



Synergistic effect of nitrogen-containing donors on extraction of divalent metal ions using *p*-tert-octylphenoxyacetic acid



Tatsuya Oshima*, Keisuke Kaneizumi, Kaoru Ohe, Yoshinari Baba

Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, 1-1 Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan

ARTICLE INFO

Article history:

Received 20 October 2014
Received in revised form 28 November 2014
Accepted 29 November 2014
Available online 18 December 2014

Keywords:

Liquid–liquid extraction
Synergistic effect
Synergistic extraction
Phenoxyacetic acid
Nitrogen-containing donor

ABSTRACT

p-tert-Octylphenoxyacetic acid (^tOP-OCH₂COOH) was a better extractant for Cu(II) than was a commercial aliphatic carboxylic acid extractant, namely Versatic 10. In the present study, the synergistic effect of nitrogen-containing donors (N-donors) on the extraction of divalent base-metal ions using ^tOP-OCH₂COOH was studied. Pyridine (Py), 2,2'-bipyridine (Bpy), and 1,10-phenanthroline (Phen) were added as synergists. The addition of N-donors to organic phases containing ^tOP-OCH₂COOH enhanced the extractabilities of the divalent metals Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). Addition of Phen was the most effective for the enhancement of metal extraction, but the selectivity was low. Synergistic extraction using a mixture of ^tOP-OCH₂COOH and Py was more effective for the separation of divalent metal ions. A mixture of ^tOP-OCH₂COOH and Bpy gave moderate extraction and selectivity; the following reaction was suggested for the extraction of Cu(II): $\text{Cu}^{2+}_{(\text{aq})} + \text{Bpy}_{(\text{org})} + 1.5(^t\text{OP-OCH}_2\text{COOH})_{2(\text{org})} \rightleftharpoons \text{Cu}^{2+}(\text{Bpy})(^t\text{OP-OCH}_2\text{COOH})(^t\text{OP-OCH}_2\text{COO}^-)_{2(\text{org})} + 2\text{H}^+_{(\text{aq})}$.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

A synergistic effect is defined as cooperation between two extractant molecules to increase the extractability compared with that of a single extractant. The separation factor of metal ions can also be increased by certain combinations of extractants. When a combination of an acidic extractant and an electron donor is used for the extraction of metal cations, the acidic extractant complexes with the metal ions and neutralizes charges, and the electron donor promotes dehydration of the metal ion by replacing a water molecule and occupying a coordination site. To date, a number of synergistic extraction systems has been developed to improve extractability and/or selectivity [1–4].

Alkylated carboxylic acid extractants, as well as organophosphates, are representative acidic extractants for metal cations. Several carboxylic acid extractants such as Versatic 10, and naphthenic, 2-bromodecanoic, and 3,5-diisopropylsalicylic acids have been developed for the extraction of various metal ions [5]. The commercial tertiary carboxylic acid Versatic 10 has been used in a number of solvent extraction systems [6–9]. Various synergistic extraction systems using Versatic 10 and other extractants have also been studied. Pyridinecarboxylate esters have a synergistic

effect in the extraction of divalent base-metals using Versatic 10 [10]. The addition of 4-(5-nonyl)pyridine also shows a synergistic effect in the extraction of Ni(II) with Versatic 10, thereby improving separation of Ni(II) and Ca(II) [11]. The combination of Versatic 10 and an aliphatic hydroxyoxime extractant LIX 63 also shows a synergistic effect for divalent base metals [12–14]. A synergistic extraction system using LIX 63 and Versatic 10 was developed for the separation of Co(II) and Zn(II) from Mn(II), Mg(II), and Ca(II) [15].

Alkylated phenoxyacetic acids have been developed as a new series of acidic extractants. Alkylated phenoxyacetic acids generally give higher extractabilities than aliphatic alkylated carboxylic acid extractants at low pH, because of the higher acid dissociation constants. *sec*-Nonylphenoxyacetic acid (CA-100) is used for the extraction of various metal ions such as rare-earth metals, Ga(III), and In(III) [16–20]. A phenoxyacetic acid extractant, namely 2-(4-nonylphenoxy)acetic acid, and its analog 2-[(4-octylphenyl)amino]acetic acid have also been used for the separation of In(III), Ga(III), and Zn(II) [21]. Synergistic extractions of metal ions using mixtures of CA-100 and other extractants have also been studied. Mixtures of CA-100 and *o*-phenanthroline (Phen) showed higher selectivities for the separation of lanthanoids and yttrium compared with CA-100 alone [22]. The synergistic extraction of In(III) from a chloride medium using a mixture of CA-100 and a trialkylamine has also been studied [23]. Furthermore, synergistic effects in Ho(III), Y(III), and Er(III) extractions using mixtures of

* Corresponding author. Tel.: +81 985 58 7321; fax: +81 985 58 7323.

E-mail addresses: oshimat@cc.miyazaki-u.ac.jp (T. Oshima), okaoru@cc.miyazaki-u.ac.jp (K. Ohe), t0g202u@cc.miyazaki-u.ac.jp (Y. Baba).

bis(2,4,4-trimethylpentyl)monothio phosphinic acid (Cyanex 302) and CA-100 have been investigated [24]. Combinations of alkylated phenoxyacetic acid and nitrogen-containing donors (N-donors) could therefore be developed for synergistic extraction systems.

The aim of the present study was to evaluate the synergistic effects of N-donors in the extraction of divalent metal ions using *p*-*tert*-octylphenoxyacetic acid [*p*-(1,1,3,3-tetramethylbutyl)phenoxyacetic acid, ^tOP-OCH₂COOH] as an acidic extractant. The extractions of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) using ^tOP-OCH₂COOH and mixtures of ^tOP-OCH₂COOH and N-donors were compared in terms of extractability and metal ion selectivity. Pyridine (Py), 2,2'-bipyridine (Bpy), and 1,10-phenanthroline (Phen) were used as synergists. The reaction in the synergistic extraction of Cu(II) using ^tOP-OCH₂COOH and Bpy was studied by slope analysis.

2. Experimental section

2.1. Apparatus

The pH values of aqueous solutions were measured using a pH meter (HM-30S, DKK-TOA Co., Tokyo, Japan). A polarized Zeeman atomic absorption spectrometer (AAS; Hitachi Z-2310, Hitachi High-Technologies Co., Tokyo, Japan) was used for determination of metal concentrations, using an air–acetylene flame.

2.2. Materials and reagents

Analytical-grade manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) chlorides (Wako Pure Chemical Industries Ltd., Osaka, Japan) were used for the metal ion solutions. Fig. 1 shows the molecular structures of ^tOP-OCH₂COOH and N-donors. Analytical-grade Py for the extraction tests was purchased from Wako Pure Chemical Industries Ltd. Analytical-grade Bpy and Phen were purchased from the Tokyo Kasei Co., Ltd. (Tokyo, Japan). Versatic 10, which is a synthetic tertiary carboxylic acid consisting of a mixture of highly branched isomers of C₁₀ monocarboxylic acids, was kindly supplied by Shell Chemicals Japan Ltd. and used as received. ^tOP-OCH₂COOH was prepared by reacting ethyl bromoacetate with *p*-*tert*-octylphenol, followed by alkaline hydrolysis, according to a previously reported procedure [21,25]. All other reagents were reagent grade and used as received. The log*P* values of N-donors were estimated using MarvinSketch 6.2.1 (ChemAxon Ltd., Hungary) by the KLOP method [26].

2.3. Liquid–liquid extraction tests

Aqueous solutions of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) of concentrations 0.10 mM were prepared. The pH of the aqueous solution was adjusted using 100 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer and a small amount of

HCl or NaOH. An organic solution was prepared by dissolving 12 mM Versatic 10 or ^tOP-OCH₂COOH in chloroform. For the synergistic extraction tests, 12 mM Py, Bpy, or Phen were also added to the organic phase. Equal volumes (5.0 cm³) of the aqueous and organic solutions were mixed in a stoppered Erlenmeyer flask and shaken (120 rpm) in a thermostated water bath at 30 °C. After 24 h, when the extraction attained equilibrium, each phase was separated and the equilibrium pH was measured. The initial and equilibrium concentrations of metal ions in the aqueous phases were determined using AAS. The extraction percentage and distribution ratio (*D*) of the metal were calculated using Eqs. (1) and (2), respectively.

$$\text{Extraction [\%]} = \frac{[M]_{\text{org,eq}}}{[M]_{\text{aq,init}}} \times 100 = \frac{[M]_{\text{aq,init}} - [M]_{\text{aq,eq}}}{[M]_{\text{aq,init}}} \times 100 \quad (1)$$

$$D = \frac{[M]_{\text{org,eq}}}{[M]_{\text{aq,eq}}} = \frac{[M]_{\text{aq,init}} - [M]_{\text{aq,eq}}}{[M]_{\text{aq,eq}}} \quad (2)$$

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

The reaction for the extraction of Cu(II) using ^tOP-OCH₂COOH and Bpy was also investigated by slope analysis. The effect of the equilibrium pH on the distribution ratio (*D*) of Cu(II) was investigated using 12 mM ^tOP-OCH₂COOH and 0.1 mM Bpy. The effects of the ^tOP-OCH₂COOH and Bpy concentrations on *D* were investigated at pH 3.5.

3. Results and discussion

3.1. Synergistic effects of N-donors on extraction of metal ions

Fig. 2 shows the extraction profiles of Cu(II) using Versatic 10 in the absence (synergist free) and presence of N-donors (Py, Bpy, and Phen). As the extraction of metal ions using an acidic extractant such as Versatic 10 proceeds by proton exchange, extraction increased with increasing pH. Cu(II) was quantitatively extracted with Versatic 10 at pH greater than 7. The addition of N-donors slightly affected the extraction of Cu(II) using Versatic 10. In the presence of Py and Bpy, Cu(II) was quantitatively extracted (99% extraction) with Versatic 10 at pH 6.5 and 6.6, respectively. The addition of Phen did not enhance extraction.

Fig. 3 shows the extraction profiles of Cu(II) using ^tOP-OCH₂COOH in the absence and presence of N-donors. Cu(II) was extracted with ^tOP-OCH₂COOH at a lower pH than with Versatic 10, and quantitatively extracted at pH less than 6. ^tOP-OCH₂COOH has a phenyl group close to the carboxyl group, so the acid dissociation constant must be higher than that of Versatic 10 [21].

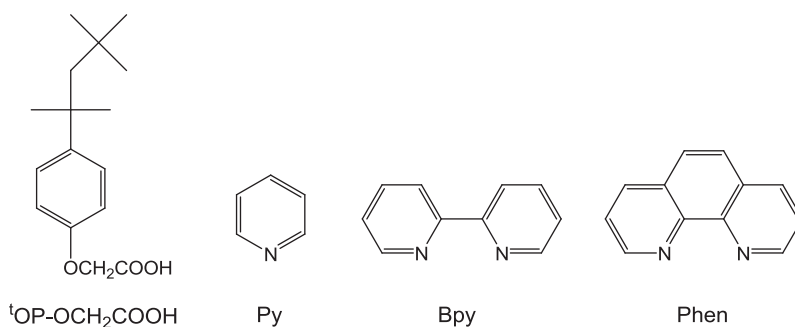


Fig. 1. Molecular structures of ^tOP-OCH₂COOH and N-donors.

Download English Version:

<https://daneshyari.com/en/article/640685>

Download Persian Version:

<https://daneshyari.com/article/640685>

[Daneshyari.com](https://daneshyari.com)