The Extraction of Bis(8-picolylideneaminoquinoline)iron(II) Perchlorate into Nitrobenzene[1)]

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The green chelate cation of bis(8-picolylideneaminoquinoline)iron(II) can be extracted into nitrobenzene as the form of the ion-pair with various univalent anions. The extractability with these anions is decreased in the order of $B(C_6H_5)_4^- \approx ClO_4^- > SCN^- > I^- \gg NO_3^- > Br^- > Cl^- \gg CH_3COO^-$. The extractive reaction with perchlorate ions has been applied to the spectrophotometric determination of minute amounts of iron(II). The nitrobenzene extract gives two characteristic charge-transfer ($d \rightarrow \pi^*$) bands at 663 and 569 nm. Under the optimum conditions of pH, ligand concentration and shaking time, Beer's law is obeyed up to 1.2×10^{-4} M iron(II) in the organic phase. The molar absorptivity is 7.04×10^3 l·mol^{-1}·cm^{-1} at 663 nm. The proposed method is selective and can be used for the determination of iron(II) in the presence of fairly large amounts of various ions, provided high concentrations of the ligand or suitable masking agents are used. A kinetic study made to obtain an information on the extraction mechanism of the ion-pair of this type showed that the rate equation can be represented as

$$-\frac{d[Fe^{2+}]}{dt} = k_0[Fe^{2+}][8\text{-PAQ}]^2_{org}(1+k_1[ClO_4^-])$$

where k_0 and k_1 are respectively the rate constant and a constant.

2,2′,2″-Terpyridine, an important colorimetric reagent for iron(II), has been known as a representative tridentate ligand which contained the functional grouping N=C–C=N–C·C·N (points denote single or double bonds). Lions and his coworkers[2)] reported briefly on the preparation and use of 8-picolylideneaminoquinoline (abbreviated as 8-PAQ) as a tridentate chelating agent with constitutional features similar to those of terpyridine and showed that it coordinated with iron(II) salts similarly to the latter. They also showed that bis(8-PAQ)iron(II) iodide is obtained as a diamagnetic crystalline solid, which gives an intense green color when dissolved in water. Later, Kurmholz[3)] recorded the visible absorption spectra of iron(II) complexes with a series of "terpyridine-like" tridentate imine ligands including 8-PAQ and interpreted the observed spectral patterns on the basis of the molecular models and the geometrical considerations.

We have found that the iron(II) chelate of 8-PAQ can be quantitatively transferred into nitrobenzene as the form of the ion-pair in the presence of such anions as perchlorate, iodide, thiocyanate, or tetraphenylborate ions. This paper deals mainly with the application of 8-PAQ to the extractive spectrophotometric determination of minute amounts of iron(II) in the presence of perchlorate ions. The method proposed here is simple and highly selective for iron(II). The interference from certain metals can be avoided by adding suitable masking agents or by using a large excess of the ligand. The only interfering metal that forms a colored chelate with the ligand is cobalt(II). In order to get a semi-quantitative information on the extraction mechanism of the ion-pair of this type, a kinetic study has also been made spectrophotometrically. The extraction rate was found to be first order with respect to the concentration of iron(II) in the aqueous phase, and second order with respect to the ligand concentration in the organic phase. The rate of the extraction is also affected by the concentration of perchlorate ions in the aqueous phase.

Experimental

Reagents. 8-PAQ and bis(8-PAQ)iron(II) perchlorate were prepared according to the procedures described in the literature. The latter, sparingly soluble black needles, decomposed above 271 °C. Found: C, 49.65; H, 3.24; N, 11.37; Cl, 9.87%. Calcd for $Fe(C_{15}H_{11}N_3)_2(ClO_4)_2 \cdot 0.5H_2O$: C, 49.34; H, 3.17; N, 11.51; Cl, 9.71%.

A stock solution of iron(II) sulfate was standardized complexometrically. Sodium perchlorate was prepared and purified as described previously.[4)] Nitrobenzene obtained from the Katayama Kagaku Co. was distilled under reduced pressure. All the other reagents used were of analytical grade.

Apparatus. The absorbance measurements were made with a Hitachi model 124 double-beam spectrophotometer equipped with quartz cells of 10 mm pathlength. The pH determinations were carried out with a Toa Dempa model HM-6A pH meter.

General Procedure. All of the extraction procedures and the absorbance measurements were made at 25 °C. A centrifuging tube (volume, 50 ml) with a glass stopper was used to equilibrate the organic and aqueous phases. The aqueous phase contained solutions of iron(II) sulfate, ascorbic acid, sodium perchlorate and an acetate buffer. A 5.0 ml portion of the aqueous solution and a 5.0 ml portion of 8-PAQ in nitrobenzene were placed in the tube, and the two phases were agitated vigorously by a mechanical shaker for a required period. When the agitation was stopped, the two phases in the tube were immediately centrifuged for 2 min at 1000 rpm. The iron contents in the two phases were determined from the initial iron concentration and the absorbance of the organic phase at 663 nm.

Results and Discussion

The Extraction of Iron(II) into Nitrobenzene with 8-PAQ in the Presence of Various Anions. In Fig. 1 the extraction behavior of iron(II) on changing counter anion is shown by plotting the percentage extraction of iron(II) as a function of the concentration of the anion. The order of extractability as a measure of half-extrac-

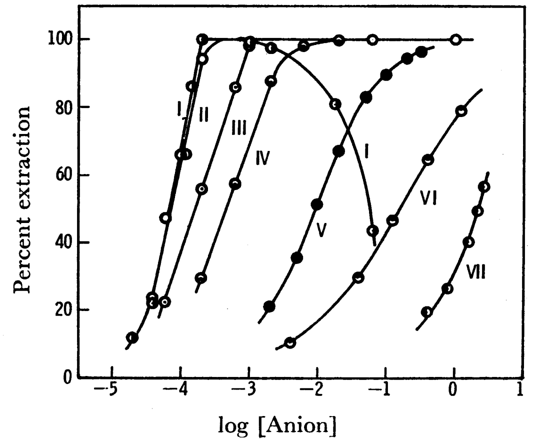

Fig. 1. Extraction of iron(II) as the 8-PAQ chelate with various anions.
Fe^{2+}, 8.0×10^{-5}M; anion ----I, $B(C_6H_5)_4^-$: II, ClO_4^-: III, SCN^-: IV, I^-: V, NO_3^-: VI, Br^-: VII, Cl^-: pH, 3.20; 8-PAQ in $C_6H_5NO_2$, 5.0×10^{-3}M

tion is as follows: $B(C_6H_5)_4^- \approx ClO_4^- > SCN^- > I^- \gg NO_3^- > Br^- > Cl^- \gg CH_3COO^-$, SO_4^{2-}. This sequence suggests that the enthalpy of hydration of the anion is the major factor governing the extractability of the iron(II)–8-PAQ chelate cation as the form of the ion-pair. The percentage extraction increases remarkably when the enthalpy of hydration of the anions is below 70—80 kcal/mol. With strongly hydrated anions, such as acetate and sulfate ions, the iron(II) chelate is scarcely extracted at all. This result is in good agreement with those obtained by Gibson and Weatherburn[5] with the quaternary phosphonium and arsonium cations, by Biswas and Mandal[6] with surfactant cations, and by Takamatsu[7] with the tris(1,10-phenanthroline)-ruthenium(II) cation.

In addition, as is evident in Fig. 1, an abnormal decrease in the percentage extraction at higher concentrations of sodium tetraphenylborate is observed. A similar result has been obtained in the extraction of tris(1,10-phenanthroline)ruthenium(II) into various organic solvents with tetraphenylborate ions.[7] This phenomenon, therefore, may be explained in terms of the hydrotropism[8,9] which is often encountered in the solution of an electrolyte with a large ion.

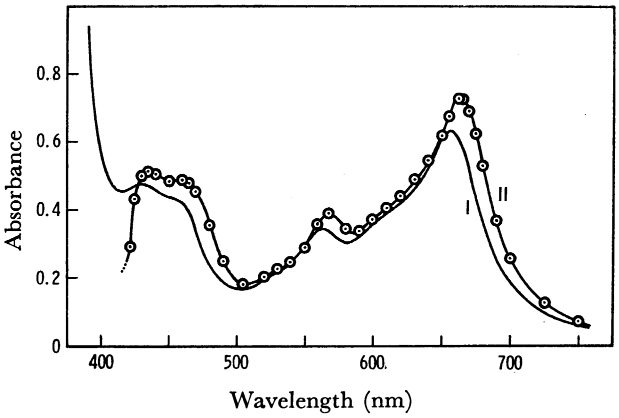

Fig. 2. Visible absorption spectra of 1.03×10^{-4}M $Fe(8\text{-}PAQ)_2(ClO_4)_2$ in 50 v/v % aqueous methanol and nitrobenzene.
I, solid $Fe(8\text{-}PAQ)_2(ClO_4)_2$ dissolved in 50 v/v % aqueous methanol; II, solid $Fe(8\text{-}PAQ)_2(ClO_4)_2$ dissolved in nitrobenzene; —, prepared by extracting 1.03×10^{-4}M iron(II) from a pH 3.2 solution containing 0.02 M $NaClO_4$

Absorption Spectra. The visible absorption spectra of 50 v/v% aqueous methanol and nitrobenzene solutions of bis(8-PAQ)iron(II) perchlorate are shown in Fig. 2.

It has generally been accepted that the visible absorption of diamagnetic iron(II) complexes of tridentate imine ligands as well as that of α-diimine ligands is caused by an electron migration from the filled 3d orbitals of the metal to the lowest vacant molecular orbitals of the ligands. In a 50 v/v% aqueous methanol solution, the main absorption band of the iron(II) complex of 8-PAQ is found at 657 nm (molar absorptivity, $\varepsilon=6.35\times10^3$). This peak is accompanied by a weak shoulder toward shorter wavelengths. A distinct second peak, which is not found in the visible absorption spectrum of the bis(terpyridine)iron(II) complex, is found at 563 nm ($\varepsilon=3.38\times10^3$), also accompanied by a weak shoulder toward shorter wavelengths. The appearance of the second transition has been assigned to the splitting of the filled T_{2g} orbitals by non-cubic field components.[3] An additional absorption band appearing in the 410—470 nm region ($\varepsilon=4.61\times10^3$ at 427 nm) may probably be attributed to the charge-transfer from the 3d orbitals of iron(II) to the second lowest vacant molecular orbitals of the ligand.[10]

In nitrobenzene, as is shown in Fig. 2, the main and the second peaks are shifted toward longer wavelengths along with an increase in intensity. These are found at 663 ($\varepsilon=7.04\times10^3$) and 569 nm ($\varepsilon=3.82\times10^3$) respectively. Figure 2 also shows that the visible absorption spectrum of the nitrobenzene extract obtained according to the general procedure is completely identical with that of the synthesized complex. In both the aqueous methanol and the organic solvent, the free ligand did not show any absorption in the visible region above 450 nm.

The ultraviolet absorption spectrum of the iron(II) complex measured in a 50 v/v% aqueous methanol solution is composed of three intense peaks at 372 ($\varepsilon=4.42\times10^4$), 352 ($\varepsilon=4.24\times10^4$), and 232 nm ($\varepsilon=5.98\times10^4$) and two shoulders at about 332 ($\varepsilon=2.9\times10^4$) and 315 nm ($\varepsilon=1.9\times10^4$). The magnitude of the molar absorptivities suggests that all the absorption bands are caused by $\pi\rightarrow\pi^*$ transitions.

Application to the Spectrophotometric Determination of Iron(II). The Effect of pH: The absorbance of the organic phase was measured as a function of pH of the aqueous phase, the result being shown in Fig. 3. The iron(II)–8-PAQ chelate is formed above pH 1. The absorbance of the extract is at its maximum at pH 2.0—4.2. It is of interest to note that the ion-pair once extracted into nitrobenzene can not be decomposed in the presence of perchlorate ions, unless high concentrations of hydrochloric acid (above 6 M) or sodium hydroxide (above 0.5 M) are used.

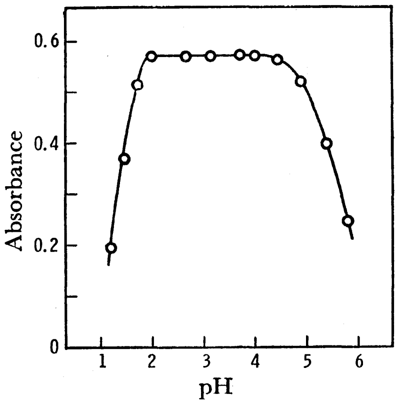

Fig. 3. Effect of pH.
Fe^{2+}, 8.0×10^{-5}M; $NaClO_4$, 0.02 M; 8-PAQ in $C_6H_5NO_2$, 5.0×10^{-3}M

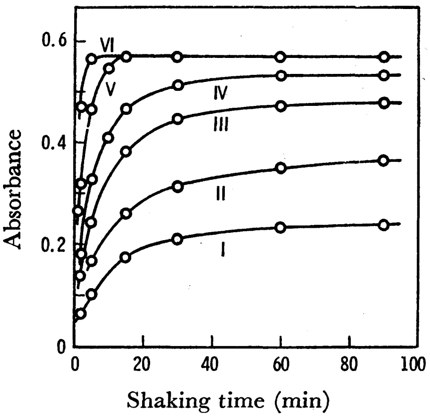

Fig. 4. Effect of the ligand concentration and the shaking time.
Fe^{2+}, 8.0×10^{-5}M; $NaClO_4$, 0.02 M; pH, 3.20; 8-PAQ in $C_6H_5NO_2$——I, 1.25×10^{-3}M: II, 1.59×10^{-3}M: III, 2.01×10^{-3}M: IV, 2.50×10^{-3}M: V, 3.75×10^{-3}M: VI, 6.25×10^{-3}M

The Effects of the Ligand Concentration and the Shaking Time: Figure 4 shows the effects of the ligand concentration and the shaking time on the extraction of iron(II). A shaking period of about 15 min is enough to obtain the maximum extraction, when the initial concentration of the ligand in nitrobenzene is 3.75×10^{-3} M which is about 50 fold molar excess over iron(II). The shaking period can be reduced by using the higher concentrations of the ligand.

The Effect of Solvents and the Stability of the Color: Several organic solvents were examined for their ability to extract the ion-pair. Of all the solvents tested, chloroform, 1,2-dichloroethane and nitrobenzene were capable of extracting the ion-pair, while in the other cases a precipitate was observed at the interface. In chloroform and 1,2-dichloroethane, however, the green color of the ion-pair tended to fade away gradually. The absorbance of the nitrobenzene extract did not change at all for at least 48 hr, indicating that the ion-pair is very stable in nitrobenzene.

The Effect of Volume of the Aqueous Phase: The absorbance of the organic phase was decreased with increasing the volume of the aqueous phase to organic phase, but it could be avoided by using higher concentrations of the ligand or by lengthening the shaking time.

Adherence to Beer's Law: To the series of sample solutions containing up to 34 μg (1.2×10^{-4} M in the final concentration) of iron(II or III), the general procedure described above was applied. The conditions used were: 8-PAQ in nitrobenzene, 5.0×10^{-3} M; sodium perchlorate, 0.02 M; ascorbic acid added as a reducing agent for iron(III), 0.4%; pH of the aqueous phase, 3.20; shaking period, 15 min. It was found that Beer's law is obeyed between the absorbance of the organic phase and the concentration of iron over

TABLE 1. EFFECT OF DIVERSE IONS FOR THE DETERMINATION OF 22.4 μg (0.4 μmol) OF IRON

Ion	Added (μmol)	Fe found (μg)	Difference (μg)
Zn	2	22.1	−0.3
	4	17.2	−5.2
	10	6.6	−15.8
	10[a]	22.1	−0.3
Cd	5	20.7	−1.7
	5[a]	22.4	±0.0
	10	15.6	−6.8
	10[a]	22.2	−0.2
Co(II)	0.2	22.8	+0.4
	1	24.3	+1.9
	10	24.5	+2.1
Ni	2	22.2	−0.2
	5[a]	22.7	+0.3
	10	15.6	−6.8
	10[a]	22.9	+0.5
Cu	4	22.6	+0.2
	10	3.5	−18.9
	10[b]	22.3	−0.1
Ru(III)	1.2	22.9	+0.5
	6	17.6	−4.8
	6[a]	22.5	+0.1
Mo(VI)	5	22.1	−0.3
	10	21.1	−1.3
	10[c]	22.5	+0.1
W(VI)	0.5	20.6	−1.8
	2	15.5	−6.9
	10	4.4	−18.0
	10[c]	22.0	−0.4
F^-	100	22.4	±0.0
	200	22.4	±0.0
$S_2O_3^{2-}$	200	22.3	−0.1
	500	22.4	±0.0
$C_2O_4^{2-}$	2	22.1	−0.3
	10	21.6	−0.8
	100	16.5	−5.9
$C_4H_4O_6^{2-}$	100	22.4	±0.0
	300	22.4	±0.0
PO_4^{3-}	100	22.2	−0.2
	200	22.0	−0.4
EDTA	0.05	21.9	−0.5
	0.1	21.4	−1.0
	1	12.4	−10.0

a) Reagent concentration: 1.0×10^{-2} M b) 1 ml of 0.2 M sodium thiosulfate solution was added. c) 1 ml of 0.2 M sodium tartrate solution was added.

the entire range examined.

The Effect of Diverse Ions: The extent of interference by a number of metal ions and anions in the determination of 22.4 μg of iron(II) was studied. The following metal ions did not interfere, even if they were present at a concentration level of several ten times that of iron: silver, thallium(I), beryllium, magnesium, calcium, strontium, barium, mercury(II), tin(II), lead, manganese(II), yttrium, lanthanoid, aluminum, gallium, indium, bismuth, chromium(III, VI), osmium(VIII), rhodium, irridium, platinum(II, IV), thorium, titanium, zirconium, vanadium(IV, V), and uranium(VI).

Table 1 shows the effect of several metal ions and anions on the determination of iron. Zinc, cadmium, nickel, copper(II), ruthenium(III), and molybdenum(VI) do not interfere up to concentrations of several times that of the amount of iron. The negative errors observed in the presence of larger amounts of these ions may be due to the consumption of the reagent by the formation of colorless complexes with these cations; the error can be eliminated by the use of a fairly large amount of the reagent, except for copper(II) which still interferes to some extent. The interference from copper(II) can be eliminated by the addition of thiosulfate. The addition of tartrate is also effective to prevent the interference from molybdenum and tungsten. The most difficult interference is that from cobalt(II), which forms an extractable brown complex with the reagent and gives a positive error. The extraction of cobalt(II) seemed to be accompanied by a transformation of $\mathrm{Co(8\text{-}PAQ)_2(ClO_4)_2}$ into an inert complex such as $\mathrm{Co(8\text{-}PAQ)_2(ClO_4)_3}$. Anions, such as fluoride, tartrate, thiosulfate and phosphate do not interfere, even when they are present at a large concentration. However, as is expected for iron(II), EDTA and a large amount of oxalate interfere with the determination by the formation of complexes with iron(II).

It is clear from these results that 8-PAQ is highly selective for iron(II), and that this reagent, although it is not very stable, can be used as a spectrophotometric reagent for iron in the presence of fairly large amounts of various ions.

A Kinetic Study. *Statistical Treatments*: Assuming that the diffusion or the transport of materials can be neglected from consideration, the rate of the extraction of iron(II) with the ligand and perchlorate ions may be generally described as follows:

$$-\frac{\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = k_0[\mathrm{Fe}^{2+}]^a[\text{8-PAQ}]^b_{\mathrm{org}}[\mathrm{H}^+]^c[\mathrm{ClO_4}^-]^d \qquad (1)$$

As the concentrations of the ligand and perchlorate ions are in considerably excess to iron(II), and as the aqueous phase is buffered, the rate can be described as follows:

$$-\frac{\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = q[\mathrm{Fe}^{2+}]^a \qquad (2)$$

where q is the multiplication of the rate constant, k_0, and the other concentrations which are kept at certain values. When the reaction order with respect to iron(II) is unity, Eq. (2) can be rewritten by integration as:

$$-\log[\mathrm{Fe}^{2+}] = q\cdot t + c_0 \qquad (3)$$

where c_0 is a constant. Equation (3) shows that the log $[\mathrm{Fe}^{2+}]$ *vs*. t plot should be a straight line with a slope of $-q$.

The reaction order with respect to the other species can be determined from the rate measurements when two of the concentrations out of these three are kept at certain values. For example, when the concentrations of the hydrogen and perchlorate ions are kept at C and D, then the quantity q_{L} can be defined as follows:

$$\log q_{\mathrm{L}} = \log k_0C^cD^d + b\log[\text{8-PAQ}]_{\mathrm{org}} \qquad (4)$$

Thus, the reaction order with respect to the ligand, b, can be determined by plotting $\log q_{\mathrm{L}}$ *vs*. $\log[\text{8-PAQ}]_{\mathrm{org}}$.

By similar treatments, the rest of the values of the c and d reaction orders can be determined from the slope of the plot given by the following equations:

$$\log q_{\mathrm{H^+}} = \log k_0B^bD^d + c\log[\mathrm{H}^+] \qquad (5)$$

$$\log q_{\mathrm{ClO_4^-}} = \log k_0B^bC^c + d\log[\mathrm{ClO_4}^-] \qquad (6)$$

However, as will be seen below, the reaction order with respect to the perchlorate ions, d, was not a constant, but changed as the perchlorate concentration was changed; the following equation should therefore be used instead of Eq. (6):

$$\log q_{\mathrm{ClO_4^-}} = \log k_0B^bC^c + \log(1+k_1[\mathrm{ClO_4}^-]+ \cdots +k_n[\mathrm{ClO_4}^-]^n) \qquad (6a)$$

The Reaction Order with Respect to Fe^{2+}: In Fig. 5 are shown some of the experimental values of $-\log[\mathrm{Fe}^{2+}]$ as a function of t. It is seen that the points lie on straight lines, indicating that the reaction order with respect to iron(II) is always unity.

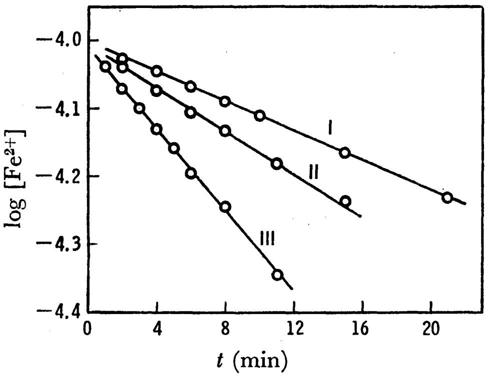

Fig. 5. Dependence of the rate of iron(II) extraction on the Fe^{2+} concentration.

pH, 3.30; $\mathrm{NaClO_4}$, 0.1 M; 8-PAQ in $\mathrm{C_6H_5NO_2}$---- I, 1.13×10^{-3}M: II, 1.33×10^{-3}M: III, 1.52×10^{-3}M

The Reaction Order with Respect to the Ligand: The rate of extraction was determined in the ligand concentration range between 0.95×10^{-3} M and 2.3×10^{-3} M, the results being plotted in Fig. 6. As may be seen from Fig. 6, the rate of extraction was concluded to be proportional to the square of the ligand concentration under these conditions.

The Reaction Order with Respect to the Hydrogen Ion: The pH of the aqueous phase was varied from 3.02 to 4.50 while the concentrations of the ligand and the perchlorate were kept at 1.35×10^{-3} M and 0.1 M

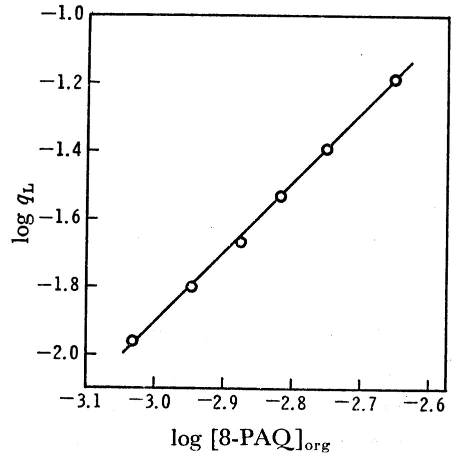

Fig. 6. Dependence of the rate of iron(II) extraction on the 8-PAQ concentration in the organic phase.
pH, 3.30; $NaClO_4$, 0.1 M

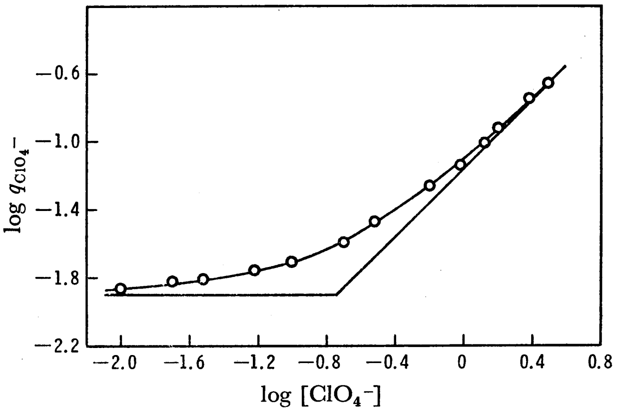

Fig. 7. Dependence of the rate of iron(II) extraction on the perchlorate-ion concentration.
pH, 3.30; 8-PAQ in $C_6H_5NO_2$, 1.35×10^{-3}M. The curve fitted is $\log q_{ClO_4^-} = -1.88 + \log(1 + 5.0[ClO_4^-])$. The intersect of the two asymptotes is (−0.72, −1.88).

respectively. As the result, it was found that the rate of extraction was almost independent of the hydrogen ion concentration of the aqueous phase under these conditions.

The Effect of Perchlorate Ions: The rate was determined as a function of the perchlorate-ion concentration in the aqueous phase when the ligand concentration of the organic phase was 1.35×10^{-3} M and when the pH of the aqueous phase was 3.30. Figure 7 gives the $\log q_{ClO_4^-}$ *vs.* $\log [ClO_4^-]$ plot. The data in this figure were also analysed by the curve fitting method.[11,12] As may be seen from Fig. 7, the slope for the plot approaches zero in the lowest $\log [ClO_4^-]$ region, but it increases with the increase in $\log [ClO_4^-]$ until it approaches unity. The increase in $q_{ClO_4^-}$ with the perchlorate concentration should not seem to be due to the ionic strength effect. Thus, it was concluded that there are two mechanisms for the extraction and they can be represented by Eq. (6b).

$$\log q_{ClO_4^-} = \log k_0 B^b C^c + \log(1 + k_1[ClO_4^-]) \qquad (6b)$$

The first order dependence of the rate on the perchlorate concentration is probably due to the first-step association of $Fe(8\text{-}PAQ)_2^{2+}$ chelate cation with perchlorate ions in the aqueous phase. This is contradictory to the conclusion of Yamamoto[13] in a similar study with tris(1,10-phenanthroline)iron(II) perchlorate; he concluded that this ion-pair is completely dissociated in water and also in nitrobenzene. On the other hand, it has also been found that the ion-pairs formed between tris(1,10-phenanthroline)ruthenium(II) and anions such as perchlorate, iodide, and thiocyanate are extracted into various organic solvents mainly as the associated form and that the degree of association is considerable even in water.[7]

The rate equation, therefore, can be expressed as:

$$-\frac{d[Fe^{2+}]}{dt} = k_0[Fe^{2+}][8\text{-}PAQ]^2_{org}(1 + k_1[ClO_4^-]) \qquad (7)$$

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