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Mutual separation of indium(III), gallium(III) and zinc(II) with alkylated aminophosphonic acids with different basicities of amine moiety

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ABSTRACT

New aminophosphonic acid extractants, α-(4-*n*-octylanilino)benzylphosphonic acid monobutyl ester (OABPM) and α-dodecylaminobenzylphosphonic acid monobutyl ester (DABPM) with different amino moiety basicities were synthesized to examine the effect of the basicity on their extraction selectivities for In(III), Ga(III), Zn(II), Cu(II), Se(IV) and Se(VI). The extraction order for metals using OABPM was In(III) > Ga(III) > Cu(II) > Zn(II), while Se(IV) and Se(VI) were not extracted. On the other hand, DABPM exhibited the reverse extraction order for Cu(II) and Zn(II). The mutual separation ability of DABPM for these metals was higher than that of OABPM as is determined by the basicity of the amino moiety of their extractants. The extraction equilibria for Ga(III) and Zn(II) with OABPM and DABPM were discussed using slope analysis. It was observed that only Ga(III)- and Zn(II)-DABPM complexes contained nitrate ions, because the phosphonic acid moiety of DABPM was hard to participate in the metal extraction.

1. Introduction

The demand for indium and gallium which are used in liquid crystal displays and light-emitting diodes has increased because of the chemical and physical properties of these metals. In recent years, these metals have also attracted attention for applications in copper-indium-gallium-selenide (CIGS) solar cells. The manufacturing costs of CIGS solar cells is lower than that of crystalline-based solar panels, and their deterioration in power generation performance through aging is also low. For these reasons, it is predicted that the demand for indium and gallium will continue to increase in the future. However, both metals have generally been produced as by-products from zinc refinery residues, so the development of selective separation techniques for indium and gallium over zinc is desired. In addition, the future development of recovery techniques for separating indium and gallium from copper and selenium in CIGS solar cell wastes is desirable.

The separation of In(III) and Ga(III) using organophosphorus compounds [1–9] has been reported, and in particular di-(2-ethylhexyl)phosphoric acid (D2EHPA) [1,2,6–8] and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A) [1,8,9] have been used as industrial extractants. The extraction selectivity for In(III) and Ga(III) was increased through the synergistic extraction using primary amines [10], trialkyl amine [11] and 3,5-dichlorophenol [12] as synergists. In addition, tris(2-hydroxy-3,5-dimethylbenzyl)amine (H3tdmba) [13] showed high extraction selectivity towards Ga(III) to In(III) and Al(III) through a steric hindrance mechanism. However, mutual separation of In(III), Ga(III) and Zn(II) using these extractants is difficult. In our previous study, bis(2-ethylhexyl)amino]methylphosphonic acid monobutyl ester (BEAMP) [14] and [N,N-di(2-ethylhexyl)amino]methylphenylphosphinic acid (DEAPP) containing an amino moiety [15] showed high selectivities for In(III), Ga(III) and Zn(II) compared with D2EHPA and PC-88A. In addition, [di-(2-ethylhexyl)amino]acetic acid (DEHAA) containing an amino moiety [16] showed a similar extraction behavior to BEAMP and DEAPP. It is considered that the amine moieties in these extractants play an important role in the mutual separation of In(III), Ga(III) and Zn(II). However, it is not known how the basicity of the amine moieties in BEAMP and DEAPP affect their extraction selectivity towards these metals.

In this study, aminophosphonic acid extractants with different basicities of amine moiety were synthesized to elucidate the causes of their extraction selectivity. We selected aniline and aliphatic amines as amine moieties with lower and higher basicities, respectively, and examined their extraction selectivity towards In(III), Ga(III), Zn(II) and Cu(II). In addition, the extraction equilibria for Ga(III) and Zn(II) were examined to identify the extracted species.

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2. Experimental section

2.1. Reagents

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%) and 4-*n*-octylaniline (>95.0%) were obtained from Tokyo Chemical Industry Co., Ltd. Benzaldehyde (>98.0%) and potassium hydroxide (>85.0%) 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. All other reagents and solvents were of analytical grade and used without further purification.

2.2. Synthesis of α-(4-n-octylanilino)benzylphosphonic acid monobutyl ester (OABPM)

OABPM was synthesized by the Mannich reaction using 4-*n*-octylaniline (24.6 g, 0.12 mol), dibutyl phosphite (24.3 g, 0.125 mol) and benzaldehyde (14.9 g, 0.14 mol) in 100 cm^3 ethanol in the presence of anhydrous iron(III) chloride (1.95 g, 0.012 mol) as a catalyst at room temperature for 24 h. The ethanol was evaporated and the product was then dissolved in chloroform. The chloroform solution was washed with aqueous sodium chloride solution to remove 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 a silica gel. The intermediate (24.4 g, 0.05 mol) and potassium hydroxide (22.4 g, 0.4 mol) were dissolved in 500 cm^3 of ethanol/water (9:1) mixture, and the mixture was heated at 60 °C for 48 h (Scheme 1). The mixture was neutralized by concentrated hydrochloric acid, and ethanol was then evaporated *in vacuo* and the crude product was dissolved in chloroform, washed with aqueous sodium hydroxide solution, hydrochloric acid and distilled water to remove unreacted raw materials, and dried over anhydrous sodium sulfate. After filtration, the chloroform was evaporated *in vacuo* and a brown liquid was obtained. The resulting product was identified by ^1H NMR, FT-IR (JASCO, Co., FT-IR 4200, Tokyo, Japan) and ESI-MS (Thermo Fisher, Q Exactive, MA, USA). ^1H NMR (400 MHz) spectra of the extractants in $CDCl_3$ were recorded with a nuclear magnetic resonance spectrophotometer model AV400 M (Bruker Co., Rheinstetten, Germany). The following properties of OABPM were identified as follows: ^1H NMR (400 MHz, $CDCl_3$, *r.t.*): $\delta = 8.83$ (br, 1H, PO*H*), 7.45 (d, 2H, H_{Ar}), 7.20 (m, 3H, H_{Ar}), 6.77 (m, 4H, H_{Ar}), 4.66 (d, 1H, NHC*H*), 3.66 (m, 2H, $POCH_2$), 2.39 (t, 2H, $PhCH_2$), 1.46 (m, 2H, $POCH_2CH_2$), 1.37 (m, 2H, $PhCH_2CH_2$), 1.26–1.18 (m, 12H, CH_2), 0.86 (t, 3H, CH_3), 0.79 (t, 3H, CH_3); FT-IR (KBr disc): ν(N—H) 3387 cm^{-1}, ν(P=O) 1198 cm^{-1}; ESI-MS: *m*/*z* calcd for $C_{25}H_{38}NO_3P = 431.26$ [$M+H^+$]; found: 432.26.

2.3. α-dodecylaminobenzylphosphonic acid monobutyl ester (DABPM)

DABPM was synthesized by the Mannich reaction using dodecylamine (37.1 g, 0.2 mol), dibutyl phosphite (40.8 g, 0.21 mol) and benzaldehyde (26.5 g, 0.25 mol) in 100 cm^3 ethanol in the presence of iron(III) chloride anhydride (3.24 g, 0.02 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 to that for OABPM. The intermediate (23.4 g, 0.05 mol) and potassium hydroxide (22.4 g, 0.4 mol) were dissolved in an ethanol/water (9:1) mixture 500 cm^3, and the mixture was reacted at 60 °C for 48 h (Scheme 1). Post-treatment was again performed in a similar manner to that for OABPM.

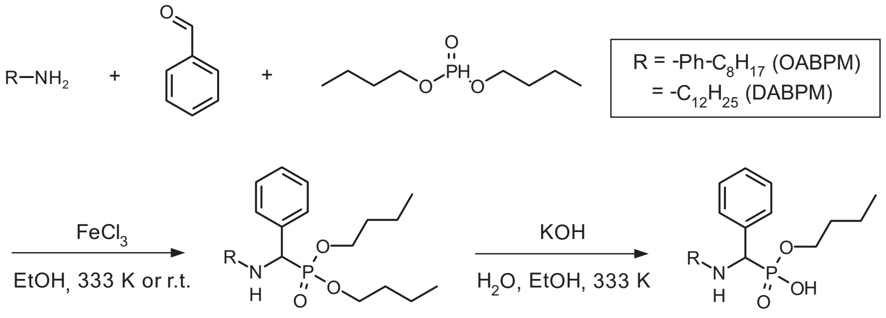
The yellow powder product was recrystallized with ethyl acetate at least three times and a white powder was obtained. ^1H NMR (400 MHz, $CDCl_3$, r.t.): $\delta = 10.7$ (br, 1H, PO*H*), 7.74 (br, 2H, H_{Ar}), 7.37 (br, 3H, H_{Ar}), 4.23 (br, 1H, NHC*H*), 3.43 (br, 2H, $POCH_2$), 2.62 (br, 2H, $NHCH_2$), 1.92 (br, 2H, $POCH_2CH_2$), 1.35–1.11 (m, 20H, CH_2), 0.82 (t, 6H, CH_3); FT-IR (KBr disc): ν(N—H) 1088 cm^{-1}, ν(P=O) 1217 cm^{-1}; ESI-MS: *m*/*z* calcd for $C_{23}H_{43}NO_3P = 411.29$ [$M+H^+$]; found: 412.30.

2.4. Potentiometric measurement of OABPM and DABPM

All potentiometric measurements were performed in a jacketed titration cell thermostated at 25 °C under a nitrogen atmosphere. The extractant was dissolved in ethanol/water (65:35, 70:30, 80:20 v/v, respectively) containing 0.1 mol dm^{-3} NaCl. Combined pH electrodes were calibrated by Gran's method [17], which determined the standard potential, E^0. The p*K*a was determined using an automatic potentiometric titrator.

2.5. Extraction tests for metal ions with OABPM and DABPM

All extraction tests for metal ions were performed in an aqueous solution containing a single metal ion. To evaluate the extractability of OABPM and DABPM, liquid-liquid extraction was carried out using 1.0 M aqueous ammonium nitrate solution containing 1 mM metal ions as an aqueous phase. The pH was adjusted using 1 M HNO_3 or $NH_3{\cdot}H_2O$. Toluene was used as a diluent of the organic phase containing 50 mM OABPM or DABPM. In a 10 cm^3 stoppered test tube, equal volumes (2.5 cm^3) of the aqueous and organic phases were shaken mechanically 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 a pH 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) using an air-acetylene flame. The metal ion concentration in the organic phase was calculated from a mass balance between the aqueous and organic phases. Extraction



Scheme 1. Synthesis of α-(4-*n*-octylanilino)benzylphosphonic acid monobutyl ester (OABPM) and α-dodecylaminobenzylphosphonic acid monobutyl ester (DABPM).