Interfacial Adsorption of Iron(II)-4,7-Diphenyl-1,10-phenanthroline Complex in Ion-Association Extraction Systems

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The interfacial adsorptivity of an iron(II)-4,7-diphenyl-1,10-phenanthroline (DPP) complex in chloroform/aqueous salt solution systems was investigated by means of a high-speed stirring method and interfacial tension measurements. The interfacial spectra observed in the stirred system suggested that the adsorbed species at the interface is the tris-DPP complex. A minor effect of the anion concentration on the adsorptivity suggested that the tris-complex adsorbed as an ion-pair in a 0.1 M anion concentration. The interfacial adsorption of the ion-pair under stirring was analyzed by the Langmuir isotherm. The adsorptivity increased, depending on the counter ions, in the order $ClO_4^- < CCl_3COO^- \simeq Br^- < Cl^- < SO_4^{2-}$, i.e. the order of increasing hydration energies of these anions.

Interfacial phenomena in solvent extraction processes have recently become an attractive subject in both fields of fundamental solvent extraction chemistry[1] and practical solvent extraction technology.[2]

Many studies have been reported concerning the solvent extraction mechanisms of ion-association extraction equilibria. The reactions in the ion-association extraction systems are usually thought to occur in two bulk phases, and the influence of the interface which exists between two liquid phases is completely ignored. Therefore, the extraction constants in the ion-association extraction equilibria are usually represented by using the ion-pair formation constants in bulk phases and the distribution constant of the ion-pair.

In our recent studies, some observations suggested a significant role of the interface in ion-association extraction processes. For example, methyl or phenyl derivatives of 1,10-phenanthroline adsorbed at the interface of chloroform/aqueous dilute hydrochloric acid, more abundantly at lower pH.[3] A tris(1,10-phenanthroline)iron(II) complex, which did not adsorb at the air/water interface,[4] showed the characteristic interfacial adsorptivity, depending on the kinds of organic solvents.[5] The distribution equilibrium of 4,7-diphenyl-1,10-phenanthroline under stirring was affected by the addition of zinc(II) or copper(II) ion, probably because of the interfacial adsorption of a metal complex of the ligand.[6] These findings required extensive investigations concerning the interfacial adsorption of the metal complexes, including 1,10-phenanthroline or its derivatives, in order to clarify the role of the interface in the ion-association extraction mechanism.

In the present study the interfacial adsorptivity of an iron(II) complex with 4,7-diphenyl-1,10-phenanthroline (abbreviated as DPP or L) was investigated in both static and highly agitated chloroform/aqueous electrolyte solution systems. Here, the adsorption isotherm and the effect of counter anions on the adsorptivity are discussed.

Experimental

Chemicals. DPP, Wako G. R., was used as purchased. A stock solution of iron(II) was prepared by dissolving recrystallized iron(II) chloride in dilute hydrochloric acid with hydroxylamine hydrochloride or iron(II) sulfate in dilute sulfuric acid with ascorbic acid. A solution of iron(II)–DPP complex in chloroform was prepared by a batch extraction method in a glass-stoppered centrifuge tube or by extraction in a high-speed stirring apparatus in advance. Sodium salts of perchlorate, bromide, trichloroacetate, chloride, and sulfate (all G. R. grade reagents) were used for the preparation of the aqueous electrolyte solutions. Chloroform (Wako G. R.) was washed three times with water prior to use. Water was purified by means of a Millipore Milli-QII system. Other chemicals used in the present study were of analytical reagent grade.

Interfacial Tension. Interfacial tensions, γ, were measured by means of a drop-volume method at 25±0.1 °C. The apparatus used in this study was the same as described previously.[5] The liquid–liquid systems used for the measurements were prepared by shaking 10 ml of 3×10^{-6}—3×10^{-3} M DPP (1 M=1 mol dm^{-3}) in chloroform and 10 ml of 1×10^{-3} M or 5×10^{-3} M Fe^{2+} in 0.1 M aqueous salt solution for 30—60 min in order to attain extraction equilibrium. The concentrations of $[Fe(DPP)_3]^{2+}$ in the organic phase were determined photometrically. The volume of a detached aqueous drop from a glass capillary was measured with precision to 0.1 μl by the use of Gilmont digital micrometer-syringe. The interfacial tension was calculated by the equation reported by Lando and Oakley.[7] The densities of the aqueous phases required for the calculations of γ were determined in the present study by using a pycnometer.

Stirring Experiment. Interfacial adsorption under stirring was observed at 25±0.1 °C by means of a high-speed stirring apparatus (described in detail elsewhere[3]). Fifty ml of iron(II)–DPP complex in chloroform and an equal volume of aqueous solution containing iron(II) ($<10^{-3}$ M) and 0.1 M sodium salt, which attained extraction equilibrium, was agitated by stirring at a stirring rate of 4700 rpm. The stirring caused a reversible decrease in the organic phase absorbance. From the decrement of the absorbance at the wavelength where the ion-pair showed a maximum absorbance, the interfacial amount of the complex was calculated. The effect of pH on the interfacial amount is not significant

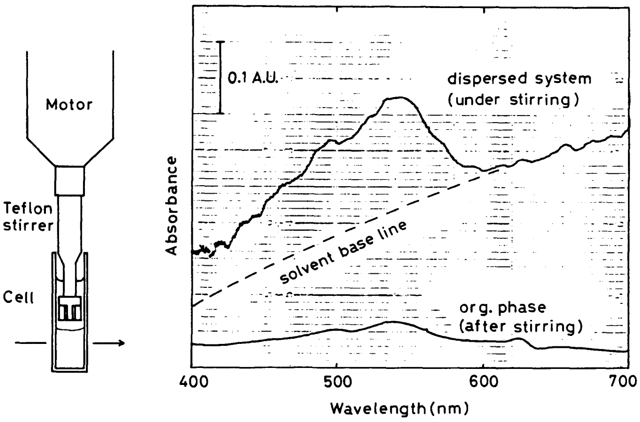

Fig. 1. Left; method for the measurements of interfacial spectra under stirring. Right; an example of the interfacial spectra, $[\mathrm{Fe}^{2+}]_{\mathrm{init}}=1.0\times10^{-3}$ M, $[\mathrm{DPP}]_{\mathrm{o,init}}=3.0\times10^{-3}$ M, and $[\mathrm{Na_2SO_4}]=0.05$ M, 3500 rpm.

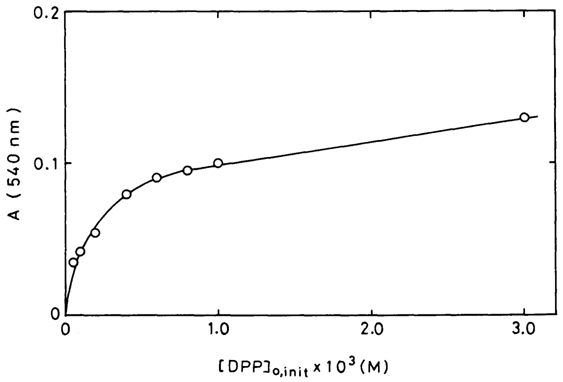

Fig. 2. Effect of DPP concentration on the interfacial spectra; $[\mathrm{Fe}^{2+}]_{\mathrm{init}}=1.0\times10^{-3}$ M, $[\mathrm{Na_2SO_4}]=0.05$ M, 3500 rpm.

over a pH range of 3.5—5.5.

Spectral Measurement. Direct measurements of the absorption spectra of the interfacially adsorbed species were attempted by using the method shown in Fig. 1. In a 1 cm optical cell mounted in a cell compartment of a Jasco Uvidec 430 spectrophotometer, a 1.5 ml chloroform solution of DPP was stirred with an equal volume of aqueous solution of iron(II) and sodium sulfate or sodium chloride by a small Teflon stirrer at the rate of 3500 rpm. The spectra of the dispersed system was recorded while maintaining stirring. The spectra of the solvent blank under stirring and that of the organic phase after stirring were also measured.

Extraction Experiment. The extractability of the ion-pair was observed in four-anion systems by a batch method. Five ml of DPP in chloroform and an equal volume of an aqueous phase containing iron(II) and 0.1 M sodium salt was shaken by a mechanical shaker for 30 min in a thermostated room at 25±1 °C. After centrifugation, the concentration of the ion-pair in the organic phase was determined photometrically. The distribution ratio of iron(II) was obtained under various concentrations of iron(II) and DPP.

Results and Discussion

Interfacial Spectra of the Stirred System. When 6.0×10^{-5}—3.0×10^{-3} M DPP in chloroform was stirred with 1.0×10^{-3} M iron(II) in a 0.05 M sodium sulfate solution, there was no appreciable extraction of the red iron(II) complex in the organic phase after stirring; nor was there an appreciable amount of it formed in the aqueous phase. However, only during stirring of the two-phase system did a reddish color appear on the dispersed mixture. A typical example of the absorption spectrum of the dispersed mixture of a $\mathrm{CHCl_3}$/$\mathrm{Na_2SO_4}$ solution system is shown in Fig. 1. The net absorbance of the spectrum under stirring is obviously larger than that after stirring. Since there was no colored species in the bulk aqueous phase, the spectrum observed under stirring was attributable to an interfacial species, which was produced only at the interface. From the shape of the spectrum (maximum at 540 nm), the interfacial species was assigned to the tris-DPP complex, $[\mathrm{Fe(DPP)_3}]^{2+}$. The net absorbance at 540 nm under stirring was increased with DPP concentration, as shown in Fig. 2. The plots showed a saturation curve which suggested that the observation was characteristically an interfacial phenomena. In a chloride system, a stirred mixture of 2.0×10^{-4} M DPP in chloroform and 1.0×10^{-3} M iron(II) in a 0.1 M NaCl solution at 3500 rpm gave 0.190 as the difference between absorbances at 537 nm and 600 nm, while the organic phase after stirring gave 0.325 as the corresponding absorbance difference; the aqueous phase showed no color. If there is no formation of the complex at the interface during stirring, the absorbance difference under stirring is equal to half of the absorbance difference of the organic phase after stirring. The experimental result (that 0.190 is larger than 0.325/2=0.1625) strongly suggested the contribution of an extra formation of $[\mathrm{Fe(DPP)_3}]^{2+}$ at the interface.

Interfacial Adsorption Isotherm. A typical example of the effect of stirring on the extraction equilibria is shown in Fig. 3 for the cases of trichloroacetate systems. The initiation of stirring of a two-phase system which had already attained an extraction equilibrium caused a decrease in the organic phase absorbance of the ion-pair $[\mathrm{Fe(DPP)_3}]\mathrm{X_2}$ (X denotes an anion) until it reached a new equilibrium under stirring. When the stirring was stopped, the absorbance was restored to that before stirring, as shown in Fig. 3.

From the absorbance before or after stirring (A) and that under stirring (A'), the absorbance decrement ($\Delta A=A-A'$) was calculated. The values of ΔA depended on the ion-pair concentration in the organic phase as well as on the anion concentration in the aqueous phase. The ion-pair concentration dependence is shown as plots of ΔA against A' for a four-

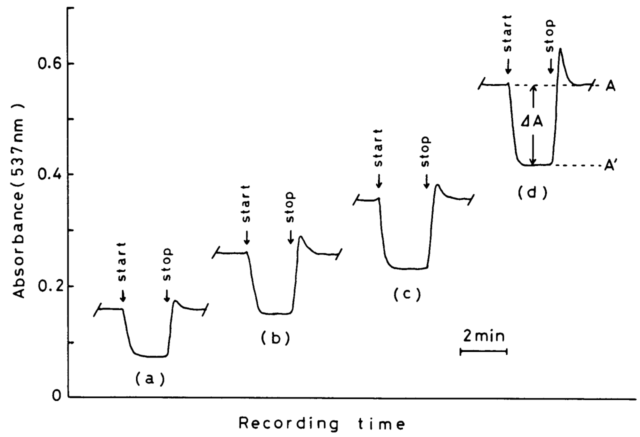

Fig. 3. A typical example of the stirring effect (4700 rpm) on the organic phase absorbance; $[\mathrm{Fe}^{2+}]_{\mathrm{init}}=1.0\times10^{-3}$ M, $[\mathrm{DPP}]_{\mathrm{o,init}}=3.57\times10^{-5}$ M (a), 5.03×10^{-5} M (b), 6.48×10^{-5} M (c), and 9.35×10^{-5} M (d).

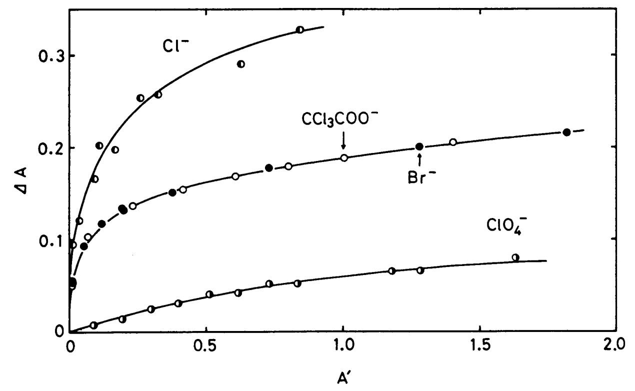

Fig. 4. Adsorption isotherm of $[\mathrm{Fe(DPP)_3}]\mathrm{X_2}$ under stirring; anion (X) concentration in aqueous phase is 0.1 M in all cases.

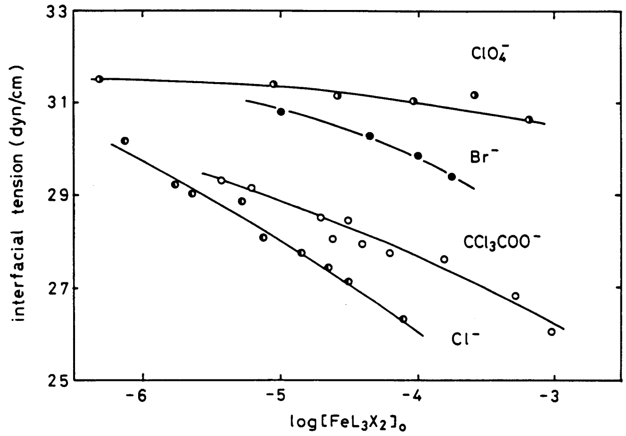

Fig. 5. Lowering of the interfacial tension as a function of the organic phase concentration of $[\mathrm{Fe(DPP)_3}]\mathrm{X_2}$ in the ion-association equilibria; anion (X) concentration in aqueous phase is 0.1 M.

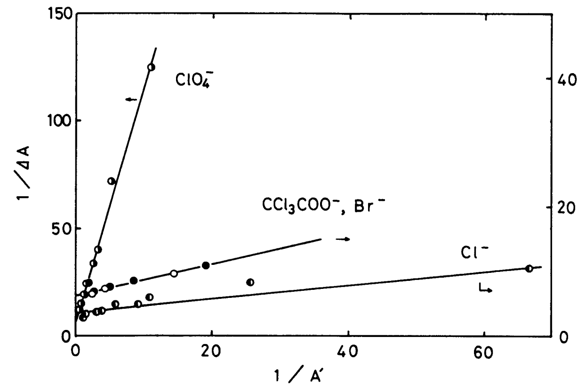

Fig. 6. Langmuir plot for the interfacial adsorption of $[\mathrm{Fe(DPP)_3}]\mathrm{X_2}$ under stirring.

anion systems in Fig. 4. The value of ΔA was largest in a chloride system and smallest in a perchlorate system, when compared at a given A'. If the observed stirring effects were responsible for the interfacial adsorption of the iron(II)–DPP complex, the interfacial tension in those systems must also be changed with the concentration of the ion-pair in the organic phase. The interfacial tension of the chloroform/aqueous phase system was indeed lowered with an increase in the concentration of the ion-pair in organic phase, depending on the anions (Fig. 5). The order of the lowering in the interfacial tension was found from Fig. 5 to be perchlorate<bromide<trichloroacetate<chloride, which can be understood as the order in the effect of anions on the adsorptivity of the ion-pair. It must be noticed, however, that the interfacial tension lowering in a trichloroacetate system includes the contribution of the adsorption of the anion, itself.

The above results suggest an interfacial adsorption of the complex; thus, the results of stirring were analyzed as follows. The mass balance equation of the tris-complex, $\mathrm{FeL_3}^{2+}$ under stirring is represented by

$$[\mathrm{FeL_3}^{2+}]_{\mathrm{o,init}}V_\mathrm{o} = [\mathrm{FeL_3}^{2+}]_\mathrm{o}V_\mathrm{o} + [\mathrm{FeL_3}^{2+}]_\mathrm{i}A_\mathrm{i}, \tag{1}$$

where subscripts o, i, and init refer to the organic phase, interface, and initial concentration, respectively. V_o refers to the volume of the organic phase (l) and A_i to the total interfacial area (cm²). The interfacial concentration was assumed to obey the Langmuir isotherm,

$$[\mathrm{FeL_3}^{2+}]_\mathrm{i} = \frac{aK'[\mathrm{FeL_3}^{2+}]_\mathrm{o}}{a + K'[\mathrm{FeL_3}^{2+}]_\mathrm{o}} \tag{2}$$

where a refers to the saturated interfacial concentration (mol cm⁻²) and K' to the adsorption constant (l cm⁻²) defined by $K'=[\mathrm{FeL_3}^{2+}]_\mathrm{i}/[\mathrm{FeL_3}^{2+}]_\mathrm{o}$ at infinitly diluted concentration of $\mathrm{FeL_3}^{2+}$. From Eqs. 1 and 2, the relation between ΔA and A' can be derived as

$$\frac{1}{\Delta A} = \left(\frac{1}{a} + \frac{\varepsilon}{K'A'}\right)\frac{V_\mathrm{o}}{\varepsilon A_\mathrm{i}}\ , \tag{3}$$

where ε is the molar absorptivity of the ion-pair in the organic phase. Based on Eq. 3, $1/\Delta A$ was plotted against $1/A'$ for the four-anion systems (Fig. 6). The

Table 1. Interfacial Adsorption of $[FeL_3]X_2$ in the Stirred Chloroform/Aqueous Phase Systems at 25 °C

Anion (0.1 M)	$\varepsilon \times 10^4$ (λ_{max})	$\log K_{ex}^{*}$ a)	$aA_i \times 10^7$ b)	$K'A_i$
			mol	l
ClO_4^-	2.14 (534 nm)	14.7	4.26 ± 1.40	$(4.52 \pm 0.14) \times 10^{-3}$
CCl_3COO^-	1.99 (537 nm)	14.2	4.13 ± 0.19	$(2.03 \pm 0.30) \times 10^{-1}$
Br^-	2.05 (573 nm)	13.4	3.90 ± 0.10	$(2.07 \pm 0.14) \times 10^{-1}$
Cl^-	1.58 (537 nm)	10.6	8.82 ± 0.60	$(4.73 \pm 0.32) \times 10^{-1}$

a) Conditional extraction constant, $K_{ex}^{*} = [FeL_3X_2]_o/[Fe^{2+}][L]_o^3$ estimated when $[X^-] = 0.1$ M, where L=DPP.
b) Using $a = 2.5 \times 10^{-11}$ mol cm^{-2} obtained from Fig. 5, A_i is estimated as 2.3×10^4 cm^2.

linear relations in Fig. 6 strongly support the interfacial adsorption mechanism for the stirring effect. From the slopes and the intercepts of the plots in this figure, parameters aA_i and $K'A_i$ were obtained (Table 1).

Effect of Anions on the Interfacial Adsorption. The saturated interfacial amount of the complex, aA_i (Table 1), shows an order of 10^{-7} mol irrespective of the anions, while the values of $K'A_i$ obviously depend on the anions: largest in chloride ion and smallest in perchlorate ion. The results of the interfacial spectra and the stirring effect showed that the effect of the anions on the adsorptivity increased in the order $ClO_4^- < CCl_3COO^- \simeq Br^- < Cl^- < SO_4^{2-}$, essencially corresponding to the same order in the hydration energies of the anions.[8] This order was reversed concerning the effect of anions on the conditional extraction constants, K_{ex}^{*}, of the ion-pair, as listed in Table 1. Similar results were reported in the interfacial adsorption of tridodecylmethylammonium and trioctylmethylammonium salts in *o*-xylene/2 M aqueous acid systems, in which the adsorptivity increased in the order $ClO_4^- < CH_3COO^- < NO_3^- < Cl^-$.[9] As opposed to this, the interfacial adsorptivity of tetrabutylammonium halides increased in the order $Cl^- < Br^- < I^-$.[10] From these results, it can be concluded that when the cation which adsorbs at the interface is highly hydrophobic and the interfacial adsorption takes place from the organic phase side, as in the present case of $[Fe(DPP)_3]^{2+}$, the cation is more adsorbable when a counter anion is more hydrophilic and less extractable. On the other hand, when the cation which adsorbs is soluble in water and its interfacial adsorption occurs from the aqueous phase side, as in the case of tetrabutylammonium ion, interfacial adsorption is more favorable in a less hydrophilic and more extractable anion system.

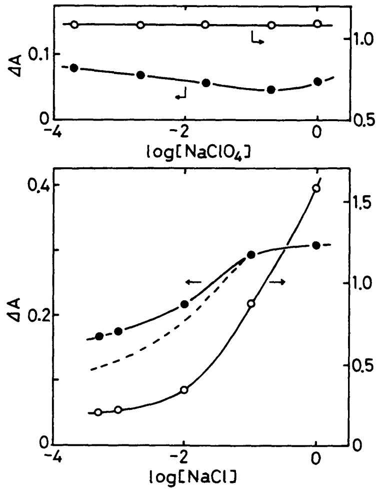

Fig. 7. Effect of the salt concentrations on ΔA and A; upper figure, $[Fe(DPP)_3X_2]_{o,init} = 3.0 \times 10^{-5}$ M, lower figure, $[Fe^{2+}]_{init} = 1.0 \times 10^{-3}$ M, $[DPP]_{o,init} = 3.3 \times 10^{-4}$ M. Dotted line shows hypothetical ΔA when A is the plotted one in [NaCl]=0.1 M.

It is important to know whether $[Fe(DPP)_3]^{2+}$ exists at the interface as an ion-pair or a free cation. Figure 7 shows the effect of the concentrations of ClO_4^- and Cl^- on both ΔA and A. In the ClO_4^- system, the ion-pair concentration in the organic phase (shown by A) was not affected by the anion concentration, while the interfacial amount (shown by ΔA) slightly decreased with an increase in the ClO_4^- concentration. In the Cl^- system, although the ion-pair concentration steeply increased with an increase in the Cl^- concentration, the interfacial amount gradually increased with an increase of the Cl^- concentration and became almost constant around $[Cl^-] = 0.1$ M.

A comparison between the change in ΔA observed by varying the NaCl concentration and that observed by varying the $[Fe(DPP)_3]^{2+}$ concentration at [NaCl]= 0.1 M under the same values of A (Fig. 7) indicated that the values of ΔA slightly increased at lower concentrations of Cl^- than 0.1 M. From these results it is supposed that the effect of the anion concentration on the adsorbed amount is not ascribable to an ion-pair formation at the interface but, rather, to the extraction equilibrium between bulk phases. Hence, the interfacial species in 0.1 M anion concentrations is probably the ion-pair.

In conclusion, interfacial adsorption in the ion-association extraction equilibria of a tris-DPP iron(II) complex was clarified and the extent of the contribution was found to be more remarkable in systems of a more dilute complex concentration (as shown by the observation of Langmuir isotherm) and in less extractable anions. These results strongly suggest that the extraction reaction in this system takes place at the interface, opposite to the usual assumption that the extraction mechanism comprises ion-pair formation in the aqueous phase and a distribution of the ion-pair between two-phases. The role of the interface in the extraction mechanism will be further clarified by kinetic studies which are now in progress.

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