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Solvent Extraction of Divalent Metal Ions Using 2-Pyridinealdoxime in Ionic Liquid

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Abstract

The extraction and separation of the divalent metals was studied by using ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) including the extractant of 2-pyridinealdoxime (2-PA). The divalent metals used here are Cd²⁺ and Pb²⁺ for the toxic and Ni²⁺ and Zn²⁺ for the valuable metals in industry. These metal ions in potassium nitrate of 0.10 mol dm⁻³ concentration were examined to be extractable. It was observed that Cd²⁺ was extracted into ionic liquid phase better than Pb²⁺ and Zn²⁺ in the pH range of 5.15-9.83 and its extractability was reached to >99% in the pH of 7.93-9.83. The extraction equilibrium of Cd²⁺ with 2-PA into BMIM-PF₆ was found to be $\text{Cd}^{2+} + 3\text{HL}_{(\text{o})} \rightleftharpoons \text{CdL}_2\text{HL}_{(\text{o})} + 2\text{H}^+ + \text{cit}^{3-}$, whose mechanism is the same way as that into chloroform (CHCl₃). The mutual separation of Cd²⁺, Pb²⁺, Ni²⁺, and Zn²⁺ can be achieved by using the different pH values of the aqueous phase in 2-PA/ BMIM-PF₆ extraction system. From these results, it can be stated that the 2-PA/ BMIM-PF₆ extraction system is useful to extract and separate the divalent metal ions examined in this work.

Key words: solvent extraction, 2-Pyridinealdoxime, ionic liquid

1 Introduction

2-Pyridinealdoxime was found to be a selective extractant for Cd²⁺ and Pb²⁺ among the representative heavy metal ions by one of the present authors.[1,2] However, since 2-PA is fairly hydrophilic, of which its distribution constant between CHCl₃ and water is 0.18, 2-PA can not be dissolved in ordinary hydrophobic solvents such as 1-octanol, cyclohexane, toluene, and n-hexane other than CHCl₃, and these solvents can not be used for 2-PA extraction system. 2-PA is soluble in the solvents containing oxygen atom such as nitrobenzene, 4-methyl-2-pentanone, and ethyl acetate, but metal complexes with 2-PA are insoluble in these solvent and can not

be extracted into these solvents. Recently, because of their environmentally harmfulness, halogenated organic solvents are avoided using. Consequently, 2-PA is not practical to use unless harmless solvent capable of dissolving 2-PA is found, although it has excellent selective extractability for Cd^{2+} and Pb^{2+} .

Nowadays, new solvent, ionic liquids, attracts people's interests because of its nonvolatile and noncombustible character and is regarded to a solvent in harmony with environment. In the field of solvent extraction, ionic liquid is expected to be not only environment friendly solvent but also an extracting solvent possessing an unique extractability.[3] It was found that 2-PA considerably dissolved in BMIM- PF_6 to form a concentrated 2-PA solution, 0.10 M ($M=\text{mol dm}^{-3}$). In the present study, although nowadays there several kinds of ionic liquids are available, BMIM- PF_6 was mainly used in this study since it is used most widely and has a good solubility to 2-PA. Ni^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} were arbitrarily selected as an analyte according to the environmental significance and were subjected to the extraction with 2-PA BMIM- PF_6 solution.

2 Experimental

2.1 Reagents and apparatus

A Varian model Vista-Pro ICP-AES spectrophotometer was used to measure the metal ion concentration and a Horiba F-21 pH meter was used to measure pH. 2-PA was obtained from Tokyo Kasei Kogyo Co. Ltd. and was purified by recrystallization from chloroform. The other reagents were all of analytical grade.

2.2 Extraction procedure

A 2.0 ml portion of 0.20 mM metal ion solution, which was masked and buffered with 0.010 M tripotassium citrate (K_3cit) and was maintained ionic strength to be 0.10 M with potassium nitrate, was equilibrated with an

Fig.1 Distribution ratios of some divalent metals as a function of pH.

Organic phase: $[\text{2-PA}]_{\text{BMIM-PF}_6}=0.10\text{ }M$. Aqueous phase: $[\text{M}^{2+}]=0.20\text{ }mM$, $[\text{KNO}_3]=0.10\text{ }M$, $[\text{K}_3\text{cit}]=0.010\text{ }M$.

Pb^{2+} , $\text{---}\bullet\text{---}$; Cd^{2+} , $\text{---}\blacklozenge\text{---}$; Ni^{2+} , $\text{---}\blacksquare\text{---}$; and Zn^{2+} , $\text{---}\blacktriangle\text{---}$ for BMIM- PF_6 extraction system:

Pb^{2+} , $\text{---}\circ\text{---}$; Cd^{2+} , $\text{---}\diamond\text{---}$; Ni^{2+} , $\text{---}\square\text{---}$; and Zn^{2+} , $\text{---}\triangle\text{---}$ for CHCl_3 extraction system:

equal volume of 0.10 M 2-PA BMIM-PF₆ solution in a 10 ml extraction vial by shaking vigorously for 1 h, followed by separating phases by centrifugation. After determining the equilibrated pH of aqueous phase, 1.0 ml of the BMIM-PF₆ phase was subjected to the back-extraction with 1.0 ml of 1.0 M HCl solution for 1 h. Then, the metal ion concentrations in both aqueous phases were determined by ICP-AES, and the extraction ratio was obtained from the determined metal ion concentrations in both aqueous phases. To evaluate the extractability of BMIM-PF₆, metal extraction was carried out separately by using CHCl₃ as an extracting solvent under the same extraction conditions.

3 Results and Discussion

3.1 Effect of pH

In the previously reported 2-PA CHCl₃ extraction system, only Cd²⁺ and Pb²⁺ were extracted into organic phase, while others were not. As for Cd²⁺, Pb²⁺, and Zn²⁺, roughly speaking, the extraction curves obtained by BMIM-PF₆ extraction system looked similar to those obtained by the 2-PA CHCl₃ extraction system, but there are several differences in detail. First, in the present extraction system, pH_{50%} values were 6.45 for Cd²⁺ and 8.86 for Pb²⁺, respectively, and were worse compared to those in the 2-PA CHCl₃ extraction system, 5.15 for Cd²⁺ and 7.89 for Pb²⁺. Second, the maximum of extraction curve for Pb²⁺ did not reach to 100% in the present system as seen in Fig.1, while that attained to more than 99% in the 2-PA CHCl₃ extraction system. The worse extractability of BMIM-PF₆ for these metal 2-PA complexes compared to CHCl₃ may be attributed to its poor solubility, if these metals were extracted in the form of 2-PA chelate complexes, as described in section 3.2. BMIM-PF₆ does not dissolve in CHCl₃ or in water mutually and form three layers when mixed them. Therefore, chemical properties such as polarity are thought to be fairly different each other between CHCl₃ and BMIM-PF₆.

As for Ni²⁺, there is a striking contrast in the extraction behavior with between CHCl₃ and BMIM-PF₆. That is, the percent extraction of Ni²⁺ was less than 3% in the entire pH region examined in the 2-PA CHCl₃ extraction system, but that was greater than 90% in the pH region of 3.9-4.3 in the 2-PA BMIM-PF₆ extraction system.

3.2 Extraction equilibrium

It is known that components in ionic liquid react with metal chelate complex to form an ion association complex in the some metal extraction systems.[4] Therefore, the extraction of these metals with CHCl₃ solution containing 1-butyl-3-methyl imidazolium chloride and 2-PA and the extraction of these metals

Fig.2 Distribution ratio of Cd²⁺ as a function of 2-PA concentration.

pH was maintained at 6.64 ± 0.05 .

from aqueous phase containing hexafluorophosphoric acid into 2-PA CHCl_3 solution were examined. The both experimental results showed that the components of BMIM- PF_6 did not affect 2-PA CHCl_3 extraction at all. Therefore, it was considered that BMIM- PF_6 worked simply as a diluent and metals were extracted in the form of chelate complex without forming ion association complex.

In the 2-PA CHCl_3 extraction system, it was ascertained by the slope analysis that Cd^{2+} was extracted in accordance with the following equilibrium,

where the subscript (o) denotes the organic phase and (w) means the aqueous phase and CdCit^- and cit^{3-} are the cadmium citrate complex and citrate anion, respectively. If same things hold in the present 2-PA BMIM- PF_6 extraction system, the plots of $\log D$ vs. pH and $\log D$ vs. $\log[2\text{-PA}]$ for Cd^{2+} should produce the line with slopes of 2 and 3, respectively. The plots of $\log D$ vs. pH for Cd^{2+} , which was obtained from the data shown in Fig.1, exhibited slope of 1.9 ($r^2=0.981$), and the plots of $\log D$ vs. $\log[2\text{-PA}]$ showed slope of 2.9 ($r^2=0.997$), as can be seen in Fig.2. Since the slopes of the $\log D$ vs. pH and $\log D$ vs. $\log[2\text{-PA}]$ plots are close to 2 and 3, it can be concluded that 2-PA BMIM- PF_6 solution extracted Cd^{2+} in the same way to the 2-PA CHCl_3 extraction system. As for Pb^{2+} and Zn^{2+} , neither metals were extracted sufficiently, so that further examination was not carried out in this study. While, the slope of the $\log D$ vs. pH plots of Ni^{2+} was -0.2, and did not give the integral number. Although it was suspected that components in ionic liquid react with Ni-complex with 2-PA to form an adduct, details have not been proved yet.

3.3 Separation between Ni^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+}

In the present 2-PA BMIM- PF_6 extraction system, extraction behavior of Ni^{2+} was quite different from those of Cd^{2+} , Pb^{2+} , and Zn^{2+} , so that Ni^{2+} can be easily separated from these metal ions by carrying out its extraction in the acidic pH region. At pH 7.2, percent extractions of Pb^{2+} and Zn^{2+} were both 0%, while that of Cd^{2+} was 92%, therefore, Cd^{2+} can also be fully separated from Pb^{2+} and Zn^{2+} by extracting Cd^{2+} at pH 7.2. The separation of Pb^{2+} and Zn^{2+} is also possible by extracting them at pH 9.8, since the extractabilities of Pb^{2+} and Zn^{2+} at pH 9.8 were 67% and 3%, respectively.

In conclusion, it can be said that the separation between Ni^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} can be achieved by the present 2-PA BMIM- PF_6 extraction system.

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