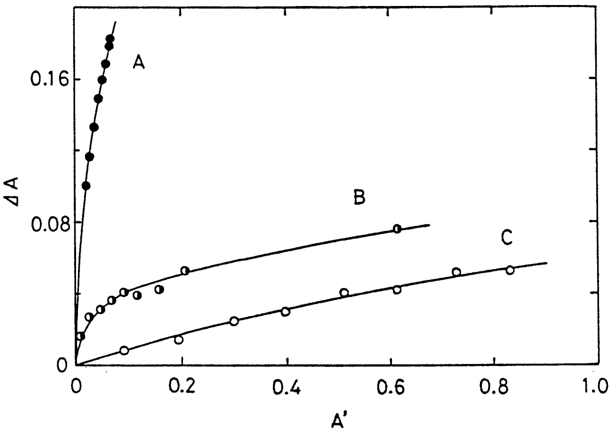

Fig. 5. Interfacial adsorption isotherm of the ion pairs shown as the plots of ΔA against A' in vigorously agitated chloroform/0.1 M $NaClO_4$ at 4700 rpm: (A) phen; (B) DMP; (C) DPP.

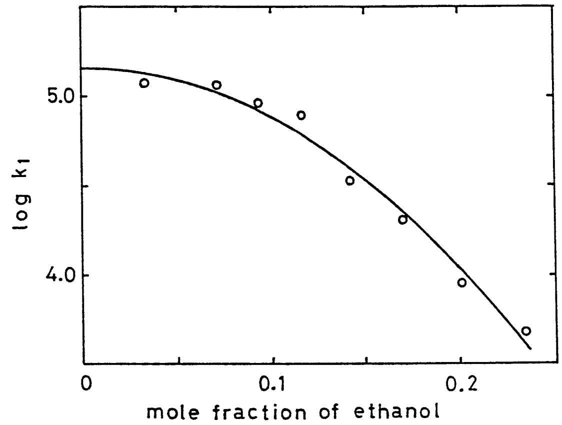

Fig. 6. Variation of the formation rate constants ($M^{-1}sec^{-1}$) of $[Fe(DPP)_3]^{2+}$ in aqueous ethanol, $[Fe^{2+}]_{init}=4.0\times10^{-7}$ M, $[DPP]_{init}=1.2\times10^{-5}$ M, $[SO_4^{2-}]=0.0333$ M. The extrapolation afforded $\log k_1=5.32$ as the value in aqueous phase.

Table 1. Summary of the Distribution, Adsorption, and Kinetic Parameters in the Ion-Association Extraction of Iron(II) with 1,10-Phenanthrolines at 25 °C

Ligands	Anion (0.1 M)	$\log K_D$	aA_i / mol	$K'A_i$ / dm^3	k_{obs} / $M^{-1}s^{-1}$	$\log k_1$[a] (obsd)	$\log k_1$[b] (calcd)	$\log k_1'$[c]
Phen	ClO_4^-	2.85	1.2×10^{-6}	0.368	49.8	5.65	5.46	not detd.
DMP	ClO_4^-	3.62	3.0×10^{-7}	0.278	68.7	5.70	6.26	6.36
DPP	ClO_4^-	7.45	4.3×10^{-7}[d]	0.00452	19.3	5.52	8.77	5.00
	CCl_3COO^-	—	4.1×10^{-7}[d]	0.203	59.4	—	9.61	6.18[h]
	Br^-	—	3.9×10^{-7}[d]	0.207	2.06	—	8.15	4.72[h]
	Cl^-	7.13[e]	8.8×10^{-7}[d]	0.473	0.38	—	7.73	4.30[h]
	SO_4^{2-}[f]	7.14	—	>1	31.3[g]	5.32	8.64	5.19

a) Stopped-flow method. b) Calculated by Eq 9. c) Calculated by Eq 12. d) Ref 13. e) Ref 12. f) 0.0333 M. g) Decreasing rate constant of $[DPP]_o$. h) Calculated by using $\log k_1$ =5.52.

As suggested from Eq. 3, the linearity between $1/\Delta A$ and $1/A'$ was confirmed for each ligand system and the values for aA_i and $K'A_i$ were obtained from the intercept and the slope of $1/\Delta A$ vs. $1/A'$ plots. The results of the values are listed in Table 1.

Formation Rate Constants. The second-order rate constants, k_1, for the reaction of iron(II) and phen, DMP, and DPP in aqueous solution were determined and are listed in Table 1. In DPP systems, k_1 was estimated from an extrapolation of the results obtained in an aqueous ethanol media, as shown in Fig. 6.

Discussion

Extraction Mechanism. The rate law given in Eq. 1, which was determined experimentally, suggests that the rate-controlling step of the ion-association extraction is the formation of the mono-complex, $[\mathrm{FeL}]^{2+}$. It is also concluded from the high-speed stirring experiments that the interfacial adsorption of the ion pair occurs during extraction in every system studied. The organic phase concentration of the ion pair is thought to be in equilibrium with the interfacial concentration following the Langmuir isotherm at any event throughout extraction. Therefore, the total complex concentration at a certain time, $[\mathrm{FeL_3X_2}]_\mathrm{T}$, which is equal to the organic phase concentration when A_i is zero, can be represented by

$$[\mathrm{FeL_3X_2}]_\mathrm{T}=[\mathrm{FeL_3X_2}]_\mathrm{o}+[\mathrm{FeL_3X_2}]_\mathrm{i}\frac{A_\mathrm{i}}{V_\mathrm{o}}. \tag{4}$$

The aqueous phase concentration $[\mathrm{FeL_3}^{2+}]$ was negligibly low in the present systems. Since $[\mathrm{FeL_3X_2}]_\mathrm{o}$ is rather dilute during the initial stage of extraction, $[\mathrm{FeL_3X_2}]_\mathrm{i}$ is assumed to be proportional to $[\mathrm{FeL_3X_2}]_\mathrm{o}$ from Eq. 2,

$$[\mathrm{FeL_3X_2}]_\mathrm{i}=K'[\mathrm{FeL_3X_2}]_\mathrm{o}. \tag{5}$$

From Eqs. 1, 4, and 5,

$$\left(\frac{\mathrm{d}[\mathrm{FeL_3X_2}]_\mathrm{T}}{\mathrm{d}t}\right)_{t=0}=k_\mathrm{obs}\left(1+\frac{K'A_\mathrm{i}}{V_\mathrm{o}}\right)[\mathrm{Fe}^{2+}]_\mathrm{init}[\mathrm{L}]_\mathrm{o,init} \tag{6}$$

was derived. If the rate-controlling reaction takes place in the bulk aqueous phase, as postulated for the Co(II)-DPP system,[9] the following reaction should be considered:

$$\mathrm{Fe}^{2+}+\mathrm{L}\longrightarrow \mathrm{FeL}^{2+} \tag{7}$$

$$\left(\frac{\mathrm{d}[\mathrm{FeL_3X_2}]_\mathrm{T}}{\mathrm{d}t}\right)_{t=0}=k_1[\mathrm{Fe}^{2+}]_\mathrm{init}[\mathrm{L}]_\mathrm{init}, \tag{8}$$

where k_1 stands for the rate constant for the formation of $[\mathrm{FeL}]^{2+}$. In this case, the observed rate constant k_obs is represented by

$$k_\mathrm{obs}=\frac{1}{1+\dfrac{K'A_\mathrm{i}}{V_\mathrm{o}}}\cdot\frac{k_1}{K_\mathrm{D}}. \tag{9}$$

The calculated values of k_1 from Eq. 9 for phen, DMP, and DPP system are listed in Table 1. In the phen and DMP systems the calculated values of $\log k_1(\mathrm{calc})$ are not very far from $\log k_1(\mathrm{obs})$ determined by the stopped-flow method; in DPP systems, however, $k_1(\mathrm{calc})$ is over 10^3-times larger than $k_1(\mathrm{obs})$. The insufficiency of Eq. 9 could also be shown by the discrepancy between the observed extraction rate constants, k_obs, and the calculated extraction rate constants, k_calc, from Eq. 9 by introducing the observed values for k_1, K_D, and $K'A_\mathrm{i}$ into it: $k_\mathrm{calc}/k_\mathrm{obs}=1.5$ for phen, 0.26 for DMP and 5.5×10^{-4} for DPP, all in $\mathrm{ClO_4^-}$ systems. The value of 5.5×10^{-4} in DPP is much smaller than unity. For this reason, it is difficult to explain the extraction rate only in terms of the aqueous phase reaction. Hence, we took into account the interfacial reaction

$$\mathrm{Fe}^{2+}+\mathrm{L_i}\xrightarrow{k_1'}\mathrm{FeL_i}^{2+}, \tag{10}$$

as well as the aqueous reaction of Eq. 7. Equations 7 and 10 afford the following rate equation:

$$\left(\frac{\mathrm{d}[\mathrm{FeL_3X_2}]_\mathrm{T}}{\mathrm{d}t}\right)_{t=0}=k_1[\mathrm{Fe}^{2+}]_\mathrm{init}[\mathrm{L}]_\mathrm{init}+k_1'[\mathrm{Fe}^{2+}]_\mathrm{init}[\mathrm{L}]_\mathrm{i}\frac{A_\mathrm{i}}{V_\mathrm{o}}, \tag{11}$$

where k_1' stands for the rate constant for the formation of $[\mathrm{FeL}]^{2+}$ at the interface. The factor $A_\mathrm{i}/V_\mathrm{o}$ in Eq. 11 was introduced in order to convert the interfacial extraction rate ($\mathrm{mol\,cm^{-2}\,s^{-1}}$) to the initial extraction rate ($\mathrm{mol\,dm^{-3}\,s^{-1}}$). In this case, k_obs is represented by the following equation, instead of Eq. 9:

$$k_\mathrm{obs}=\frac{1}{1+\dfrac{K'A_\mathrm{i}}{V_\mathrm{o}}}\left(\frac{k_1}{K_\mathrm{D}}+k_1'K_\mathrm{L}'\frac{A_\mathrm{i}}{V_\mathrm{o}}\right), \tag{12}$$

where K_L' refers to the adsorption constant of L defined by $K_\mathrm{L}'=[\mathrm{L}]_\mathrm{i}/[\mathrm{L}]_\mathrm{o}$ for infinite dilution of L. The values of $K_\mathrm{L}'A_\mathrm{i}$ were estimated as $7.1\times10^{-6}\,\mathrm{dm^3}$ for DMP and $1.0\times10^{-5}\,\mathrm{dm^3}$ for DPP, assuming that $K_\mathrm{L}'A_\mathrm{i}=K_\mathrm{LH}'A_\mathrm{i}/K_\mathrm{D}$, where $K_\mathrm{LH}'=[\mathrm{LH^+}]_\mathrm{i}/[\mathrm{LH^+}]$, the adsorption constant of protonated DMP or DPP.[12] The values of $\log k_1'$ were calculated according to Eq. 12 while employing the values of k_obs, $k_1(\mathrm{obs})$, $K'A_\mathrm{i}$, K_D and $K_\mathrm{L}'A_\mathrm{i}$. The results are listed in Table 1. The values of $\log k_1'$ in DPP systems are much closer to those of $\log k_1(\mathrm{obs})$ than those of $\log k_1(\mathrm{calc})$; the magnitude of $\log k_1'$ is thus considered to be reasonable as the formation rate constant of $[\mathrm{FeL}]_\mathrm{i}^{2+}$, which may be produced at the aqueous phase side of the interface.

Effect of Ligands. From the parameters obtained from the experiments involving 0.1 M $\mathrm{ClO_4^-}$ for phen, DMP, and DPP systems (Table 1), the effect of the ligands on the extraction kinetics of iron(II) can be compared. The adsorptivity of the tris-complex shown by $K'A_\mathrm{i}$ in Table 1 decreases in the order $[\mathrm{Fe(phen)_3}]^{2+}>[\mathrm{Fe(DMP)_3}]^{2+}>[\mathrm{Fe(DPP)_3}]^{2+}$, corresponding to the order of increasing hydrophobicity of the ligands; this is indicated by the value of K_D. Although the value of $K'A_i$ of $[Fe(phen)_3]^{2+}$ is the largest among the three systems, the least adsorptivity of phen, which was actually undetectable, makes the contribution of the interfacial reaction, Eq. 10, negligibly small. The extraction rate with phen can thus be understood to be governed by an adsorption of the tris-complex and a bulk aqueous reaction, Eq. 7; the extraction rate constant can be represented by Eq. 9. The value of $k_{calc}/k_{obs}=1.5$, which means k_{obs}, is 33% less than k_{calc}, may suggest that the mass-transfer rate of phen is somewhat inhibited by the interfacial film of $[Fe(phen)_3]^{2+}$. As for the DMP system, the contribution of the interfacial reaction was not ignored, since the value of K_D of DMP is larger than that of phen and $HDMP^+$ showed moderate adsorptivity.[12] The percentage of the interfacial reaction was estimated as being about 70% from a calculation of $100\times(k_{obs}-k_{calc})/k_{obs}$. In the DPP system, the value of K_D is very large and the aqueous phase concentration is negligibly small; the interfacial concentration of DPP, however, is not ignored and, hence, extraction with DPP proceeds completely via an interfacial reaction.

Effect of Anions. The effect of the five anions on the extraction behavior of $[Fe(DPP)_3]^{2+}$ was examined. As noted in Table 1, though the values of K_D are independent of the anions, those of $K'A_i$ depend significantly on anions in the order $ClO_4^- < CCl_3COO^- \approx Br^- < Cl^- < SO_4^{2-}$, corresponding to the order of increasing hydration energy.[17]

The values of $\log k_1'$ determined in the various anion systems are close to the observed $\log k_1$ and show little dependence on the anions, except for the CCl_3COO^- system. Recalling the interfacial adsorptivity of CCl_3COO^-, itself, which was pointed out in the interfacial tension measurements,[13] the higher value of 6.18 as $\log k_1'$ may be attributable to an analogous effect to a miceller catalysis of anionic surfactants on the chelate formation rate.[18]

In conclusions, the role of the interface on the ion-association extraction rate of $[FeL_3]X_2$ under high-speed stirring could be clarified as: (1) interfacial catalysis in the formation of $[FeL]^{2+}$ promoted by an interfacial adsorption of the ligands, which is favorable for the ligand of larger K_D and (2) interfacial trapping of an ion pair during extraction, which is more remarkable for an ion pair with a less-hydrophobic ligand e.g. $[Fe(phen)_3](ClO_4)_2$, or in the ion pair with more hydrophilic anion, e.g. $[Fe(DPP)_3]SO_4$. Usually, the extraction constant of ion-association extraction is represented by the product of the formation constant of an ion pair in the aqueous phase and the distribution constant of the ion pair by a tacit assumption of an "aqueous phase mechanism". However, as concluded in the present kinetic study, there are alternative cases in which extraction proceeds completely via an interfacial reaction, as shown in DPP systems. In such cases, it is not reasonable to assume the "aqueous phase mechanism". Much more attention concerning interfacial phenomena should be paid in any analysis of the extraction mechanism of ion-association extraction systems.

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