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Synthesis of Aminophosphonic Acid Extractants and the Effect of the Alkyl Chain on Their Extraction Selectivities for Indium(III), Gallium(III), and Zinc(II)

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New extractants with different alkyl chains, α-(octylamino)-4-*tert*-butylbenzylphosphonic acid monobutyl ester (OATPM), α-(2-ethylhexyl-amino)-4-*tert*-butylbenzylphosphonic acid monobutyl ester (EATPM), and α-1-(dodecylamino)octyl-phosphonic acid monobutyl ester (DAOPM) were synthesized by the Mannich reaction. The extraction selectivities of α-dodecylaminobenzylphosphonic acid monobutyl ester (DABPM), EATPM, OATPM and DAOPM were examined using In(III), Ga(III), Cu(II) and Zn(II) from a 1 M aqueous NH_4NO_3 solution. The extraction order for these metals using DABPM, EATPM, and OATPM was In(III) > Ga(III) > Zn(II) > Cu(II), whereas the order for DAOPM was In(III) > Ga(III) > Cu(II) > Zn(II). The separation ability of DABPM and OATPM is higher than that of EATPM and DAOPM. These extractants were analyzed by ^{1}H-NMR. As a result, DABPM and OATPM were found to form intramolecular hydrogen bonds between P=O···H–N and P-OH···N-C. These hydrogen bonds allow to exist in the monomer form of DABPM and OATPM in toluene, which lead to the lower extraction ability for Zn(II).

1. Introduction

Solvent extraction is one of the most important separation techniques for metal ions, and a large number of studies on extractants with high selectivity for metal ions have been reported. The affinity between the ligand and the metal ion is important to ensure selectivity for the metal ions, and it is also necessary to design new extractants by considering metal ion size, valency, coordination number, and HSAB theory [1]. However, many cases cannot be explained by the direct interaction between the metal ion and the ligand.

Crown ethers [2] and calixarene [3], with cyclic structures, are effective for metal ions which adapt to the size of the ring. However, molecular recognition is not only carried out by cyclic compounds, *pseudo*-macrocyclic structures, formed by intermolecular interactions with the cyclic structure, show high selectivity for specific metal ions. For example, salicylaldoxime derivatives form a dimeric structure, which is selective for Cu(II) owing to the planar geometry and metal ion size [4]. Forgan *et. al*., synthesized 5-tert-butyl-3-X-salicylaldoximes (X = H, Me, *t*Bu, NO_2, Cl, Br, OMe) and investigated their extraction ability for Cu(II), which was influenced by the rigidity of the second coordination sphere of the complex with different substituents through the hydrogen bond [5]. In addition, Warr *et. al*. reported that the extraction ability of $PtCl_6^{2-}$ using tripodal ionophores incorporating multiple hydrogen bond donors linked to a protonatable bridgehead nitrogen center was increased by the hydrogen bond between Pt–Cl···H–N [6]. Organophosphorus acid and carboxylic acid extractants formed dimers in low dielectric constant solvents, and the dimer influenced the extraction ability of metal ions. Thus, the selectivity profile of metal ions not only relies on the direct interaction between the metal ion and the ligand, but also on the second coordination sphere which forms between the metal ion and the extractant through hydrogen bonding.

In recent years, In(III) and Ga(III) have attracted attention in relation to copper-indium-gallium-selenide (CIGS) solar cells. Separation of these metals was reported using industrial extractants such as di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A). However, the recovery of these elements from electric wastes is difficult, in particular, the separation of In(III) and Ga(III) from Zn(II). In our previous studies, aminophosphonic acid extractants with different basicities of the amine moiety were prepared, and exhibited high selectivity for In(III), Ga(III) and Zn(II) [7,8]. Furthermore, it was found that the high basicity of the amine moieties in the extractants played an important role in the high selectivity for these metals. In addition, DABPM(pK_a = 2.48 [8]) showed a lower extraction ability for Zn(II) compared with PC-88A(pK_a = 4.51 [9]), regardless of its low acid dissociation constant [8]. It is considered that this specific behavior is due to the intra- or intermolecular interactions of DABPM.

In this study, aminophosphonic acid extractants (Figure 1) with different alkyl chains were synthesized to elucidate the effect of the alkyl chain length on their extraction selectivity to In(III), Ga(III), Cu(II) and Zn(II), and the metal complexes were analyzed by FT-IR and ^{1}H-NMR.

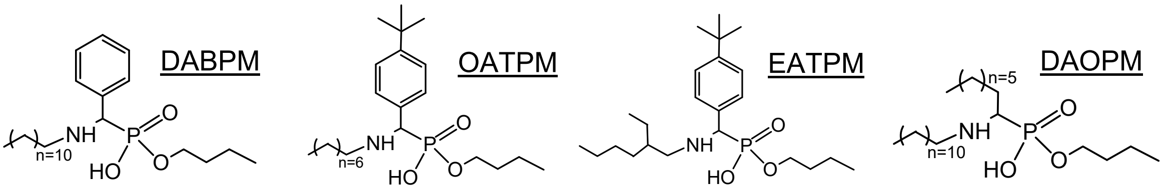

Figure 1. Chemical structure of DABPM, OATPM, EATPM and DAOPM.

2. Experimental

2.1 Materials and analysis

Metal nitrates of analytical grade (Wako Pure Chemical Industries Ltd, Tokyo, Japan.) were used to prepare test solutions of the metal ions. Dodecylamine (>97.0%), *n*-octanal (>98.0%), 4-*tert*-butylbenzaldehyde (>95.0%) and triethylamine (>99.0%) were obtained from Tokyo Chemical Industry Co., Ltd. Benzaldehyde (>98.0%), 2-ethylhexylamine (>98.0%), octylamine (>98.0%), potassium hydroxide (>85.0%) and 1-octanol (>97.0%) were obtained from Wako Pure Chemical Industries Ltd, Tokyo, Japan. Dibutyl phosphite (>96.0%) was obtained from Sigma Aldrich Co. Anhydrous iron(III) chloride (>98.0%) was obtained from Alfa Aesar Co. α-Dodecylaminobenzylphosphonic acid monobutyl ester (DABPM) was obtained during our previous study [8]. All other reagents and solvents were of analytical grade and used without further purification.

2.2 Synthesis of α- (2-ethylhexylamino)-4-*tert*-butylbenzylphosphonic acid monobutyl ester (EATPM)

EATPM was synthesized by the Mannich reaction using 2-ethylhexylamine (15.51 g, 0.12 mol), dibutyl phosphite (19.42 g, 0.10 mol) and 4-*tert*-butylbenzaldehyde (16.22 g, 0.10 mol) in 50 mL ethanol in the presence of anhydrous iron(III) chloride (1.95 g, 0.012 mol) as a catalyst at room temperature (r.t.) for 24 h, followed by reaction at 60°C for 24 h. The ethanol was evaporated and the product was dissolved in chloroform. The chloroform solution was washed with aqueous sodium chloride solution to remove the iron(III) chloride, and dried over anhydrous sodium sulfate. After filtration, the chloroform was evaporated *in vacuo*, and the residue was purified by column chromatography with silica gel. The intermediate (23.4 g, 0.05 mol) and potassium hydroxide (22.4 g, 0.4 mol) were dissolved in 500 mL of an ethanol/water (9:1) mixture, and the mixture was heated at 60°C for 48 h (Figure 2). The mixture was neutralized with concentrated hydrochloric acid, and the ethanol was evaporated *in vacuo*. After the crude product was dissolved in chloroform, it was washed repeatedly with hydrochloric acid and distilled water and then dried over anhydrous sodium sulfate. After filtration, the chloroform was evaporated *in vacuo* and a yellow powder was obtained. The yellow powder product was recrystallized with ethyl acetate at least three times and a white powder was obtained. The resulting product was identified by ^{1}H-NMR, FT-IR (JASCO, Co., FT-IR 4200, Tokyo, Japan) and ESI-MS (Thermo Fisher, Q Exactive, MA, USA). ^{1}H-NMR (400 MHz) spectra of the extractants in $CDCl_3$ were recorded with an NMR spectrophotometer model AV400 M (Bruker Co., Rheinstetten, Germany). The following properties of EATPM were identified: ^{1}H-NMR (400 MHz, $CDCl_3$, *r.t.*): δ= 10.7 (br, 1H, PO*H*), 7.68 (d, 2H, H_{Ar}), 7.36 (d, 2H, H_{Ar}), 4.23 (dd, 1H, NHC*H*), 3.42 (m, 2H, $POCH_2$), 2.70 (m, 2H, $NHCH_2$), 1.79 (m, 1H, NCH_2CH_1), 1.32 (s, 9H, $C(CH_3)_3$), 1.22–1.00 (m, 14H, CH_2), 0.79-0.59 (m, 9H, CH_3); FT-IR (liquid cell): ν(P=O) 1244 cm^{-1}; ESI-MS : m/z calcd for $C_{23}H_{42}NO_3P$=411.29, [M+H$^+$]; found: 412.29.

2.3 Synthesis of α-(octylamino)-4-*tert*-butylbenzylphosphonic acid monobutyl ester (OATPM)

OATPM was synthesized by the Mannich reaction using octylamine (15.51 g, 0.12 mol), dibutyl phosphite (19.42 g, 0.10 mol) and 4-*tert*-butylbenzaldehyde (16.22 g, 0.10 mol) in 50 mL ethanol in the presence of iron(III) chloride anhydride (1.95 g, 0.012 mol) as a catalyst at r.t. for 24 h, followed by reaction at 60°C for 24 h. The post-treatment was performed in a similar manner as that for EATPM. The intermediate (23.4 g, 0.05 mol) and potassium hydroxide (22.4 g, 0.4 mol) were dissolved in 500 mL of an ethanol/water (9:1) mixture, and then it was reacted at 60°C for 48 h (Figure 2). Post-treatment was again performed in a similar manner as that for EATPM. ^{1}H-NMR (400 MHz, $CDCl_3$, *r.t.*): δ= 10.7 (br, 1H, PO*H*), 7.69 (br, 2H, H_{Ar}), 7.37 (br, 2H, H_{Ar}), 4.23 (br, 1H, NHC*H*), 3.55 (br, 2H, $POCH_2$), 2.62 (br, 2H, $NHCH_2$), 1.91 (br, 2H, $POCH_2CH_2$), 1.34 (s, 9H, $C(CH_3)_3$), 1.11 (m, 14H, CH_2), 0.77 (t, 6H, CH_3); FT-IR (liquid cell): ν(P=O) 1242 cm^{-1}; ESI-MS : m/z calcd for $C_{23}H_{42}NO_3P$=411.29, [M+H$^+$]; found: 412.29

2.4 Synthesis of α-1-(dodecylamino)octylphosphonic acid monobutyl ester (DAOPM)

Dodecylamine (24.10 g, 0.13 mol) and *n*-octanal (16.67 g, 0.13 mol) were dissolved in toluene (500 mL), and the mixture was reacted at 130°C for 2 h using a Dean-Stark trap. The toluene was then evaporated *in vacuo*, and the product (35.47 g, 0.12 mol) was added to a mixture of dibutyl phosphite (23.31 g, 0.12 mol) and triethylamine (12.15 g, 0.12 mol) dissolved in ethanol (50 mL), and then the mixture was reacted at 80°C for 24 h. The post-treatment was performed in a similar manner as that for EATPM. The intermediate (22.04 g, 0.045 mol) and potassium hydroxide (22.4 g, 0.4 mol) were dissolved in an ethanol/water (9:1) mixture (500 mL), and then the mixture was reacted at 60°C for 48 h (Figure 2). Post-treatment was performed in a similar manner as that for EATPM, and recrystallization was carried out using acetone containing a small amount of ethanol. ^{1}H-NMR (400 MHz, $CDCl_3$, *r.t.*): δ= 10.2 (br, 1H, PO*H*), 3.92–3.78 (m, 2H, POC*H*$_2$), 2.94 (br, 1H, NHC*H*), 2.62 (br, 2H, NHC*H*$_2$), 1.85 (br, 4H, PCH_2CH_2, NHC*H*$_2$), 1.58 (m, 2H, $POCH_2CH_2$), 1.40–1.24 (m, 30H, C*H*$_2$), 0.90 (t, 9H, C*H*$_3$); FT-IR (liquid cell): ν(P=O) 1227 cm^{-1}; ESI-MS : m/z calcd for $C_{24}H_{52}NO_3P$=433.37 [M+H$^+$]; found: 434.37

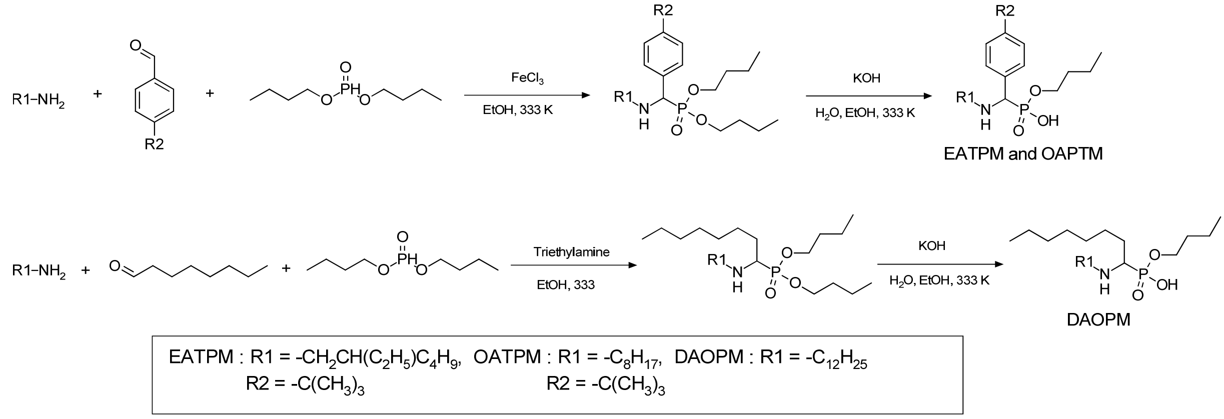

Figure 2. Synthetic schemes for OATPM, EATPM and DAOPM.

2.5 Extraction tests for metal ions with DABPM, EATPM, OATPM and DAOPM

All extraction tests for metal ions were performed in an aqueous solution containing a single metal ion. To evaluate the extractability of DABPM, OATPM, EATPM and DAOPM, liquid-liquid extraction was carried out using a 1.0 M aqueous ammonium nitrate solution containing 1 mM metal ions as the aqueous phase. The pH was adjusted using 1 M HNO_3 or NH_4OH. Toluene or 50 vol% 1-octanol/toluene solution was used as the organic phase diluent containing 50 mM DABPM, OATPM, EATPM or DAOPM. Equal volumes (2.0 mL) of the aqueous and organic phases were mechanically shaken in a 20 mL sample tube, for 24 h at 303 K. After phase separation, the pH of the aqueous solutions was measured using a pH meter (HM-30S, DKK-TOA Co., Tokyo, Japan), and was determined by acid-base titration at pH values below 0.5. The metal concentration in the aqueous solution was determined using a flame atomic absorption spectrophotometer model Z-2310 (Hitachi Co., Tokyo, Japan) with an air-acetylene flame. The metal ion concentration in the organic phase was calculated from the mass balance between the aqueous and organic phases. Extraction percentages (*E%*) and metal distribution ratios (*D*) were calculated according to Equations (1) and (2), respectively.

$$E\% = \frac{[\mathrm{M}]_{org,eq}}{[\mathrm{M}]_{aq,init}} \times 100 = \frac{[\mathrm{M}]_{aq,init} - [\mathrm{M}]_{aq,eq}}{[\mathrm{M}]_{aq,init}} \times 100 \tag{1}$$

$$D = \frac{[\mathrm{M}]_{org,eq}}{[\mathrm{M}]_{aq,eq}} = \frac{[\mathrm{M}]_{aq,init} - [\mathrm{M}]_{aq,eq}}{[\mathrm{M}]_{aq,eq}} \tag{2}$$

where $[\mathrm{M}]_{aq,init}$ represents the initial concentration of the metal ion in the aqueous phase, and $[\mathrm{M}]_{aq,eq}$ and $[\mathrm{M}]_{org,eq}$ are the total concentrations of the metal ion in the aqueous and organic phases, respectively, at equilibrium.

2.6 FT-IR analysis for metal-loaded organic phases

Liquid-liquid extraction was carried out using 1.0 M aqueous ammonium nitrate solutions containing 0 – 25 mM metal ions as the aqueous phase. Carbon tetrachloride or a 50 vol% 1-octanol/carbon tetrachloride solution was used as the diluent of the organic phase containing 100 mM DABPM, OATPM, EATPM or DAOPM. In a 20 mL sample tube, volumes of the aqueous (3 or 4 mL) and organic (1 mL) phases were shaken mechanically for 24 h at 303 K. Metal concentration and pH were determined by the same method as experiment **2.5**. The organic phase was measured by FT-IR spectroscopy using a liquid cell (25 μm). $[HR]_{org}/[M]_{org,eq}$ was defined as a guide for the quantity of loaded metal ion in the organic phase. $[HR]_{org}$ was the concentration of the extractant in the organic phase.

2.7 ^{1}H-NMR analysis for extractants

Deuterochloroform was used as the diluent of the organic phase containing 1–100 mM DABPM, OATPM, EATPM or DAOPM. The aqueous solutions less than pH 1 were prepared by changing the ratio of the solution mixture of 1.0 M NH_4NO_3 and 1.0 M HNO_3. In a 20 mL sample tube, volumes of the aqueous (5 mL) and organic (1 mL) phases were shaken mechanically for 24 h at 303 K. After phase separation, the organic phase was measured by ^{1}H-NMR.

3. Results and Discussion

3.1 Extraction selectivity for metal ions with DABPM, EATPM, OATPM and DAOPM

Figure 3 shows the effect of the equilibrium pH on the percentage extraction of metal ions from 1 M aqueous ammonium nitrate solution with DABPM, EATPM, OATPM and DAOPM. DABPM and OATPM

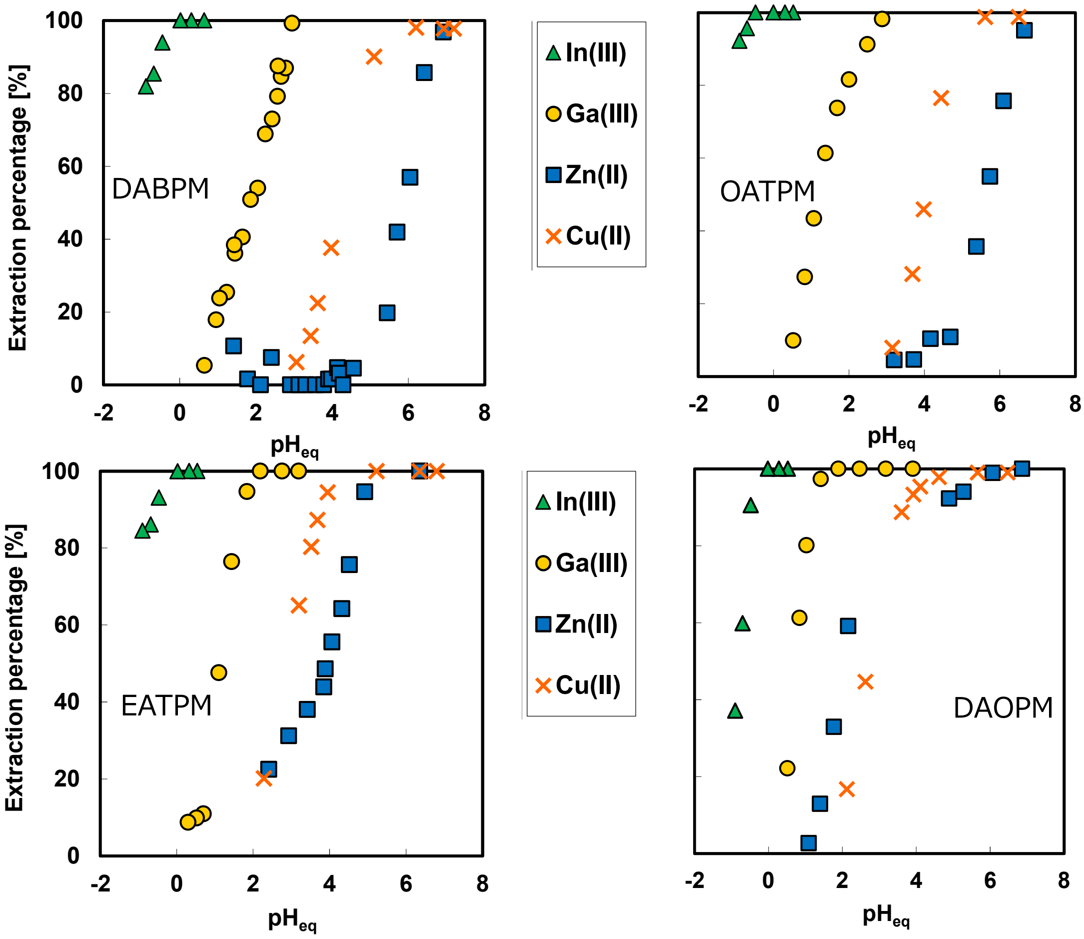

Figure 3. Effect of pH on the extraction percentage of metal ions from aqueous ammonium nitrate solution with DABPM, OATPM, EATPM and DAOPM using toluene as the diluent.

exhibited almost the same extraction behavior for metal ions, indicating that the presence of a *tert*-butyl moiety on the extractant did not affect the extraction behavior of the metal ions. Zn(II) was extracted at lower pH with EATPM and DAOPM, compared with DABPM and OATPM. This indicates that a phenyl moiety and a branched alkyl chain affected the extraction ability of Zn(II). However, EATPM contains a branched alkyl chain which increases the steric hindrance to the amine moiety. In addition, DAOPM does not contain the phenyl moiety like the other extractants. Therefore, the difference in the extraction behavior for Zn(II) cannot be explained only by steric hindrance of the different alkyl chains. The extraction order with DAOPM was Zn(II) > Cu(II), similar to that with phosphorus acid extractants such as PC-88A and D2EHPA [10]. In addition, the extraction behavior of In(III), Ga(III) and Zn(II) with DAOPM showed the same trends as for the aminophosphonic acid (BEAMP) [11] and the aminophosphinic acid (DEAPP) [7]. Therefore, it was found that the extraction behavior for these metal ions with DABPM, OATPM and EATPM are different from those with PC-88A, DEAPP and BEAMP. Comparing the extraction behavior of metal ions with each extractant, it was observed that the extraction of Zn(II) changed significantly. In order to examine the extraction of Zn(II) in more detail, the effect of the diluent on the extraction behavior of Zn(II) was also investigated. Figure 4 shows the effect of the equilibrium pH on the extraction percentage of Zn(II) from a 1 M aqueous ammonium nitrate solution with DABPM, EATPM, OATPM and DAOPM using toluene or 50 vol% 1-octanol/toluene as the diluent. Using toluene as the diluent, the extraction order of Zn(II) was DAOPM > EATPM > DABPM = OAPTM. Using 50 vol% 1-octanol/toluene as the diluent, the extraction order of Zn(II) was almost the same for all the extractants. The results for DABPM and OATPM showed that the extraction for Zn(II) in 50 vol% 1-octanol/toluene was slightly shifted to higher pH values compared with toluene while the results for DAOPM and EATPM were significantly shifted to higher pH values. This suggests that the metal-extractant complexes were distributed less in the organic phase with the increasing dielectric constant of the diluents. The extraction of metal ions with D2EHPA and PC-88A using protic solvents such as alcohols have already been reported [12–14]. For example, Cu(II)

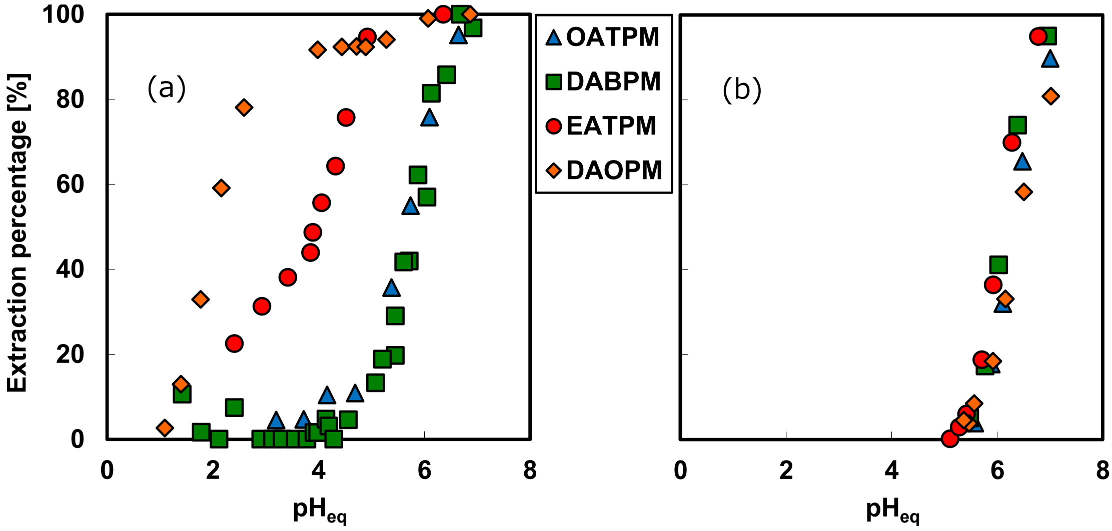

Figure 4. Effect of pH on the extraction percentage of Zn(II) from aqueous ammonium nitrate solution with DABPM, OATPM, EATPM and DAOPM using toluene (a) or 50 vol% 1-octanol/toluene (b) as the diluent.

was extracted into an organic phase as CuL_2 owing to the low degree of dimerization of D2EHPA in octanol, so its extraction ability the for Cu(II) was increased [12]. In addition, the extraction ability for Ni(II) with PC-88A was enhanced by stabilization of the associated water with alcohols in the metal complex [13]. In contrast, the extraction ability for Ga(III) was decreased with an decrease in the dimer activity [14]. As mentioned above, the extraction ability of metal ions using alcohol as a diluent was sometimes increased, and sometimes decreased. This cannot be fully explained, as this behavior is dependent on the type of metal ion (coordination number, geometry). Therefore, in this study, a decrease in the extraction ability for Zn(II) is thought to be due to a decrease in dimer activity.

To elucidate how the amino moieties participate in the formation of metal-extractant complexes, the metal-loaded organic phases were analyzed using an FT-IR spectrometer.

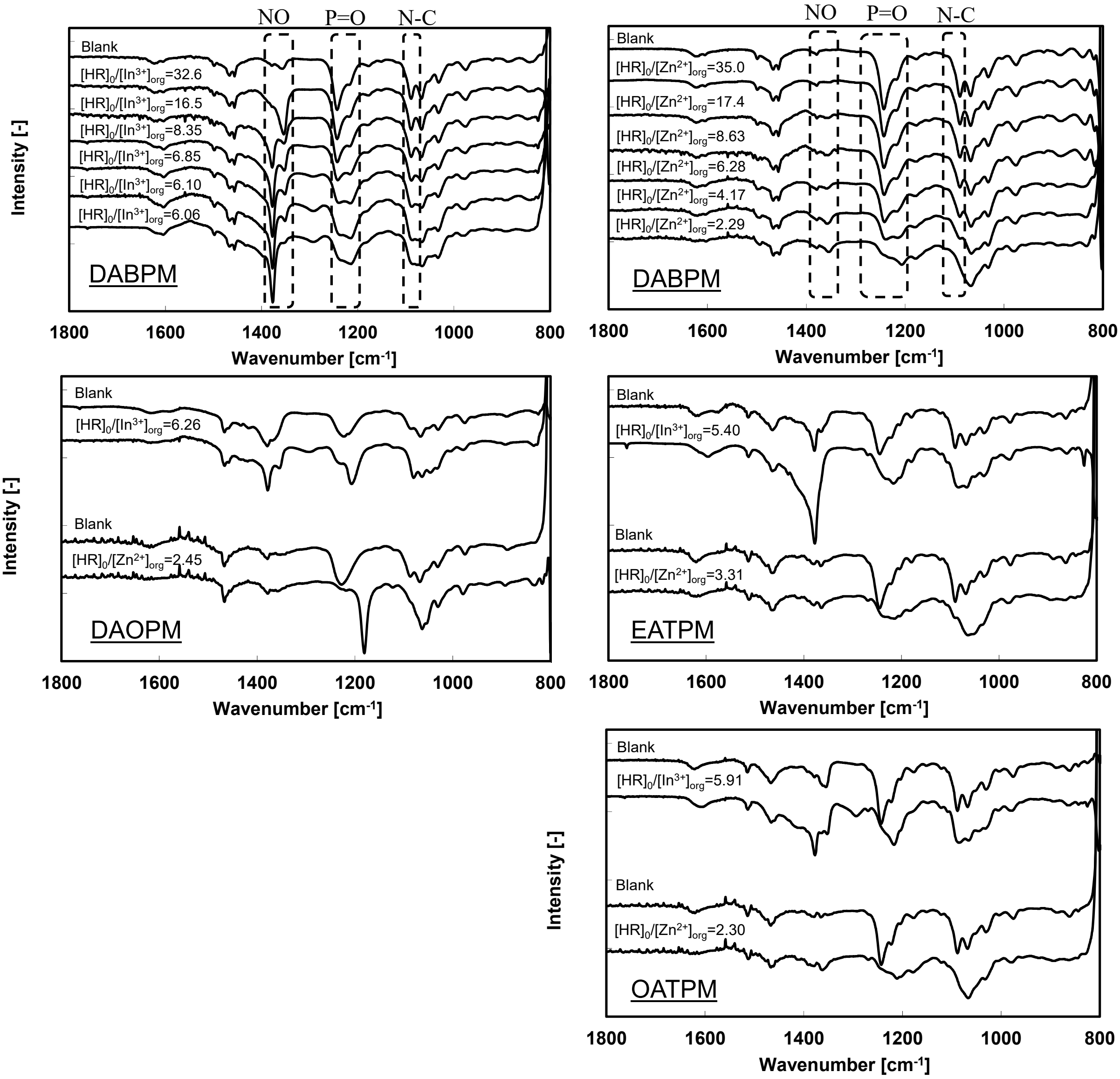

Figure 5. FT-IR spectra of DABPM, OATPM, EATPM and DAOPM at increasing concentrations of In(III) and Zn(II) using carbon tetrachloride as the diluent.

3.2 FT-IR analysis of the metal-loaded organic phase

Figure 5 shows the effect of the amount of loaded metal ion using carbon tetrachloride on the FT-IR spectra. All samples of Ga(III) were precipitated, so measurements for Ga(III) were not carried out. The P=O [15–17] and C–N [18] groups in each extractant were observed at around 1240 and 1090 cm^{-1}, respectively. The P=O peak intensity in DABPM was decreased with an increase in the amount of In(III) loaded in the organic phase. The electrons of the ligand were withdrawn from the metal ions when ligands coordinated to metal ions, and the covalent bounding ability of the ligands decreases. As a result, the peak intensity of P=O decreased. It was therefore inferred that the P=O in DABPM was coordinated to In(III). In addition, a new NO_3^- peak was observed at 1355 cm^{-1}, which shifted to 1377 cm^{-1} with an increase in the In(III) loading in the organic phase. This change indicated that the outer sphere molecule of nitric acid is weakly hydrogen bonded to the inner-sphere molecule of nitric acid. A similar effect was reported in the extraction of nitric acid with tri-*n*-butyl phosphate [19]. Decreased intensity, shifting, or appearance of the peak in the FT-IR spectra on extraction of Zn(II) with DABPM were observed at P=O, C–N and NO_3^-, respectively, and so it was inferred that these ligands participated in the formation of the DABPM-Zn(II) complex. A decrease and shift of peaks was also observed with other extractants, and the results are presented in Table 1.

Table 1 Participation of the ligand in the extraction of metal ions with each extractant.

	DABPM		OATPM		EATPM		DAOPM	
ligand	In(III)	Zn(II)	In(III)	Zn(II)	In(III)	Zn(II)	In(III)	Zn(II)
P=O	○	○	○	○	○	○	○	○
N-C	×	○	×	○	×	○	×	○
NO_3^-	○	○	○	○	○	×	○	×

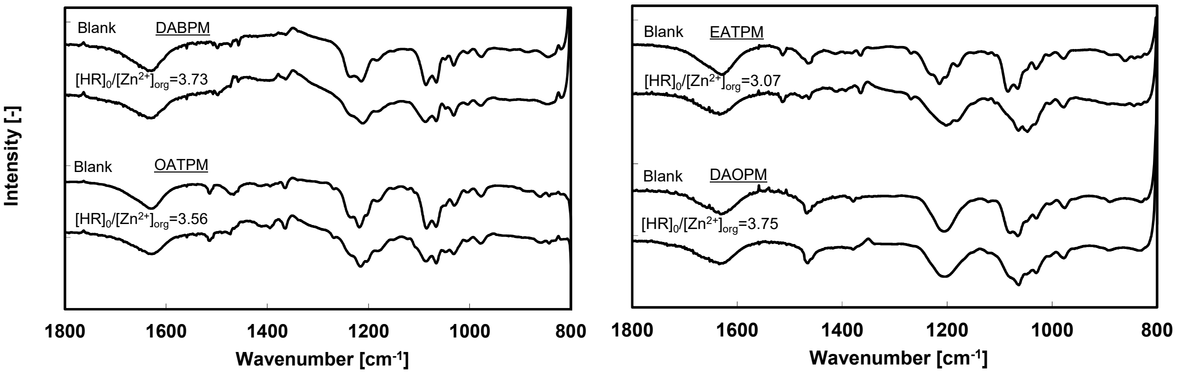

Figure 6. FT-IR spectra of DABPM, OATPM, EATPM and DAOPM with increasing concentration of In(III) and Zn(II), using 50 vol% 1-octanol/carbon tetrachloride as the diluent.

Figure 6 shows the effect of the amount of loaded In(III) or Zn(II) using 50 vol% 1-octanol/carbon tetrachloride on the FT-IR spectra. The interaction of the ligand with the In(III) or Zn(II)-extractant complex only involved P–OH, because the peak shift was not observed at P=O and C-N when using 1-octanol/carbon tetrachloride as the diluent. This result correlated with Figure 4(b), and it can be explained that the extraction behavior of Zn(II) with each extractant was almost the same when using 1-octanol/carbon tetrachloride. Despite the fact that the extraction behavior of Zn(II) using toluene was significantly different with each extractant, it was found that the participating ligand in the Zn(II) extraction using carbon tetrachloride was the same. It is not thought that the significant change of extraction behavior for Zn(II) with each extractant is due to the slight changes of amine basicity and phosphonic acid acidity in each extractant. Consequently, this cannot explain the differences in the extraction behavior for Zn(II) with the ligands participating in the metal-extraction complex.

3.3 ^{1}H-NMR analysis of the extractants

Figure 7 shows the effect of extractant concentration on the ^{1}H-NMR spectra of the extractants. The N–H proton peaks of DABPM, OAPTM and DAOPM were observed at low magnetic fields. In general, the aliphatic amine was observed at high magnetic fields, and the peak was shifted to lower magnetic fields when the N–H proton formed a hydrogen bond. Therefore, it is thought that DABPM, OATPM and DAOPM form an N–H･･･O=P hydrogen bond. The N–H and P–OH peaks in DABPM and OATPM were not shifted by decreasing the extractant concentration, suggesting the formation of an intramolecular hydrogen bond. Therefore, DABPM and OATPM have two intramolecular hydrogen bonds namely N‐H···O=P and P‐OH···N-C. On the other hand, the P–OH peak was shifted to a higher magnetic field with decreasing extractant concentration, suggesting an intermolecular hydrogen bond. However, the N–H peak was not shifted. DAOPM formed an intramolecular hydrogen bond, however it has been suggested that DAOPM also forms a dimer in the same way as PC-88A and D2EHPA. This indicates that the intermolecular steric hindrance in DAOPM is less than that in DABPM and OATPM, because DAOPM does not contain a phenyl group, unlike DABPM and OATPM. Only the P–OH peak was observed for

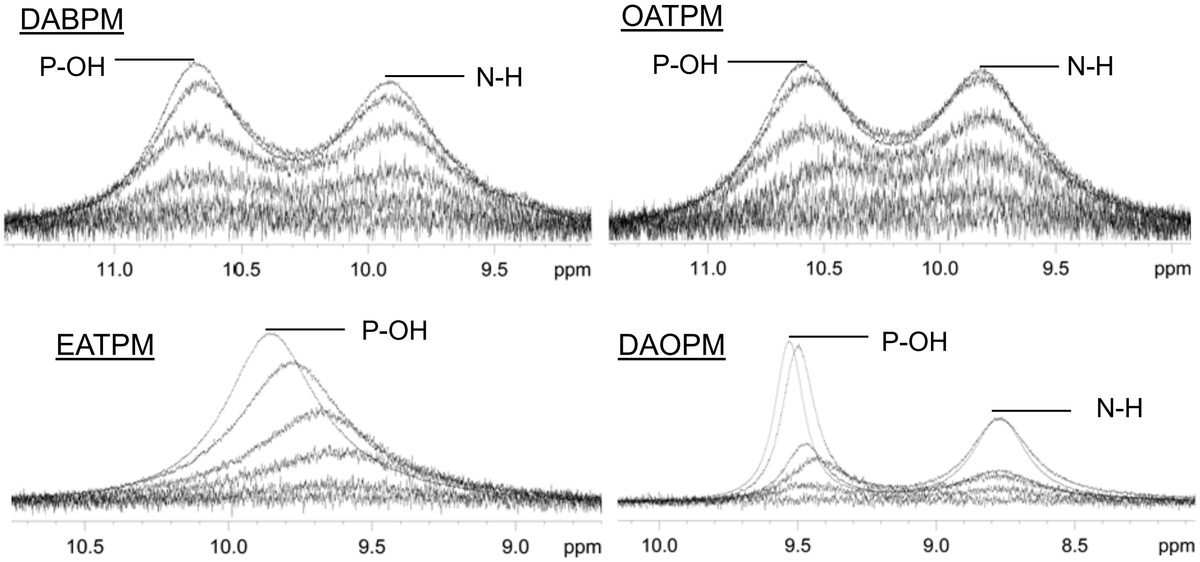

Figure 7. Effect of extractant concentration on the ^{1}H-NMR spectra. [HR] = 1, 5, 10, 25, 50, 100 mM.

EATPM, indicating that the hydrogen bond from the N–H was blocked by the branched alkyl chain. Therefore, EATPM formed a dimer in the same way as PC-88A, as the P–OH peak was shifted to higher magnetic fields with decreasing extract concentration.

The FT-IR and ^{1}H-NMR results established that the P=O and C–N groups of each extractant participated in the extraction of Zn(II). DABPM and OATPM exist as monomers, and EATPM and DAOPM form dimers. The extraction order of Zn(II) and Cu(II) with D2EHPA and PC-88A was Zn(II)>Cu(II), which does not follow the Irving-Williams order [20]. The order of D2EHPA and PC-88A is due to dimer formation, involving 8-membered rings with bond angles (O-M-O) of the dimer-metal complex greater than 90°, where the angle is adapted to a tetrahedral metal ion, such as Zn(II) [10]. This coordination geometry produces an increased extraction ability for Zn(II) compared with Cu(II). According to Figure 4, the monomers DABPM and OATPM showed a low extraction ability for Zn(II), whereas the dimers DAOPM and EATPM showed a high extraction ability. This behavior agrees with the data above, and demonstrates that it is important for the extraction ability of Zn(II) whether the extractant forms dimer or not. On the contrary, In(III) and Ga(III) form octahedral complexes, which leads to a slight shift of extraction pH for these metals compared with Zn(II).

4. Conclusions

EATPM, OATPM and DAOPM, with different alkyl chains, were synthesized by the Mannich reaction. The separation ability for In(III), Ga(III) and Zn(II) with DABPM and OATPM is higher than that of EATPM and DAOPM. This selectivity showed that straight alky chain and phenyl moieties play an important role in the mutual separation of these metals. When using 50 vol% 1-octanol/toluene as the diluent, Zn(II) was extracted at the same pH with all extractants. It is considered that these selectivities are determined by the structures (monomer or dimer) of the extractants in an organic solution. The ^{1}H-NMR results showed that DABPM and OATPM exist as monomers, and EATPM and DAOPM form dimers through intra- or inter-molecular hydrogen bonding caused by different alkyl chains. Therefore, DABPM and OATPM, as monomers, showed low extraction ability for Zn(II), leading to high separation ability for In(III), Ga(III) and Zn(II).

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