

## Ion-pair extraction of metalloporphyrins into a mixture of acetonitrile with water

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**Abstract:** Extraction mechanism and solvent structure were studied for the solvent extraction of cationic porphyrin (5,10,15,20-tetrakis(1-methyl-pyridinium-4-yl) porphyrin;  $H_2(tmpyp)^{4+}$ ) and its metalloporphyrins ( $MP^{(n+2)+}$ ) into an acetonitrile phase separated from a 1:1 (v/v) mixture of acetonitrile with water by addition of sodium chloride.  $M^{n+}$  denotes  $Cu^{2+}$ ,  $Co^{3+}$ ,  $Fe^{3+}$ ,  $Li^+$ ,  $Mn^{3+}$ , and  $Zn^{2+}$  and  $H_2P^{4+}$  is the free base form of  $H_2tmpyp^{4+}$ . The separated acetonitrile phase contains a lot of water (more than 4 mol  $dm^{-3}$ ) and sodium chloride ( $1 \times 10^{-2}$  mol  $dm^{-3}$ ) that are necessary to extract the highly charged chemical species of the above porphyrin or metalloporphyrins which can not be extracted into normal organic solvents such as chloroform. The extracted chemical species dissociate in the acetonitrile phase and exist in ionized forms.

X-ray diffraction analysis indicates the formation of clusters of acetonitrile in the mixed-aqueous organic solvent. An acetonitrile molecule interacts with 2 neighbors at 3.45 Å in antiparallel and 4.10 Å in parallel through dipole-dipole interaction. Water molecules that form hydrogen bonding between water molecules surround the acetonitrile clusters. The porphyrin or metalloporphyrins are preferentially solvated by acetonitrile molecules and are surrounded by acetonitrile clusters.

### INTRODUCTION

When inorganic salts are added to a mixture of a water-miscible organic solvent and water, phase-separation occurs due to decreased solubility of the organic solvent in the aqueous solution. The separated organic solvent contains water and salts and shows high polarity compared with the corresponding pure organic solvent (ref. 1). The salting-out technique has been used for the extraction of metal chelates, ion-pair complexes, organic compounds, prior to atomic absorption spectrophotometry (ref. 2), high performance liquid chromatography (ref. 3,4) and polarography (ref. 5) and absorption spectrophotometry (ref. 6). One of the advantages of using salting-out techniques is to be able to extract highly charged analytes which are not extracted into conventional organic solvents such as chloroform (ref. 7). We found that cationic water-soluble porphyrin (5,10,15,20-tetrakis(1-methyl-pyridinium-4-yl) porphyrin;  $H_2(tmpyp)^{4+}$ ) (Fig. 1) and its metalloporphyrins ( $MP^{(n+2)+}$ ) are extracted into an acetonitrile phase separated from a 1:1 (v/v) mixture of acetonitrile with water by addition of sodium chloride in the presence of perchlorate. The complexes were not extracted into chloroform and 1,2-dichloroethane.  $M^{n+}$  denotes  $Cu^{2+}$ ,  $Co^{3+}$ ,  $Fe^{3+}$ ,  $Li^+$ ,  $Mn^{3+}$  and  $Zn^{2+}$ , and  $H_2P^{4+}$  is the free base form of porphyrin,  $H_2tmpyp^{4+}$ .

Several studies were conducted to better understand the role of salts and solvents in the salting-out technique. Most of the theories concerned with the salting-out effect have used salting-out coefficients (Setschenow constant) defined as  $k_0 = 1/m(\log S_0/S)$ , where  $S_0$  and  $S$  are the solubilities of the organic

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solvent in water and in an electrolyte solution of molality,  $m$ , respectively (ref. 8-10). However, microscopic chemical properties such as  $E_T(30)$  and solvent structures of the solvents separated by salting-out have not been studied.

In this paper we describe the mechanism of extraction of ion-pair complexes of metalloporphyrins into acetonitrile layers separated by salting-out and have developed a new and useful method for the determination of metal ions. Furthermore, the  $E_T(30)$  and  $D_{II,I}$  (ref. 11,12) values and the solvent-structure determined by X-ray diffraction are reported here for the acetonitrile layers in order to better understand the salting-out phenomenon.

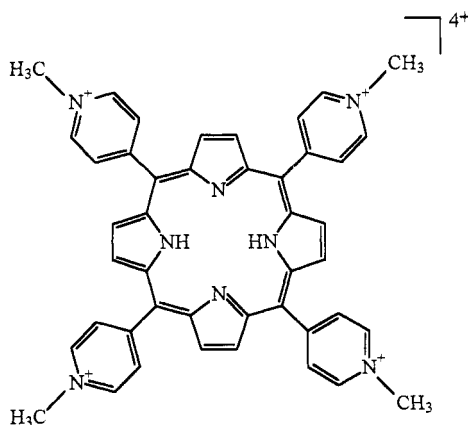


Fig.1 H<sub>2</sub>(tmpyp)<sup>4+</sup>

## EXPERIMENTAL

### Procedure

**Solvent Extraction.** Into a stoppered graduated tube, a 5-cm<sup>3</sup> volume of aqueous sample solution was taken, then sodium chloride was added to the solution. When the salt had dissolved a 5-cm<sup>3</sup> volume of organic solvent was added to the aqueous solution. The mixed solvent was shaken for about 1 min. The two phases were allowed to stand for a few minutes. The volumes of the organic and the aqueous phases were measured, and the concentrations of chloride in separate organic layers were determined by argentometry. The concentration of water was determined by Karl Fisher titration on a Karl Fisher Moisture Titrator (MKL-200, Kyoto Electronics, Japan). Absorption spectra of porphyrins were measured by a Shimadzu UV-vis spectrophotometer Z-2100. The concentration of sodium was determined by a PERKIN ELMER atomic absorption spectrophotometer (A ANALYST 100). A 1.00 x 10<sup>-2</sup> mol dm<sup>-3</sup> perchloric acid aqueous solution containing the same concentration of sodium chloride as found in the aqueous phase after salting-out, was used as a standard for the hydrogen ion concentration (-log[H<sup>+</sup>] = 2.000).

**X-ray diffraction.** All X-ray diffraction measurements were made at room temperature (25 °C) on a rapid X-ray diffractometer combined with an imaging plate (IP) detector (MAC Science Co. Ltd. DIP301). Detail of the diffractometer and its performance have previously been described

(ref. 13,14). X-rays were generated at a rotary Mo anode operated at 50 kV and 200 mA and then monochromized by a graphite crystal to obtain Mo  $K\alpha$  radiation ( $\lambda = 0.7107$ ). Sample solutions were sealed in a glass capillary of 1 mm inner diameter and measured in transmission geometry. The observed range of the scattering angle ( $2\theta$ ) was  $0.2^\circ$  to  $109^\circ$ , corresponding to the scattering vector ( $s = 4\pi\lambda^{-1} \sin \theta$ ) of 0.03 to  $14.4 \text{ \AA}^{-1}$ . The exposure time to X-rays was 3 h per sample solution. All X-ray diffraction data were analyzed by the programs KURVLR (ref. 15) and NIPLSQ.

TABLE 1. Data of phase-separation by salting-out using sodium chloride

	acetonitrile phase	aqueous phase
Volume/cm <sup>3</sup>	4.17	6.11
NaCl/mol dm <sup>-3</sup>	$2.49 \times 10^{-2}$	3.37
H <sub>2</sub> O/mol dm <sup>-3</sup>	4.53	—
CH <sub>3</sub> CN/mol dm <sup>-3</sup>	—	3.47
$E_T(30)/\text{kJ mol}^{-1}$	228	—
$D_{II,I}/\text{kJ mol}^{-1}$	48.0	60.6

## RESULTS AND DISCUSSION

### $E_T(30)$ and $D_{II,I}$ values of solvents

One would expect that water and sodium chloride dissolved in the acetonitrile phase would profoundly alter the chemical properties of the solvent. The values of  $E_T(30)$  and  $D_{II,I}$  were determined to know the donor and acceptor properties of the solvents. Figs. 2 and 3 show the  $E_T(30)$  and  $D_{II,I}$  values measured in pure solvents, phase-separated organic solvents and the mixed aqueous-organic solvents. All these data suggest that the donor and acceptor properties of the phase-separated solvents increased after salting-out compared to the mixed solvents before salting-out. A large change in the chemical properties of solvents by salting-out was observed for acetonitrile, 1,4-dioxane, tetrahydrofuran and 2-propanol. The main factor for the change in  $E_T(30)$  value is the increased concentration of water in the phase-separated solvent: acceptability of the phase-separated solvents increases by incorporation of water that has a high acceptor number (AN = 54.8). Typical data are summarized in Table 1 for acetonitrile. The  $E_T(30)$  and  $D_{II,I}$  values of the acetonitrile phase are larger than those of nitrobenzene (ref. 11) and indicate the high donor and acceptor abilities due to a large amount of water dissolved in the solvent. This is a unique characteristic of the solvents separated by salting-out compared with other organic solvents. The high polarity is an advantage for the extraction of ionic compounds which are not extracted into conventional organic solvents such as chloroform.

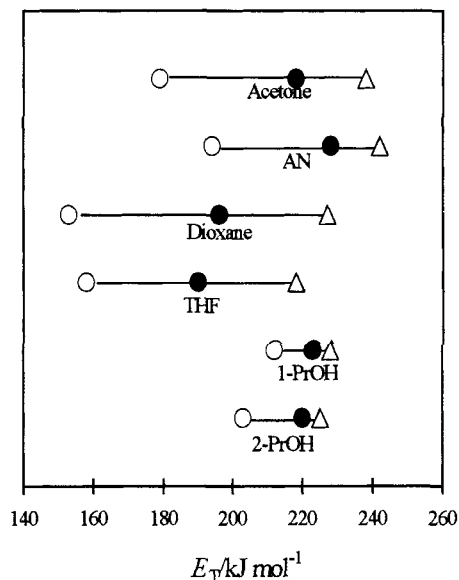


Fig.2  $E_T$  values of water-miscible pure solvents (O), organic phase after the salting-out (●), and 1:1 mixed aqueous solutions (Δ).  $E_T = 1.196 \times 10^5/\lambda$  /kJ mol<sup>-1</sup>

### Effect of salting-out agents

The phase separation depends on the salting-out agents. The effect of salting-out decreases in the following order:

$\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} \gg \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Li}^+$ , and  $\text{SO}_4^{2-} > \text{Cl}^-$ . The main driving force of the salting-out is hydration of these cations and anions. The hydration energies ( $\text{kJ mol}^{-1}$ ) of these ions are 4612 ( $\text{Al}^{3+}$ ), 2198 ( $\text{Mg}^{2+}$ ), 1592 ( $\text{Ca}^{2+}$ ), 1317 ( $\text{Ba}^{2+}$ ), 501.8 ( $\text{Na}^+$ ), 424.5 ( $\text{K}^+$ ), 2198 ( $\text{Li}^+$ ) (ref. 16). With the exception of lithium ion, the salting-out is correlated with the hydration energies of the ions. The small salting-out effect of lithium ion may be due to the large solubility of lithium chloride in acetonitrile.

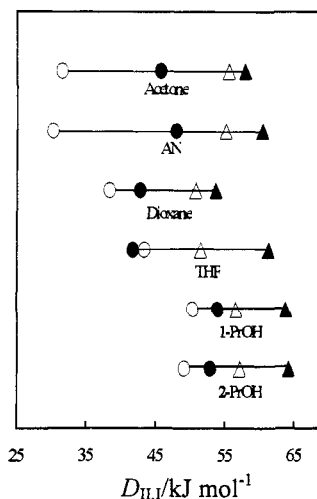


Fig. 3  $D_{\text{III}}$  values of water-miscible pure solvents (O), organic phase after the salting out (●), and 1:1 mixed-aqueous solutions (Δ) and aqueous phase (▲).  $D_{\text{III}} = (1.196 \times 10^5 / \lambda) / \text{kJ mol}^{-1}$

### Extraction of $\text{H}_2(\text{tmpyp})^{4+}$ , $[\text{M}(\text{tmpyp})]^{n+2}$ , ( $\text{M}^{n+} = \text{Cu}^{2+}$ , $\text{Co}^{3+}$ , $\text{Mn}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Zn}^{2+}$ )

The above free-base porphyrin and metalloporphyrins were readily extracted into the acetonitrile phase separated by salting-out by addition of sodium perchlorate. Typical extraction data are given as a function of concentration of perchlorate ions in the aqueous phase in Fig. 4.  $\text{H}_2(\text{tmpyp})^{4+}$ ,  $[\text{Cu}(\text{tmpyp})]^{4+}$ ,  $[\text{Co}(\text{tmpyp})\text{Cl}]^{4+}$ ,  $[\text{Mn}(\text{tmpyp})\text{Cl}]^{4+}$ ,  $[\text{Fe}(\text{tmpyp})\text{Cl}]^{4+}$  and  $[\text{Zn}(\text{tmpyp})]^{4+}$ .  $\text{H}_2(\text{tmpyp})^{4+}$ ,  $[\text{Cu}(\text{tmpyp})]^{4+}$  and  $[\text{Zn}(\text{tmpyp})]^{4+}$  were quantitatively extracted into acetonitrile at  $0.08 \text{ mol dm}^{-3}$  sodium perchlorate, and  $[\text{Co}^{\text{III}}(\text{tmpyp})\text{Cl}]^{4+}$ ,  $[\text{Fe}^{\text{III}}(\text{tmpyp})\text{Cl}]^{4+}$  and  $[\text{Mn}^{\text{III}}(\text{tmpyp})\text{Cl}]^{4+}$  were extracted at perchlorate concentrations  $> 0.3 \text{ mol dm}^{-3}$ . The metalloporphyrins of cobalt(III), iron(III) and manganese(III) have an octahedral structure with water molecules in the axial position.

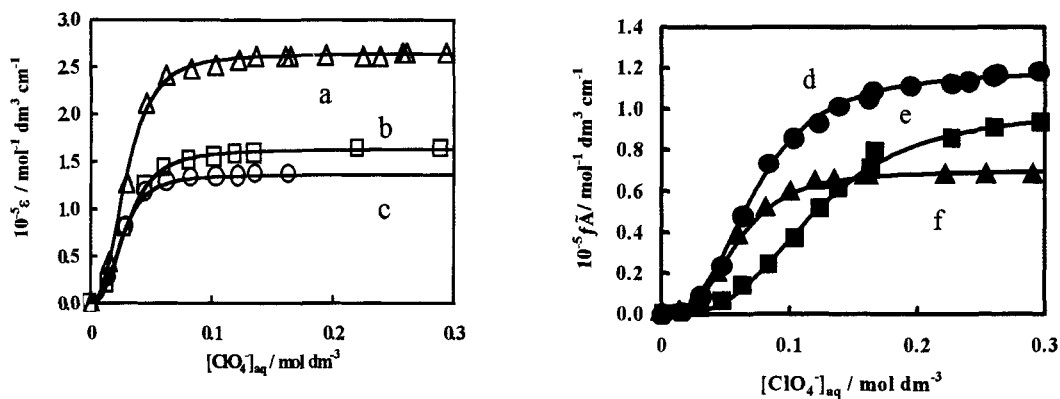
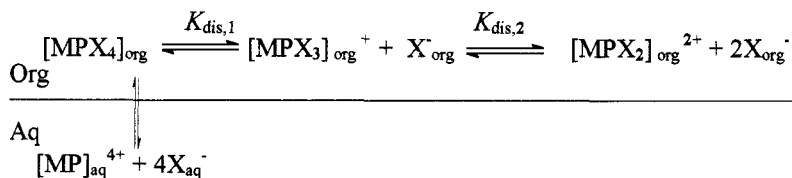


Fig. 4 Extraction into the acetonitrile phase of (a)  $\text{H}_2(\text{tmpyp})^{4+}$ , (b)  $[\text{Zn}(\text{tmpyp})]^{4+}$ , (c)  $[\text{Cu}(\text{tmpyp})]^{4+}$ , (d)  $[\text{Co}(\text{tmpyp})\text{Cl}]^{4+}$ , (e)  $[\text{Mn}(\text{tmpyp})\text{Cl}]^{4+}$ , (f)  $[\text{Fe}(\text{tmpyp})\text{Cl}]^{4+}$ .

Thus metalloporphyrins of the trivalent metal ions were not readily extracted into acetonitrile-phase. In contrast,  $[\text{Cu}(\text{tmpyp})]^{4+}$  is planar with no bound water molecule. The plot of the log value of absorbance ratio of the organic phase to the aqueous phase against the concentration of perchlorate ion in the aqueous phase gives a straight line for these metalloporphyrins: the slopes of the straight lines are  $2.75 \pm 0.07$ ,  $2.56 \pm 0.15$ ,  $2.59 \pm 0.06$ ,  $3.01 \pm 0.06$ ,  $2.82 \pm 0.05$  and  $3.01 \pm 0.04$  for  $[\text{Cu}(\text{tmpyp})]^{4+}$ ,  $\text{H}_2(\text{tmpyp})^{4+}$ ,  $[\text{Zn}(\text{tmpyp})]^{4+}$ ,  $[\text{Fe}(\text{tmpyp})\text{Cl}]^{4+}$ ,  $[\text{Co}(\text{tmpyp})\text{Cl}]^{4+}$ ,  $[\text{Mn}(\text{tmpyp})\text{Cl}]^{4+}$ , respectively. Smaller slopes than 3 indicate the binding of two or three perchlorate ions to the porphyrins in the acetonitrile phase. Thus, the partition of the free base porphyrin or the metalloporphyrins ( $\text{MP}^{4+}$ ) between aqueous and acetonitrile phases in the presence of perchlorate ion ( $\text{X}^-$ ) is expressed by the following scheme:



where  $\text{X}^-$  denotes perchlorate ion and  $K_{\text{ex}} = \frac{[\text{MPX}_4]_{\text{org}}[\text{MP}^+]_{\text{aq}}^{-1}[\text{X}^-]_{\text{aq}}^{-4}}{[\text{MPX}_3^+]_{\text{org}}[\text{X}^-]_{\text{org}} \times [\text{MPX}_4]_{\text{org}}^{-1}}$  and  $K_{\text{dis},2} = \frac{[\text{MPX}_2^{2+}]_{\text{org}}[\text{X}^-]_{\text{org}}[\text{MPX}_3^+]_{\text{org}}^{-1}}{[\text{MPX}_4]_{\text{org}}}$ . The apparent molar absorptivity ( $\epsilon$ ) of the porphyrins in the organic phase is correlated to the above  $K_{\text{ex}}$ ,  $K_{\text{dis},1}$  and  $K_{\text{dis},2}$  as follows:

$$\epsilon = \frac{\text{Abs}_{\text{org}}}{C_{\text{MP}}} = \frac{\epsilon_1 K_{\text{ex}} K_{\text{dis},1} K_{\text{D}} [\text{X}^-]_{\text{aq}}^3 + \epsilon_2 K_{\text{ex}} K_{\text{dis},1} K_{\text{dis},2} [\text{X}^-]^2}{K_{\text{D}}^2 (V_{\text{aq}} V_{\text{org}}^{-1}) + K_{\text{ex}} K_{\text{dis},1} K_{\text{D}} [\text{X}^-]_{\text{aq}}^3 + \epsilon_2 K_{\text{ex}} K_{\text{dis},1} K_{\text{dis},2} [\text{X}^-]^2}$$

The values of  $K_{\text{ex}}$ ,  $K_{\text{dis},1}$  and  $K_{\text{dis},2}$  were determined using a least square minimization program, assuming  $\epsilon_1 = \epsilon_2$ . Since the extracted chemical species  $[\text{MPX}_4]$  completely dissociates to  $[\text{MPX}_3]^+$ , the  $K_{\text{dis},1}$  value could not be determined. The extraction and dissociation constants determined are summarized in Table 2.

**Determination of Copper(II) by Extraction in Acetonitrile.**

*Calibration Curve*  $[\text{Cu}(\text{tmpyp})]^{4+}$  is completely extracted into the acetonitrile phase after salting-out at a wide pH range (1-12). However,  $\text{H}_2(\text{tmpyp})^{4+}$  is not extracted into the acetonitrile-phase at  $\text{pH} < 2$ . The results imply an extraction of only  $[\text{Cu}(\text{tmpyp})]^{4+}$  in an excess of  $\text{H}_2(\text{tmpyp})^{4+}$  at pH 1-2 and hence that copper(II) could be determined without any overlapping of absorbance of unreacted  $\text{H}_2(\text{tmpyp})^{4+}$ .

	$K_{\text{ex}} K_{\text{dis},1} / (\text{mol}^{-3} \text{dm}^9)$	$K_{\text{dis},2} / (\text{mol} \text{dm}^{-3})$
$\text{H}_2(\text{tmpyp})^{4+}$	$(7.2 \pm 1.3) \times 10^4$	$(2.9 \pm 1.4) \times 10^{-2}$
$[\text{Zn}(\text{tmpyp})]^{4+}$	$(6.4 \pm 0.9) \times 10^4$	$(3.1 \pm 1.1) \times 10^{-2}$
$[\text{Cu}(\text{tmpyp})]^{4+}$	$(1.35 \pm 0.13) \times 10^5$	$(8.0 \pm 4.9) \times 10^{-3}$
$[\text{Co}(\text{tmpyp})\text{Cl}]^{4+}$	$(4.8 \pm 0.6) \times 10^3$	$(5.1 \pm 2.2) \times 10^{-2}$
$[\text{Fe}(\text{tmpyp})\text{Cl}]^{4+}$	$(1.23 \pm 0.05) \times 10^4$	—
$[\text{Mn}(\text{tmpyp})\text{Cl}]^{4+}$	$(1.42 \pm 0.07) \times 10^3$	—

The calibration graph was linear for copper concentration of  $1.0 \times 10^{-8} - 5.0 \times 10^{-6} \text{ mol dm}^{-3}$ , with a high

correlation factor ( $r = 0.998$ ). The blank absorbance was 0.008 at 421 nm, and molar absorptivity  $\epsilon = 3.1 \times 10^5 \text{ mol dm}^{-3} \text{ cm}^{-1}$ . A sample solution containing  $5.00 \times 10^{-7} \text{ mol dm}^{-3}$  copper was determined with a precision of 1.3 % (RSD). The high sensitivity and the low blank absorbance were developed into a method for determination of subnanogram amount of copper(II) by the solvent extraction of  $[\text{Cu}(\text{tmpyp})]^{4+}$ .

**Effect of Foreign Ions** Acetonitrile can extract Zn(II), Mn(II), Fe(III) and Co(II) as their metalloporphyrins of  $\text{H}_2(\text{tmpyp})^{4+}$ . But,  $[\text{Zn}(\text{tmpyp})]^{4+}$  completely dissociates to Zn(II) and  $\text{H}_4\text{tmpyp}^{6+}$  at pH 2, and Mn(II), Fe(III) and Co(II) react with  $\text{H}_2(\text{tmpyp})^{4+}$  at very slow rate. Thus, these metal ions do not interfere with the determination of copper(II). Other metal ions and anions usually encountered in natural water did not interfere with determination of Cu(II). The method was applied to determine copper(II) in hot-spring waters.

### X-ray Diffraction of the mixed solvents of water and acetonitrile

In order to know why the mixture of acetonitrile with water can extract such highly charged ion-pair complexes we carried out an X-ray diffraction and an IR studies at different molar ratio of acetonitrile:  $X_{\text{AN}} = 0.2, 0.25, 0.4, 0.6, 0.8$  and 1.0. The corresponding radial distribution functions (RDFs) in the form of  $D(r) - 4\pi r^2 \rho_0$  are shown in Fig. 5. The predominant peaks are observed around 1.2, 2.6, and 3~5 Å in the RDF for pure acetonitrile ( $X_{\text{AN}} = 1.0$ ). The first two peaks are mainly assigned to intramolecular interactions of acetonitrile and nonbonding interaction within an acetonitrile molecule. The third broad peak at 3~5 Å corresponds to the interactions between nearest neighbor acetonitrile molecules. The broad peak at 3~5 Å in the RDF was explained well only when both antiparallel and parallel dipole-dipole orientations are assumed for the first-neighbor and the second-neighbor molecules, respectively, as proposed by Kratochwill *et al.* (ref. 17). It has also been found that the dipole centers of the first-neighbor molecules are shifted by 1.47 Å from a central molecule. A small broad peak observed at distances  $r \geq 6.5$  Å suggests that there is no significant long-range structure in pure acetonitrile due to the dipole-dipole interaction. Thus, the 6.5-Å peak was not analyzed in the present analysis; instead, an even electron distribution was assumed for the long-range interaction beyond 6 Å. Fig. 6 (a) shows the most likely structure for pure acetonitrile proposed from the present X-ray diffraction data. As shown in a side view of Fig. 6(a), acetonitrile molecules are alternately aligned to form a zigzag cluster. The distances between the first-neighbor molecules is 3.45 Å ( $\text{C}_1 \cdots \text{N}'$  and  $\text{N} \cdots \text{C}_1'$ ), and the dipole centers are shifted by 1.47 Å for the  $\text{C}_1\text{-C}_2$  bond length. The number of the first-neighbor acetonitrile molecules is 2.0 (1). The distance and number of the second-neighbor molecules in parallel are 4.10 (3) Å and 2.0 (1), respectively. It is likely that such arrangements are repeated to form a zigzag cluster consisting of 4-6 acetonitrile molecules.

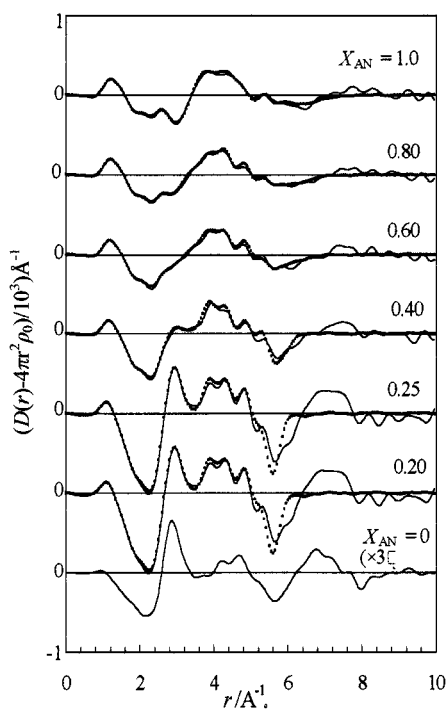


Fig. 5 X-ray diffraction curves of mixtures of acetonitrile and water

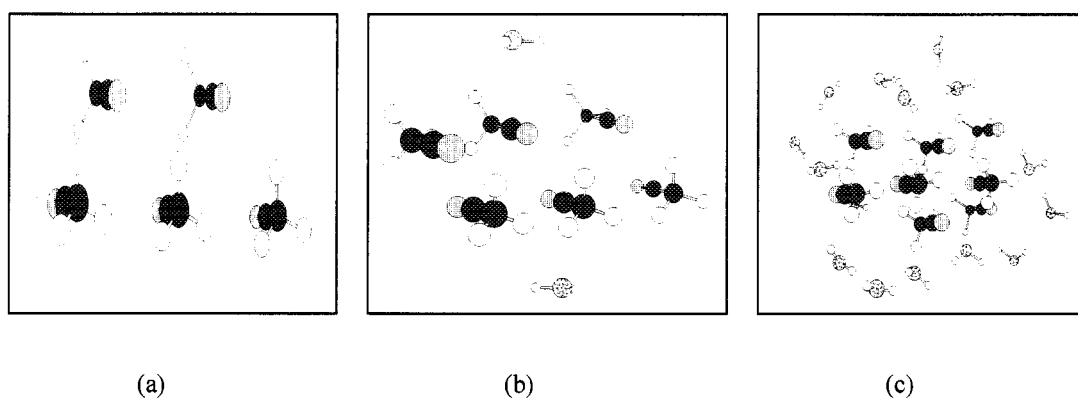


Fig. 6. Proposed structures of the mixtures of acetonitrile with water at (a)  $X_{AN} = 1.0$ , (b)  $0.6 \leq X_{AN} \leq 0.8$ , (c)  $0.2 \leq X_{AN} < 0.6$ .

*Structure of Acetonitrile-Water Mixtures.* As seen in Fig. 5, the RDFs at  $X_{AN} = 0.6$  and  $0.8$  do not drastically change by addition of water to pure acetonitrile, except that a trough around  $3.0 \text{ \AA}$  in the RDF at  $X_{AN} = 1.0$  gradually disappear with decreasing acetonitrile concentration. The enhancement of the RDF at  $3.0 \text{ \AA}$  indicates that a new interaction grows in the mixtures with increasing water content. This peak probably arises from the interactions between acetonitrile and water molecules due to antiparallel dipole-dipole interaction on the basis of their large dipole moments and van der Waals radii. From a consideration that an oxygen atom of water molecule is placed by  $3.00 \text{ \AA}$  ( $C_1 \cdots O$ ) above  $C_1$  atom of an acetonitrile molecule, the  $C_2 \cdots O$  and  $N \cdots O$  distances are estimated to be  $3.34$  and  $3.21 \text{ \AA}$ , respectively. This model well explained the interactions around  $3.0\text{--}3.4 \text{ \AA}$  in the RDFs of the mixtures at  $X_{AN} = 0.6$  and  $0.8$ . Further addition of water to the mixtures brings about a new peak at  $2.85 \text{ \AA}$  in the RDFs at  $X_{AN} \leq 0.4$ . The new peak arises mainly from formation of hydrogen bonds among water molecules in the mixtures. Many authors have suggested  $N \cdots H-O$  hydrogen bonds between acetonitrile and water molecules (ref. 18,19). However, the present RDFs could not give strong evidence for formation of such a hydrogen bond because  $N \cdots H-O$  bonds are not distinguishable from  $O \cdots H-O$  hydrogen bonds between water molecules owing to similar X-ray scattering power of N and O atoms and comparable bond lengths. The model is characterized by linear  $CN \cdots HO$  hydrogen bonds with  $N \cdots O$ ,  $C_1 \cdots O$ , and  $C_2 \cdots O$  distances of  $2.80$ ,  $3.95$ , and  $5.42 \text{ \AA}$ , respectively.

The X-ray diffraction measurements for the acetonitrile-water mixtures suggested that the zigzag clusters as shown in pure acetonitrile remain even in the mixtures at low water contents. In the mixtures water molecules interact with acetonitrile molecules on the surface of cluster through antiparallel dipole-dipole interaction. However, X-ray diffraction measurements could not clarify the formation of acetonitrile-water hydrogen bond. When further acetonitrile is added to water, acetonitrile molecules tend to gather to form three-dimensional clusters rather than random distribution. Moreover, water molecules form hydrogen-bonded networks in the mixtures at  $X_{AN} \leq 0.4$ . Thus, both acetonitrile and water clusters coexist in the acetonitrile-water mixtures in the range of  $0.2 \leq X_{AN} < 0.6$ .

## CONCLUSION

The present study shows how mixtures of acetonitrile and water are useful for solvent extraction method, especially for highly charged ion-pair complexes. The extracted chemical species dissociate into ions in the mixed solvent. Both acetonitrile and water clusters coexist, thus, microheterogeneity occurs in the mixtures by dipole-dipole interaction between acetonitrile molecules. The unique characteristics of the solvent is ascribed to (1) increased high polarity of the solvent by involvement of water and salts in addition to high dielectric constant of acetonitrile and (2) the formation of acetonitrile clusters in which hydrophobic ion-pair complexes can dissolve. The method was applied to the determination of copper(II) in hot-spring waters.

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