Propiononitrile as an Extraction Solvent for the Ion-Pair Complexes of Water-Soluble Tetracationic Porphyrinatocopper(II) with Perchlorate: The Effect of Sodium Chloride

Kenta Fujii,[1] **Jun Nishimoto,***[,2] **Shiro Yamada,**[1] **Mizue Fukamachi,**[1] **and Masaaki Tabata**[1]

[1]Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502

[2]Analytical Research Center for Instrumental Sciences, Saga University, 1 Honjo-machi, Saga 840-8502

Received August 14, 2003; E-mail: nishimoj@cc.saga-u.ac.jp

The ion-pair extraction of 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrinatocopper(II) ($[\mathrm{Cu^{II}(tmpyp)}]^{4+}$, $\mathrm{CuP^{4+}}$) with perchlorate ion has been studied for a water–propiononitrile (PN) system in the presence of sodium chloride. The $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was extracted as $[\mathrm{CuP{\cdot}4ClO_4}]$ and dissociated to $[\mathrm{CuP{\cdot}2ClO_4}]^{2+}$ and $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$ in the PN phase. The high concentration of NaCl in the aqueous phase suppressed the extraction of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ ($n = 1$, 2) due to the increased partition of $\mathrm{ClO_4}^-$ into the PN phase. The extraction constants of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ with $\mathrm{ClO_4}^-$ into the PN phase at different concentrations of NaCl were found to be $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$ ($\mathrm{mol^{-1}\,dm^3}$) $= [\mathrm{CuP{\cdot}ClO_4}^{3+}]_\mathrm{o}[\mathrm{ClO_4}^-]_\mathrm{o}^3[\mathrm{CuP^{4+}}]_\mathrm{a}^{-1}[\mathrm{ClO_4}^-]_\mathrm{a}^{-4} = 9.1 \pm 1.9$, $(3.0 \pm 0.2) \times 10^{-1}$, and $(2.5 \pm 2.2) \times 10^{-1}$ for 0, 0.5, and 1.0 $\mathrm{mol\,dm^{-3}}$ NaCl, respectively, and $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$ ($\mathrm{mol^{-2}\,dm^6}$) $= [\mathrm{CuP{\cdot}2ClO_4}^{2+}]_\mathrm{o}[\mathrm{ClO_4}^-]_\mathrm{o}^2[\mathrm{CuP^{4+}}]_\mathrm{a}^{-1}[\mathrm{ClO_4}^-]_\mathrm{a}^{-4} = 31 \pm 18$ for 1.0 $\mathrm{mol\,dm^{-3}}$ NaCl. The extraction constants of $\mathrm{NaClO_4}$ were found to be $K_{\mathrm{ex(NaClO_4)}}$ ($\mathrm{mol^{-1}\,dm^3}$) $= [\mathrm{NaClO_4}]_\mathrm{o}[\mathrm{Na^+}]_\mathrm{a}^{-1}[\mathrm{ClO_4}^-]_\mathrm{a}^{-1} = (8.8 \pm 1.6) \times 10^{-2}$ and $(5.1 \pm 0.7) \times 10^{-2}$ for 0.5 and 1.0 $\mathrm{mol\,dm^{-3}}$ NaCl, respectively. The dissociation constants of $\mathrm{NaClO_4}$ in the PN phase were determined: $K_{\mathrm{dis(NaClO_4)}}$ ($\mathrm{mol\,dm^{-3}}$) $= [\mathrm{Na^+}]_\mathrm{o}[\mathrm{ClO_4}^-]_\mathrm{o}[\mathrm{NaClO_4}]_\mathrm{o}^{-1} = (1.5 \pm 0.3) \times 10^{-2}$ and $(2.8 \pm 0.4) \times 10^{-2}$ for 0.5 and 1.0 $\mathrm{mol\,dm^{-3}}$ NaCl, respectively, and $K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}} = [\mathrm{Na^+}]_\mathrm{o}[\mathrm{ClO_4}^-]_\mathrm{o}[\mathrm{Na^+}]_\mathrm{a}^{-1}[\mathrm{ClO_4}^-]_\mathrm{a}^{-1} = (2.37 \pm 0.05) \times 10^{-3}$ for 0 $\mathrm{mol\,dm^{-3}}$ NaCl. The detailed extraction mechanism of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ is discussed by taking into account the chemical species of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ in the PN phase and the extraction of $\mathrm{NaClO_4}$ and comparing these with the results obtained for acetonitrile.

In solvent extraction, conventional solvents such as chloroform, carbon tetrachloride, etc. have generally been used as the organic phase.[1] The solvents are suitable for the extraction of non-polar compounds or compounds with low electric charges, but it is difficult to extract water-soluble compounds with high electric charges into organic solvents. Mixed solvents of water and water-miscible organic solvents like acetonitrile are separated into aqueous and organic phases by the addition of salts like sodium chloride, due to the decrease in solubility of organic solvents in aqueous solution.[2] The water content in the acetonitrile phase after phase separation is from 1 to 10 $\mathrm{mol\,dm^{-3}}$, while that in the conventional organic solvent is 10^{-1} $\mathrm{mol\,dm^{-3}}$ or less.[3] Therefore, these water-miscible organic solvents can extract highly charged compounds.

Porphyrins are highly sensitive and selective analytical reagents for the determination of metal ions due to a high molar absorptivity and size recognition of metal ions by the rigid central porphyrin core.[4] The combination of spectrophotometry and solvent extraction leads to a much more sensitive and selective analytical method due to the elimination of a reagent blank[5,6] and the different extractabilities of metalloporphyrins.[6] The metalation rate of porphyrins, however, is usually slow in solution because of difficulties related to deformation of the rigid porphyrin structure.[4,7] Furthermore, porphyrins that are extractants are barely soluble in water, resulting in a much slower metalation rate. Thus, there are few reports on the extraction of metal ions using porphyrins.[8] To overcome this problem, the following methods have recently been reported. Ion-pair extraction of metalloporphyrins that are formed in aqueous solution by using catalysts and water-soluble porphyrins has been performed using acetonitrile separated from the aqueous mixture by salting-out.[6,9]

We have reported an equilibrium study of ion-pair extraction of a highly positive charged metalloporphyrin (4+) with perchlorate ions into the acetonitrile phase separated from the acetonitrile–water mixture by the addition of sodium chloride.[6,9] In particularly, 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrinatocopper(II) cation ($[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ ($\mathrm{CuP^{4+}}$), Fig. 1) in aqueous solution was quantitatively extracted into the acetonitrile phase. Furthermore, this technique was applied to the determination of a trace amount of Cu(II) ion (3×10^{-8}–4×10^{-6} $\mathrm{mol\,dm^{-3}}$) in water. The high concentration of water and ions in the acetonitrile phase plays an important role for the extraction of the charged species. However, salts used in the extraction affect the concentrations of water and NaCl in the organic phase, making it difficult to analyze the extraction mechanism.

In the present work, we have studied the ion-pair extraction of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ in a water–propiononitrile–NaCl system. We have paid particular attention to the effects of the salting-out reagent (NaCl) concentrations on the extraction. In the water–propiononitrile–NaCl system, the compositions of both the

Published on the web March 12, 2004; DOI 10.1246/bcsj.77.511

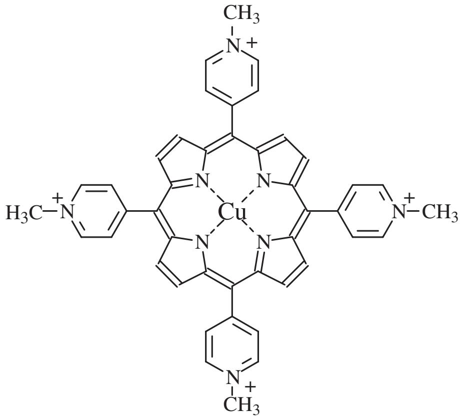


Fig. 1. 5,10,15,20-Tetrakis(*N*-methylpyridinium-4-yl)porphyrinatocopper(II) cation ($[Cu^{II}(tmpyp)]^{4+}$, CuP^{4+}).

organic and aqueous phases do not drastically change with different amounts of NaCl. Furthermore, the organic phase contains comparatively much water about 2–3 mol dm^{-3} like the acetonitrile rich phase after phase separation using sodium chloride. Thus, the propiononitrile is a good solvent to study the effects of increasing salt concentrations on the extraction of $[Cu^{II}(tmpyp)]^{4+}$. The present paper clarifies the extraction mechanism of the ion-pair complexes of $[Cu^{II}(tmpyp)]^{4+}$ with perchlorate in the presence of NaCl by determining the effects of the partition coefficients of $NaClO_4$ into the propiononitrile, as well as those of $[Cu^{II}(tmpyp)]^{4+}$. Moreover, this is the first paper using propiononitrile as an extraction solvent for ion-pair complexes.

Experimental

Reagents. Water treated with a Mill-Q SP TOC (Nippon Millipore, Japan) was used for all experiments. 5,10,15,20-Tetrakis(1-methylpyridinium-4-yl)porphyrin tetrakis(*p*-toluenesulfonate) ($H_2tmpyp^{4+}\cdot 4$(toluenesulfonate)) was purchased from Dojindo Laboratories (Japan). All other reagents are products of Wako Pure Chemical Industries (Japan).

Propiononitrile was dried for several days on 4 Å molecular sieves. After the removal of the molecular sieves, 6 g of *p*-toluenesulfonic acid was added to the propiononitrile (1 dm^{-3}) to remove basic impurities. The propiononitrile was then purified by distillation. The $[Cu^{II}(tmpyp)]^{4+}$ was synthesized by the reaction of H_2tmpyp^{4+} with an excess of copper(II) chloride and was precipitated as perchlorate.[10] The porphyrinatocopper(II) perchlorate was washed with a perchloric acid solution (10^{-2} mol dm^{-3}) and passed through an anion-exchange resin of chloride form. Sodium chloride and sodium perchlorate were dried in an electric oven at 573 K, and kept in a desiccator. All other chemicals were used without further purification.

Extraction Procedure of $[Cu^{II}(tmpyp)]^{4+}$. A 5 cm^3 aqueous solution containing 0, 0.5, and 1 mol dm^{-3} of NaCl as a salting-out reagent, $NaClO_4$ at various concentrations as the counter ion, and 5×10^{-6} mol dm^{-3} of $[Cu^{II}(tmpyp)]^{4+}$ were placed in a 10 cm^3 sample tube with a screw cap, and then 5 cm^3 propiononitrile was added. This solution was shaken for about 1 minute, followed by spinning in a centrifuge for 10 minutes to separate the two phases completely. The solution was left at 25 ± 0.1 °C for 24 h in a thermostat to reach complete equilibrium. All procedures were carried out at room temperature (25 °C). Absorption spectra were recorded on a JASCO UV–vis spectrophotometer V-550.

Composition of Propiononitrile and Aqueous Phases. The concentrations of sodium perchlorate in the aqueous and propiononitrile phases were determined by the methylene bule method.[11] Propiononitrile in the sample solution did not affect the determination of ClO_4^- after the dilution of the aqueous and propiononitrile phases more than 1000 times. The concentration of sodium chloride in the propiononitrile phase was determined by the change in absorbance of mercury thiocyanate.[12] The concentration of sodium chloride in the aqueous solution was calculated by subtracting the sodium chloride in the propiononitrile phase from the total NaCl. The amount of water in the propiononitrile phase was determined by a Karl Fisher titration on a Karl Fisher moisture titrator (MKL-200, Kyoto Electronics, Japan). The concentration of water in the propiononitrile phase was determined using the density measured by a density meter (DMA 48, ANTON paar K.G., Austria). The concentration of propiononitrile in the aqueous solution was determined by gas chromatography (GC-380, Gasukuro Kogyo, Japan) after the extraction of the propiononitrile in the aqueous solution into *m*-xylene. The volumes of propiononitrile and the aqueous phase were measured with a graduated tube.

Results and Discussion

Composition of Propiononitrile and Aqueous Phases. The volumes of the propiononitrile and aqueous phases and the concentrations of water and propiononitrile in each phase are given in Table 1. As $[NaCl]_{ini}$ increased, where the subscript ini denotes the initial concentration in aqueous solution before the addition of propiononitrile, the volume of the aqueous phase decreased, but that of the propiononitrile phase increased slightly. As the NaCl concentration increased, the water content in the propiononitrile phase decreased due to the decrease in water activity by the hydration of Na^+ and Cl^- in the aqueous phase. The propiononitrile phase can contain a lot of water compared with conventional organic solvents, such as

Table 1. Compositions of Aqueous and Propiononitrile Phases at 1, 0.5, and 0 mol dm^{-3} Initial Concentration of Sodium Chloride

	1 mol dm^{-3} $[NaCl]_{ini}$	0.5 mol dm^{-3} $[NaCl]_{ini}$	0 mol dm^{-3} $[NaCl]_{ini}$
Volume of aq. phase/cm^3[a]	5.37	5.37	5.45
Volume of org. phase/cm^3[a]	4.61	4.59	4.58
Water in org. phase/mol dm^{-3}[b]	2.38	2.50	2.63
Org. solvent in aq. phase/mol dm^{-3}	1.24[c]–1.30[d]	1.11[c]–1.20[d]	1.4[b]
$[Cl^-]$ in org. phase/mol dm^{-3}[b]	8.11×10^{-4}	6.70×10^{-4}	—
D_{NaClO_4}	0.511[e]–0.225[f]	0.319[e]–0.156[f]	

a) Average values when changing $[NaClO_4]_{ini}$ from 0 to 0.06 mol dm^{-3}. b) Values at 0 mol dm^{-3} $[NaClO_4]_{ini}$. c), d) Values at $[NaClO_4]_{ini}$ of 0[c] to 0.08[d] mol dm^{-3}. e), f) Values at $[NaClO_4]_{ini}$ of 0.01[c] to 0.06[d] mol dm^{-3}.

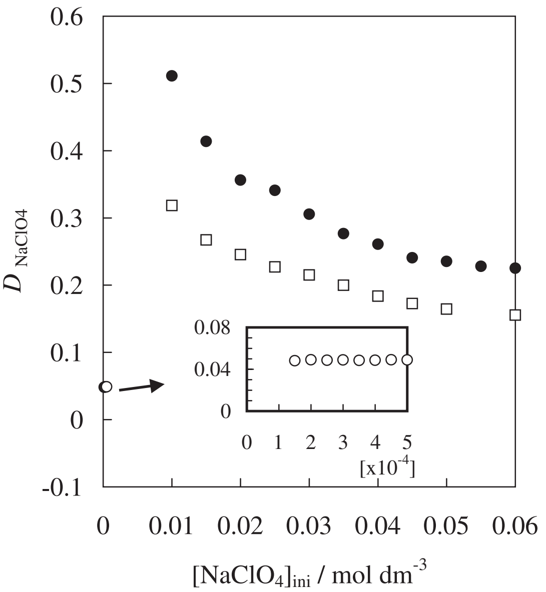


Fig. 2. Distribution ratio, $D_{\mathrm{NaClO_4}}$, of perchlorate at 0 (○), 0.5 (□), and 1 (●) mol dm^{-3} [NaCl]$_{\mathrm{ini}}$. $D_{\mathrm{NaClO_4}} = ([\mathrm{NaClO_4}]_o + [\mathrm{ClO_4}^-]_o)/[\mathrm{ClO_4}^-]_a$.

chloroform. When the initial NaCl concentration was increased, the concentration of propiononitrile in the aqueous phase decreased due to the weakened propiononitrile–water interaction by the hydration of Na^+ and Cl^-, similar to the acetonitrile–water system.[13] The change in the initial concentration of $NaClO_4$ did not have any effect on the volumes of the two phases, the concentrations of water in the propiononitrile or of propiononitrile in the aqueous phases.

Distribution of Sodium Perchlorate. To clarify the detailed ion-pair extraction mechanism of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$, it is necessary to determine the distribution coefficients of sodium perchlorate and sodium chloride between the aqueous and propiononitrile phases.

The distribution ratios of sodium perchlorate ($D_{\mathrm{NaClO_4}}$) observed at 0, 0.5, and 1.0 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$ are given in Fig. 2 as a function of $[\mathrm{NaClO4}]_{\mathrm{ini}}$. At concentrations of $[\mathrm{NaClO4}]_{\mathrm{ini}}$ as low as 10^{-4} mol dm^{-3}, $D_{\mathrm{NaClO_4}}$ was independent of $[\mathrm{NaClO4}]_{\mathrm{ini}}$ in the absence of NaCl (see the inserted figure in Fig. 2). $D_{\mathrm{NaClO_4}}$, however, decreased gradually with increasing the $[\mathrm{NaClO4}]_{\mathrm{ini}}$ at 0.5 and 1 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$, and was higher at higher NaCl concentrations. These results can be explained by taking into account the dissociation of the ion-pair complex of $NaClO_4$ extracted in the propiononitrile phase. We determined the extraction constant of sodium perchlorate between the aqueous and propiononitrile phases and the dissociation constant in the propiononitrile phase as follows:

$$\begin{aligned} D_{\mathrm{NaClO_4}} &= ([\mathrm{NaClO4}]_o + [\mathrm{ClO_4}^-]_o)/[\mathrm{ClO_4}^-]_a \\ &= (K_{\mathrm{ex(NaClO_4)}}[\mathrm{Na^+}]_a[\mathrm{ClO_4}^-]_a + K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}} \\ &\quad \times [\mathrm{Na^+}]_a[\mathrm{ClO_4}^-]_a[\mathrm{Na^+}]_o^{-1})/[\mathrm{ClO_4}^-]_a \end{aligned} \tag{1}$$

where $K_{\mathrm{ex(NaClO_4)}} = [\mathrm{NaClO4}]_o[\mathrm{Na^+}]_a^{-1}[\mathrm{ClO_4}^-]_a^{-1}$ and $K_{\mathrm{dis(NaClO_4)}} = [\mathrm{Na^+}]_o[\mathrm{ClO_4}^-]_o[\mathrm{NaClO4}]_o^{-1}$ and the subscripts a and o denote chemical species in aqueous and propiononitrile phases. In order to know $[\mathrm{Na^+}]_o$ and $[\mathrm{NaCl}]_o$, the total concentration of $([\mathrm{Cl^-}]_o + [\mathrm{NaCl}]_o)$ was determined in various initial concentrations of sodium perchlorate. The concentration of $([\mathrm{Cl^-}]_o + [\mathrm{NaCl}]_o)$ decreased and reached a constant with increasing $[\mathrm{NaClO4}]_{\mathrm{ini}}$. In the region that the concentration of $([\mathrm{Cl^-}]_o + [\mathrm{NaCl}]_o)$ is constant, almost all sodium chloride is thought to be part of an ion pair. Thus, the only ions in the propiononitrile phase are Na^+ and ClO_4^-, resulting in $[\mathrm{Na^+}]_o = [\mathrm{ClO_4}^-]_o$ for $[\mathrm{NaClO4}]_{\mathrm{ini}} \geq 0.015$ and ≥ 0.020 mol dm^{-3} at 0.5 and 1.0 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$, respectively. From $[\mathrm{Na^+}]_o = [\mathrm{ClO_4}^-]_o$ and the definition of the equilibrium constants,

$$[\mathrm{Na^+}]_o = \sqrt{K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}[\mathrm{Na^+}]_a[\mathrm{ClO_4}^-]_a}. \tag{2}$$

When $[\mathrm{Na^+}]_o$ is substituted in Eq. 1, we obtain

$$\begin{aligned} D_{\mathrm{NaClO_4}} &= K_{\mathrm{ex(NaClO_4)}}[\mathrm{Na^+}]_a \\ &\quad + \sqrt{\frac{K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}[\mathrm{Na^+}]_a}{[\mathrm{ClO_4}^-]_a}}. \end{aligned} \tag{3}$$

As expected from Eq. 3, the plot of $D_{\mathrm{NaClO_4}}$ against $[\mathrm{ClO_4}^-]_a^{-1/2}$ gave a straight line for 0.5 and 1 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$, respectively (Fig. 3), in the region where almost all sodium chloride is part of an ion-pair. The slops and intercepts of the straight lines for 0.5 and 1 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$ were $(2.5 \pm 0.1) \times 10^{-2}$ and $(4.1 \pm 0.8) \times 10^{-2}$, and $(3.7 \pm 0.1) \times 10^{-2}$ and $(4.8 \pm 0.7) \times 10^{-2}$, respectively. The values of $K_{\mathrm{ex(NaClO_4)}}$, $K_{\mathrm{dis(NaClO_4)}}$, and $K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}$ ($= [\mathrm{Na^+}]_o[\mathrm{ClO_4}^-]_o[\mathrm{Na^+}]_a^{-1}[\mathrm{ClO_4}^-]_a^{-1}$) are given in Table 2.

For the extraction of perchlorate at 0 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$, $[\mathrm{Na^+}]_a = [\mathrm{ClO_4}^-]_a$. Thus, Eq. 3 can be rearranged to

$$D_{\mathrm{NaClO_4}} = K_{\mathrm{ex(NaClO_4)}}[\mathrm{Na^+}]_a + \sqrt{K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}}. \tag{4}$$

At 0 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$, $D_{\mathrm{NaClO_4}}$ was constant, indicating that $K_{\mathrm{ex(NaClO_4)}}[\mathrm{Na^+}]_a$ is much smaller than $\sqrt{K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}}$, and the extracted sodium perchlorate dissociates completely in the propiononitrile phase at $[\mathrm{NaClO4}]_{\mathrm{ini}}$ as low as 10^{-4} mol dm^{-3}. The $K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}$ are given in Table 2. $K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}$ at [NaCl]$_{\mathrm{ini}} = 0$ mol dm^{-3} was high due

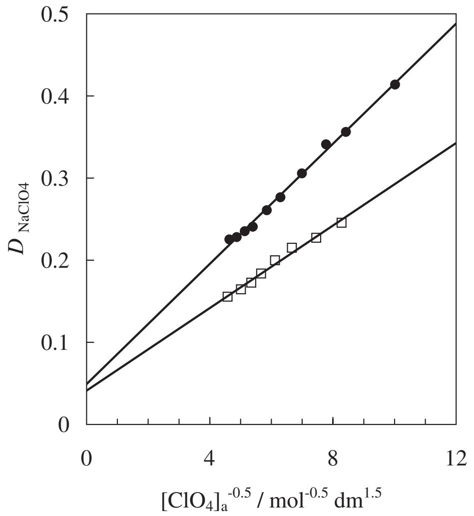


Fig. 3. Plot of distribution ratio of perchlorate, $D_{\mathrm{NaClO_4}}$, against $([\mathrm{ClO_4}^-]_a)^{-1/2}$. The symbols of (□) and (●) represent the values at 0.5 and 1 mol dm^{-3} [NaCl]$_{\mathrm{ini}}$ respectively.

Table 2. Various Equilibrium Constants Determined from Experiments and Analysis

Equilibrium constant	Initial NaCl concentration 0 mol dm^{-3}	 0.5 mol dm^{-3}	 1 mol dm^{-3}
$K_{\mathrm{ex(NaClO_4)}}$/mol dm^{-3}		$(8.8 \pm 1.6) \times 10^{-2}$	$(5.1 \pm 0.7) \times 10^{-2}$
$K_{\mathrm{dis(NaClO_4)}}$/mol^{-1}dm^3		$(1.5 \pm 0.3) \times 10^{-2}$	$(2.8 \pm 0.4) \times 10^{-2}$
$K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}$	$(2.37 \pm 0.05) \times 10^{-3}$	$(1.35 \pm 0.14) \times 10^{-3}$	$(1.44 \pm 0.08) \times 10^{-3}$
$K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$			$(3.1 \pm 1.8) \times 10^{1}$ a) $(4.4 \pm 2.1) \times 10^{1}$ b)
$K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$	9.1 ± 1.9 a)	$(3.0 \pm 0.2) \times 10^{-1}$ a) $(2.9 \pm 0.4) \times 10^{-1}$ b)	$(2.5 \pm 2.2) \times 10^{-1}$ a) $(1.9 \pm 1.2) \times 10^{-1}$ b)

a) Equilibrium constants determined by using Eq. 9. b) Equilibrium constants determined by using Eq. 8.

to the low ionic strength in the aqueous solution, compared with the case of $[\mathrm{NaCl}]_{\mathrm{ini}} = 0.5$ and 1.0 mol dm^{-3}.

Ion-Pair Extraction of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ with Perchlorate Ion. $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was extracted into the propiononitrile phase in the presence of sodium perchlorate. Its extraction behavior varied with the concentration of sodium chloride, as shown in Fig. 4. For $[\mathrm{NaCl}]_{\mathrm{ini}} = 0.5$ and 1 mol dm^{-3}, $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was almost completely extracted into the propiononitrile phase at $[\mathrm{NaClO_4}]_{\mathrm{ini}} = 0.08$ mol dm^{-3}, while for $[\mathrm{NaCl}]_{\mathrm{ini}} = 0$ mol dm^{-3} it was almost completely extracted at $[\mathrm{NaClO_4}]_{\mathrm{ini}} = 5 \times 10^{-4}$ mol dm^{-3} (see the inserted figure in Fig. 4). The extractability of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ with $\mathrm{ClO_4}^-$ decreased with increasing [NaCl]. This is ascribed to the $\mathrm{ClO_4}^-$ concentration in the propiononitrile phase in the presence of NaCl. Considering the dissociation of ion-pairs of the porphyrinatocopper(II) in the propiononitrile phase containing water (2–3 mol dm^{-3}) and the high polarity, the extraction equilibrium is written as follows:

$$(\mathrm{CuP}^{4+})_{\mathrm{a}} + 4(\mathrm{ClO_4}^-)_{\mathrm{a}} \rightleftharpoons ([\mathrm{CuP}\cdot n\mathrm{ClO_4}]^{(4-n)+})_{\mathrm{o}} + (4-n)(\mathrm{ClO_4}^-)_{\mathrm{o}}. \tag{5}$$

The distribution ratio of perchlorate ion into the propiononitrile phase depends on the concentration of NaCl in the aqueous phase (Fig. 2). A high concentration of NaCl in the aqueous phase increases the concentration of $\mathrm{NaClO_4}$ in the propiononitrile phase, resulting in the decreased extraction of $[\mathrm{CuP}\cdot n\mathrm{ClO_4}]^{(4-n)+}$ into the propiononitrile phase. More $[\mathrm{CuP}\cdot n\mathrm{ClO_4}]^{(4-n)+}$ is extracted at high $[\mathrm{ClO_4}^-]_{\mathrm{a}}$ and low $[\mathrm{ClO_4}^-]_{\mathrm{o}}$ (see Eq. 5).

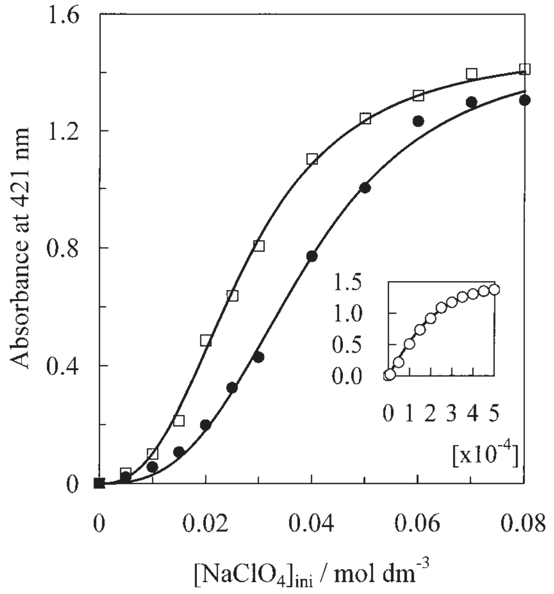
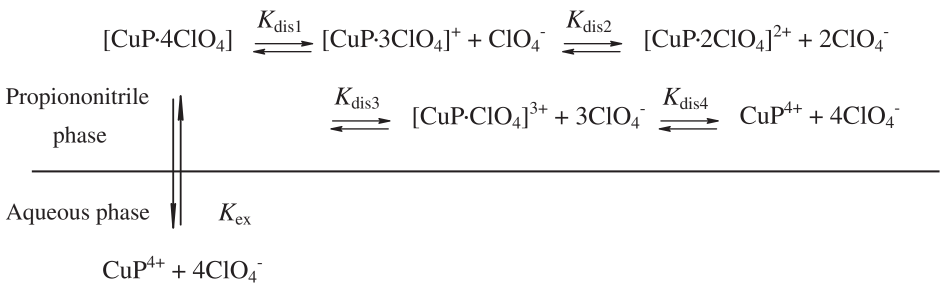


Fig. 4. The observed extraction data of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ and the calculation curve plotted against the initial concentration of perchlorate ion. Solid lines are calculated by using the determined equilibrium constants. The symbols of (○), (□), and (●) are the observed data at 0, 0.5, 1 mol dm^{-3} $[\mathrm{NaCl}]_{\mathrm{ini}}$ respectively.

Ion-Pair Species in Propiononitrile Phase. The extraction of ion-pair complexes of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ is affected by both $\mathrm{NaClO_4}$ and NaCl concentrations in aqueous solution. The chemical species of $[\mathrm{CuP}\cdot n\mathrm{ClO_4}]^{(4-n)+}$ in the propiononitrile phase was analyzed based on the reaction scheme and equation for the extraction and dissociation equilibria as shown in Scheme 1, where $K_{\mathrm{ex}} = [\mathrm{CuP}\cdot 4\mathrm{ClO_4}]_{\mathrm{o}}[\mathrm{CuP}^{4+}]_{\mathrm{a}}^{-1}[\mathrm{ClO_4}^-]_{\mathrm{a}}^{-4}$, $K_{\mathrm{dis}(5-n)} = [\mathrm{CuP}\cdot(n-1)\mathrm{ClO_4}^{(5-n)+}]_{\mathrm{o}}[\mathrm{ClO_4}^-]_{\mathrm{o}}[\mathrm{CuP}\cdot n\mathrm{ClO_4}^{(4-n)+}]_{\mathrm{o}}^{-1}$ ($n = 1$, 2, 3, and 4). The distribution ratio of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ is as follows:



Scheme 1. Extraction mechanism.

$$D_{\mathrm{CuP}} = ([\mathrm{CuP{\cdot}4ClO_4}]_o + [\mathrm{CuP{\cdot}3ClO_4}^+]_o + [\mathrm{CuP{\cdot}2ClO_4}^{2+}]_o + [\mathrm{CuP{\cdot}ClO_4}^{3+}]_o + [\mathrm{CuP}^{4+}]_o)/[\mathrm{CuP}^{4+}]_a. \qquad (6)$$

When $[\mathrm{CuP{\cdot}}n\mathrm{ClO_4}]_o$ in Eq. 6 is substituted with K_{ex} and $K_{\mathrm{dis}(5-n)}$, the following equation is derived

$$D_{\mathrm{CuP}} = [\mathrm{ClO_4}^-]_a{}^4\left(K_{\mathrm{ex}} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}}{[\mathrm{ClO_4}^-]_o} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}}{[\mathrm{ClO_4}^-]_o{}^2} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}}{[\mathrm{ClO_4}^-]_o{}^3} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}K_{\mathrm{dis4}}}{[\mathrm{ClO_4}^-]_o{}^4}\right). \qquad (7)$$

Because the concentration of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was much lower compared with the concentration of sodium perchlorate, we can assume $[\mathrm{Na}^+]_o = [\mathrm{ClO_4}^-]_o$. From Eq. 2, $[\mathrm{ClO_4}^-]_o = \sqrt{K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}[\mathrm{Na}^+]_a[\mathrm{ClO_4}^-]_a}$. $[\mathrm{ClO_4}^-]_o$ is substituted in Eq. 7, and the logarithm value of Eq. 7 is as follows:

$$\log D_{\mathrm{CuP}} = 4\log[\mathrm{ClO_4}^-]_a + \log\left(K_{\mathrm{ex}} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}}{Y[\mathrm{ClO_4}^-]_a{}^{0.5}} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}}{Y^2[\mathrm{ClO_4}^-]_a} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}}{Y^3[\mathrm{ClO_4}^-]_a{}^{1.5}} + \frac{K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}K_{\mathrm{dis4}}}{Y^4[\mathrm{ClO_4}^-]_a{}^2}\right) \qquad (8)$$

where $Y = (K_{\mathrm{ex(NaClO_4)}}K_{\mathrm{dis(NaClO_4)}}[\mathrm{Na}^+]_a)^{0.5}$. The difference in $[\mathrm{Na}^+]_a$ at higher and lower initial concentrations of sodium perchlorate was about 8%. We regarded Y as constant. In Fig. 5, the log values of the distribution ratio of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ are plotted against the log values of the perchlorate ion concentration in the aqueous phase for $[\mathrm{NaCl}]_{\mathrm{ini}} = 0.5$ and 1 mol dm^{-3}. The slopes were found to be 2.53 and 2.79 at $[\mathrm{NaCl}]_{\mathrm{ini}} = 0.5$ and 1.0 mol dm^{-3}, respectively. The results suggest that the main chemical species is $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$ at $[\mathrm{NaCl}]_{\mathrm{ini}} = 0.5$ mol dm^{-3}, and are the mixtures of $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$ and $[\mathrm{CuP{\cdot}2ClO_4}]^{2+}$ at $[\mathrm{NaCl}]_{\mathrm{ini}} = 1.0$ mol dm^{-3}. The reason is as follows: when the main chemical species is $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$, $\log D_{\mathrm{CuP}} = \log K_{\mathrm{ex}} + 2.5\log[\mathrm{ClO_4}]_a + \log(K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}/Y^3)$. Then the slope is 2.5. When main chemical species is $[\mathrm{CuP{\cdot}2ClO_4}]^{2+}$, $\log D_{\mathrm{CuP}} = \log K_{\mathrm{ex}} + 3.0\log[\mathrm{ClO_4}^-]_a + \log(K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}/Y^2)$. Then the slope is 3.0. Thus, the value of the slope, 2.79, indicates the main chemical species are $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$ and $[\mathrm{CuP{\cdot}2ClO_4}]^{2+}$. The difference in the extracted chemical species is ascribed to the concentration of perchlorate ion in the propiononitrile phase. As expected from Scheme 1, a higher concentration of perchlorate ion in the propiononitrile phase leads to the formation of $[\mathrm{CuP{\cdot}}n\mathrm{ClO_4}]^{(4-n)+}$ with a higher number of $\mathrm{ClO_4}^-$ ions.

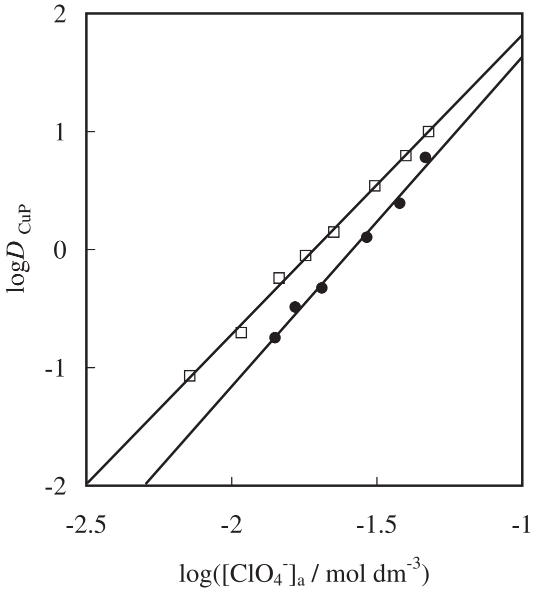


Fig. 5. Plot of log value of distribution ratio of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$, D_{CuP}, against log value of $[\mathrm{ClO_4}^-]_a$. The symbols of (□) and (●) represent the values at 0.5 and 1 mol dm^{-3} $[\mathrm{NaCl}]_{\mathrm{ini}}$ respectively.

Determination of Equilibrium Constant. To express quantitatively the ion-pair extraction of CuP^{4+} with $\mathrm{ClO_4}^-$ from the aqueous phase to the propiononitrile phase and the dissociation in the propiononitrile phase of the extracted ion-pair complex, $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$ and $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$ were determined by the Eq. 9 using a least squares minimization program.

Since the main chemical species of porphyrinatocupper(II) in the propiononitrile phase are $[\mathrm{CuP{\cdot}ClO_4}]^{3+}$ and $[\mathrm{CuP{\cdot}2ClO_4}]^{2+}$ at $[\mathrm{NaCl}]_{\mathrm{ini}} = 1.0$ mol dm^{-3}, $A = \varepsilon_{\mathrm{CuPX}}[\mathrm{CuP{\cdot}X}^{3+}]_o + \varepsilon_{\mathrm{CuP2X}}[\mathrm{CuP{\cdot}2X}^{3+}]_o)$ where A is the absorbance at 421 nm, the peak maximum of porphyrinatocupper(II) in the propiononitrile phase, and $\varepsilon_{\mathrm{CuPX}}$ and $\varepsilon_{\mathrm{CuP2X}}$ are the apparent molar absorptivities of $[\mathrm{CuP{\cdot}ClO_4}]^{2+}$ and $[\mathrm{CuP{\cdot}2ClO_4}]^{3+}$ in the propiononitrile phase respectively. Assuming that $\varepsilon_{\mathrm{CuPX}}$ and $\varepsilon_{\mathrm{CuP2X}}$ are the same, the following equation for determining $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$ and $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$ are obtained taking into account of Eq. 2 and Y;

$$A = \{C_{\mathrm{CuP}}V_{\mathrm{ini}}\varepsilon_{\mathrm{app}}[\mathrm{ClO_4}^-]_a{}^4(K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}Y[\mathrm{ClO_4}^-]_a{}^{0.5} + K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}})\}/\{V_aY^3[\mathrm{ClO_4}^-]_a{}^{1.5} + V_o[\mathrm{ClO_4}^-]_a{}^4 \times (K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}Y[\mathrm{ClO_4}^-]_a{}^{0.5} + K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}})\} \qquad (9)$$

where $\varepsilon_{\mathrm{app}}$ is the apparent molar absorptivity, $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}} = [\mathrm{CuP{\cdot}2ClO_4}^{2+}]_o[\mathrm{ClO_4}^-]_o{}^2[\mathrm{CuP}^{4+}]_a{}^{-1}[\mathrm{ClO_4}^-]_a{}^{-4}$, $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}} = [\mathrm{CuP{\cdot}ClO_4}^{3+}]_o[\mathrm{ClO_4}^-]_o{}^3[\mathrm{CuP}^{4+}]_a{}^{-1}[\mathrm{ClO_4}^-]_a{}^{-4}$, C_{CuP} is the initial concentration of porphyrinatocopper(II) in aqueous solution, and V_a, V_o, and V_{ini} are the volumes of the aqueous phase, propiononitrile phase, and initial aqueous solution (5 cm^3), respectively. The determined equilibrium constants are shown in Table 2.

Similarly, we tried to determine the $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$ and $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$ values at $[\mathrm{NaCl}]_{\mathrm{ini}} = 0$ and 0.5 mol dm^{-3}. But the $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}$ values were not determined correctly due to a large deviation. The determined equilibrium constants are summarized in Table 2 with one determined by using Eq. 8. In Fig. 4, the solid lines are the calculated values using the equilibrium constants. $K_{\mathrm{ex}}K_{\mathrm{dis1}}K_{\mathrm{dis2}}K_{\mathrm{dis3}}$ decreased with increasing $[\mathrm{NaCl}]_{\mathrm{ini}}$ because increasing the ionic strength suppresses the electrostatic attraction between CuP^{4+} and $\mathrm{ClO_4}^-$ in aqueous solution.

Comparisons of Propiononitrile with Acetonitrile and 1,4-Dioxane in Regards to Ion-Pair Extraction. With regards to the water–acetonitrile–NaCl system, the ion-pair extraction of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ with perchlorate ions into the separated organic phase was studied before in our labolatory.[6,9]

Table 3. Comparison of Propiononitrile System with Acetonitrile and 1,4-Dioxane Systems

	Water–organic solvent–NaCl system		
	Propiononitrile	Acetonitrile	1,4-dioxane
$[\mathrm{NaCl}]_{\mathrm{ini}}/\mathrm{mol\,dm^{-3}}$	1	4	4
Water in org. phase/$\mathrm{mol\,dm^{-3}}$[a)]	2.38 ± 0.06	4.53	4.94 ± 0.06
Organic solvent in aq. phase/$\mathrm{mol\,dm^{-3}}$[a)]	1.1 ± 0.1	3.47	3.48 ± 0.12
$D_{\mathrm{NaClO_4}}$	0.511–0.225	1.82 (constant)	0.188 (constant)
(n) number for $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ in org. phase	1–2	2–3	—[b)]

a) Values at 0 $\mathrm{mol\,dm^{-3}}$ $[\mathrm{NaClO_4}]_{\mathrm{ini}}$. b) No extraction of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ into organic phase was observed.

The extraction behavior and mechanism are compared with that obtained in the present water–propiononitrile–NaCl system. The separated organic phases contain a lot of water in both the acetonitrile and propiononitrile systems, and that is an important factor in extracting the highly charged porphyrinatocopper(II). The water concentrations in the propiononitrile and acetonitrile phases were 2.38 and 4.53 $\mathrm{mol\,dm^{-3}}$, respectively. Thus, the acetonitrile seems to be preferable for the charged ionic species of $\mathrm{CuP^{4+}}$ compared with propiononitrile. However, $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was quantitatively extracted into the acetonitrile phase at 0.3 $\mathrm{mol\,dm^{-3}}$ of $\mathrm{NaClO_4}$ compared to 0.08 $\mathrm{mol\,dm^{-3}}$ for propiononitrile. The extracted chemical species of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ were $[\mathrm{CuP}{\cdot}3\mathrm{ClO_4}]^{+}$ and $[\mathrm{CuP}{\cdot}2\mathrm{ClO_4}]^{2+}$ in the acetonitrile phase for acetonitrile and $[\mathrm{CuP}{\cdot}2\mathrm{ClO_4}]^{2+}$ and $[\mathrm{CuP}{\cdot}\mathrm{ClO_4}]^{3+}$ for propiononitrile. This can be explained in terms of the concentration of perchlorate ion in the aqueous and organic phases. The distribution ratio of perchlorate, $D_{\mathrm{NaClO_4}}$, is greater for the acetonitrile system than the propiononitrile system (Table 3). A high concentration of perchlorate ion in the acetonitrile phase suppresses the dissociation of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ in the organic phase more than for propiononitrile, and reduces the extraction of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ into the organic phase. Similarly, a lower concentration of perchlorate ion in the aqueous phase makes the extraction of $[\mathrm{CuP}{\cdot}n\mathrm{ClO_4}]^{(4-n)+}$ into the organic phase less efficient.

1,4-Dioxane is a water-soluble polar solvent, like acetonitrile and propiononitrile, and a 1:1 (v/v) water–1,4-dioxane mixture is separated into aqueous and organic phases by the addition of 4 $\mathrm{mol\,dm^{-3}}$ of sodium chloride. Although the organic phase for a 1,4-dioxane system has a lot of water content, $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$ was not extracted into that phase with $\mathrm{NaClO_4}$. In addition, the $[\mathrm{ClO_4}^-]_\mathrm{o}$ in the 1,4-dioxane phase was low, compared with that in the propiononitrile phase. The dielectric constant of pure 1,4-dioxane is 2.1 at 25 °C.[14] The dielectric constant of the separated 1,4-dioxane phase was calculated to be 5.1 on the basis of the reference data.[14] Thus, this behavior is explained by the low dielectric constant of the organic phase.

In the case of water miscible organic solvents, the organic phase contains a lot of water and the aqueous phase contains a lot of organic solvent. Thus, the polarity of the organic phase is high, and the difference of the polarity between the organic and aqueous phases is small, leading to easier extraction of polar compounds into the organic phase. However, the salting-out reagent, for example NaCl, has to be added to the mixture of water and water miscible organic solvent to separate the two phases. Generally, higher salt concentration in aqueous solution makes the association constants of ion-pairs in aqueous solution decrease. Moreover, our results indicate the distribution ratio of the counter ion (perchlorate ion) was very big due to the high concentration of salting out reagent, leading to a drop in the ion pair extraction of $[\mathrm{Cu^{II}(tmpyp)}]^{4+}$. The same relationship was reported.[15] Propiononitrile was superior to acetonitrile and 1,4-dioxane for the ion-pair extraction of a highly charged organic compound using perchlorate ion because two phase separation occurs without salting out reagents and the organic phase can dissolve a few molar amounts of water. The dielectric constants of solvents with mono- and di-nitrile groups are relatively high ($\varepsilon = 20$ to 60).[14,16] There are, however, few reports of ion-pair extraction using nitriles,[16] and no reports using propiononitrile. The present paper is the first paper on the extraction of ion-pair complexes using propiononitrile.

This work was partly supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (B), No. 15350046.

References

1 Y. Marcus, "Principles and Practives of Solvent Extraction," ed by J. Rydberg, C. Musikas, and G. R. Choppin, Marcel Dekker, Inc., New York (1992), pp. 21–27.

2 F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952); M. Tabata, M. Kumamoto, and J. Nishimoto, *Anal. Sci.*, **10**, 383 (1994).

3 Y. Marcus, "The Properties of Solvents," John Willey & Sons, Chichester (1998).

4 M. Tabata and M. Tanaka, *Trends Anal. Chem.*, **10**, 128 (1991).

5 H. Ishii, K. Satoh, and H. Koh, *Bunseki Kagaku*, **29**, 276 (1980).

6 M. Tabata, M. Kumamoto, and J. Nishimoto, *Anal. Chem.*, **68**, 758 (1996).

7 M. Tabata and M. Tanaka, *J. Chem. Soc., Dalton Trans.*, **1983**, 1955; M. Tabata and M. Babasaki, *Inorg. Chem.*, **31**, 5268 (1992); M. Tabata, *J. Mol. Liq.*, **65/66**, 221 (1995); M. Inamo, A. Tomita, Y. Inagaki, N. Asano, K. Suenaga, M. Tabata, and S. Funahashi, *Inorg. Chim. Acta*, **256**, 77 (1997).

8 T. Kawai, R. Fujiyoshi, S. Sawamura, and S. Tachimori, *Solv. Extr. Res. Dev. Jpn.*, **6**, 80 (1999); T. Kawai, R. Fujiyoshi, and S. Sawamura, *Solv. Extr. Res. Dev. Jpn.*, **7**, 36 (2000).

9 M. Kumamoto, J. Nishimoto, T. Takamuku, and M. Tabata, *Pure Appl. Chem.*, **70**, 1925 (1998).

10 R. F. Pasternack, E. J. Gibbs, and J. J. Villafranca, *Biochemistry*, **22**, 2406 (1983).

11 I. Iwasaki, S. Utsumi, and C. Kang, *Bull. Chem. Soc. Jpn.*, **36**, 325 (1963).

12 The Japan Society for Analytical Chemistry, "Bunseki Kagaku Binran," 3rd ed, Maruzen (1981), p. 192.

13 T. Takamuku, A. Yamaguchi, D. Matsuo, M. Tabata, M. Kumamoto, J. Nishimoto, K. Yoshida, T. Yamaguchi, M. Nagano, T. Otomo, and T. Adachi, *J. Phys. Chem.*, **105**, 6236 (2001).

14 The Chemical Society of Japan, "Kagaku Binran Kisohen II," 3rd ed, Maruzen (1984), p. 504.

15 Y. Yamamoto, E. Sumimura, K. Miyoshi, and T. Tominaga, *Anal. Chim. Acta*, **64**, 255 (1973); T. Iwachido, *Bull. Chem. Soc. Jpn.*, **45**, 1746 (1972).

16 J. D. Lamb, A. Y. Nazarenka, and R. J. Hansen, *Sep. Sci. Tech.*, **34**, 2583 (1999).