Extraction Behavior of Metal Cations Using 8-Quinolinol as an Extractant in Cyclopentyl Methyl Ether

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To date, many kinds of chelating extractants have been developed, however, many of the good extractants are insoluble in aliphatic solvents. In the present study, cyclopentyl methyl ether (CPME) was assessed as a solvent for extractants to develop new solvent extraction systems. Many of the extractants (100 mM) were soluble in CPME. The extraction behavior of metal ions using a typical chelating extractant, 8-quinolinol (HQ) in CPME, was studied. The extraction profiles of metal ions using HQ in CPME were similar to those in toluene, whereas metal ions were extracted using HQ in 1-octanol and chloroform under lower pH conditions. The extraction reaction of In(III) using HQ in CPME was confirmed by slope analysis. A 3 : 1 complex between HQ and In(III) was formed in CPME by a proton exchange reaction, and the extraction equilibrium constant was determined. In(III), extracted using HQ in CPME, was quantitatively recovered using mineral acids. From the results, CPME was found to be a potential alternative solvent to other toxic organic solvents for the development of a solvent extraction system.

1. Introduction

In order to develop effective separation processes for many kinds of metal ions, a number of powerful chelating extractants have been developed. However, many of such extractants have a solubility problem in aliphatic solvents. If the chelating extractants are soluble only in toxic organic solvents such as chloroform, the practical use of these extractants is very limited. Therefore, various dissolution techniques for the extractants have been developed. Introduction of an alkyl group to the chelate ligands is a typical strategy to improve the solubility [1-4]. Dissolution of extractants using reversed micelle formation has also been used [5, 6]. Addition of modifiers such as an alcohol into the organic solvent is also effective in improving the solubility of the extractants [7-9]. Another strategy should be the development of new solvents which can dissolve the extractant.

Authors have focused on cyclopentyl methyl ether (abbreviated as CPME, Figure 1) as a new solvent or extractant for use in solvent extraction systems [10, 11]. CPME is relatively hydrophobic (logP = 1.59) and less soluble in water (solubility in water = 1.1/100g) compared with typical ethereal solvents [12, 13]. Recently, the extraction of transition metal ions using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in CPME was studied.

(a) [Moleculer structure of (a) HQ and (b) CPME.]

(b)
The extraction reaction of Cu(II) using D2EHPA in CPME was similar to that in dodecane, and the extraction equilibrium constants were determined. In hydrochloric acid media, CPME is directly available for the extraction of Au(III) [11]. Au(III) was selectively extracted using CPME from other precious metal ions and base metal ions. CPME can load large quantities of Au(III), and the extraction rate is very rapid. CPME is a less toxic solvent and is approved by the Toxic Substances Control Act (TSCA) and the European List of Notified Chemical Substances (ELINCS) [12,13].

In the present study, CPME was used as a solvent for various popular extractants. Solubility tests for the extractants in CPME were carried out. On the basis of the results, the extraction behavior of metal ions using a chelating extractant 8-quinolinol (abbreviated as HQ, Figure 1) was studied in order to evaluate whether CPME can be used as an alternative solvent instead of toxic solvents like chloroform. HQ and its derivatives have extensively been used as chelating extractants in the field of analytical chemistry [14-24]. Various metal ions can be extracted using HQ, however, extraction using HQ has generally been conducted in toluene or chloroform because of the limited solubility of HQ. Development of solvents would expand the application of metal extraction using HQ. The extraction behavior of metal ions using HQ in CPME was compared with that in other organic solvents. Additionally, the extraction reaction for In(III) using HQ in CPME was studied by slope analysis. The back extraction of In(III) extracted using HQ into CPME phase was also studied.

2. Experimental

2.1 Reagents

Analytical grade indium(III) (Kishida Chemical Co., Ltd., Japan), iron(III), gallium(III), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) nitrates (Wako Pure Chemical Ind. Ltd., Japan) were used to prepare test solutions of the metal ions. Analytical grade CPME was supplied from Zeon Co., Japan. Analytical grade chloroform, toluene, 1-octanol, HQ, trioctylamine (TOA), diethylene glycol dibutyl ether (dibutyl carbitol, DBC) (Wako Pure Chemical Ind. Ltd., Japan), di-(2-ethylhexyl) phosphoric acid (D2EHPA), trioctylmethylammonium chloride (TOMAC), 4-tert-butylcalix[6]arene (Tokyo Kasei Co., Japan), 18-crown-6, dibenzo-18-crown-6, (Sigma-Aldrich Co., St. Louis, MO, USA), and 15-crown-5 (Merck, Hohenbrunn, Germany) for the solubility tests and the extraction tests were purchased and used without further purification. 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) was kindly supplied by Daihachi Chemical Industries, Japan. Cyanex® 923, which is a mixture of trialkylphosphine oxides including trioctylphosphine oxide, was kindly supplied by Cytec Inc., Canada. Versatic™ 10, which is a mixture of highly branched isomers of C_{10} monocarboxylic acids, was kindly supplied by Shell Chemicals Japan Ltd. All other reagents and solvents were of analytical grade and were used as received. The logarithm of the partition coefficient between 1-octanol and water (logP) is widely accepted as a quantitative indicator of the hydrophilic-lipophilic balance. The logP values of the diluents were estimated using MarvinSketch 6.2.1 (ChemAxon Ltd., Budapest, Hungary) by the KLOP method [25].

2.2 Solubility of various extractants in CPME

Solubility of each extractant in CPME at room temperature was studied by adding each extractant (HQ, D2EHPA, PC-88A, Cyanex 923, Versatic 10, TOA, TOMAC, 15-crown-5, 18-crown-6, dibenzo-18-crown-
6, and 4-tert-butylcalix[6]arene) to CPME to obtain 100 mM or 10 mM solutions. The solubility was visually checked. Additionally, solubility of HQ 68.9 mM (10.0 g/dm$^3$) in each solvent (acetone, chloroform, tetrahydrofuran (THF), toluene, 1-octanol, CPME, diphenyl ether, water, hexane, dodecane, cyclohexane, 1,2-propanediol, and isoctane (2,2,4-trimethylpentane)) was also investigated visually.

Hansen solubility parameters (HSPs) of various solvents and HQ were compared in order to study the factors of good diluents for HQ [26-28]. HSPs consist of three intermolecular bonding forces; the nonpolar (dispersion) interactions (δD), polar (dipole-dipole and dipole-induced dipole) interactions (δP), and hydrogen bonding interactions (δH). The solubility parameter distances between two materials (Ra) is given by Equation (1);

$$Ra = \sqrt{4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2}$$

(1)

where δD1, δP1, and δH1 represent the HSP values of a compound, while δD2, δP2, and δH2 represent the HSP values of the other compound. Smaller Ra value means that the HSP values of the compounds are close to each other. On the basis of the classical “like dissolves like” rule, solvents that show smaller Ra value would be good solvents [26, 27]. HSP values for HQ and solvents were obtained from HSPiP (Hansen Solubility Parameters in Practice) software ver.5 [26]. From the results of solubility tests for 68.9 mM (10.0 g/dm$^3$) HQ using 30 solvents (water, acetone, methanol, ethanol, 2-propanol, 1-pentanol, 1-octanol, 1-decanol, 1,2-propanediol, 1,4-dioxane, tetrahydrofuran (THF), CPME, diphenyl ether, ethyl acetate, diethylamine, dipropylamine, triethylamine, 2-aminoethanol, pyridine, $N,N$-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chloroform, toluene, n-hexane, cyclohexane, n-octane, isoctane, n-decane, n-dodecane, and decahydronaphthalene), the HQ Hansen sphere was also investigated [26, 29].

2.3. Extraction of metal ions using HQ in CPME

Liquid-liquid extraction tests were conducted by the batchwise method and a typical procedure was as follows: the aqueous solution was prepared by dissolving 1.0 mM of the following metal ions Fe(III), Ga(III), In(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II). The pH values of the aqueous solutions were adjusted using 100 mM HNO$_3$ or NH$_3$. Organic solutions were prepared by dissolving 50 mM HQ in CPME chloroform, toluene, or 1-octanol. Equal volumes (10 cm$^3$) 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 shaking for 24 h to attain equilibrium, each phase was separated and the equilibrium pH was measured. The initial and equilibrium concentrations of the metal ions in the aqueous phases were determined using a polarized Zeeman atomic absorption spectrometer (HITACHI Z-2310). The extraction percentages of the metal ions and the distribution ratio (D) were calculated according to Equations (2) and (3):

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

(2)

$$D = \frac{[\text{M}]_{\text{org, eq}}}{[\text{M}]_{\text{aq, eq}}} = \frac{[\text{M}]_{\text{aq, eq}} - [\text{M}]_{\text{aq, eq}}}{[\text{M}]_{\text{aq, eq}}}$$

(3)

where [M]$_{\text{aq, init}}$ and [M]$_{\text{aq, eq}}$ represent the initial and equilibrium concentrations of the metal ions in the aqueous phase. [M]$_{\text{org, eq}}$ is the total concentration of the metal ions in the organic phase after equilibrium,
which was calculated from the decrease in concentration of the metal ions in the aqueous phase after equilibrium.

2.4 Back Extraction of In(III)

The forward extraction of 1.0 mM In(III) with 50 mM HQ in CPME at pH 2.0 was performed from the aqueous to the organic phase (40 cm³/40 cm³) in a similar manner to that shown in section 2.3. The organic phase containing In(III) was divided into 5.0 cm³ portions, and each solution was contacted with a 5.0 cm³ fresh aqueous solution containing a different mineral acid. Both phases were mixed and shaken at 30°C for 24 h. The stripping solution was separated from the organic phase and the back extraction percentage (B.E. [%]) was calculated according to Eq. (4).

\[
B.E.[\%] = \frac{[\text{In(III)}]_{\text{org,init}}}{[\text{In(III)}]_{\text{aq,eq}}} \times 100
\]

where \([\text{In(III)}]_{\text{org,init}}\) represents the initial concentration of the metal ion in the organic phase and \([\text{In(III)}]_{\text{aq,eq}}\) is the total concentration of the metal ion in the aqueous phase after equilibrium.

3. Results and Discussion

3.1 Solubility of various extractants in CPME

Figure 2 shows extractants which are soluble (100 mM) in CPME. Many types of commercially available acidic extractants such as D2EHPA and Versatic 10 are soluble in CPME [10]. Basic extractants, such TOA and TOMAC, are also soluble in CPME. Moreover, macrocyclic compounds the crown ethers are also soluble in CPME. Therefore a variety of solvent extraction systems can be prepared using CPME as the diluent. However, tert-butylecalix[4]arene, tert-butylecalix[6]arene, and dibenzo-18-crown-6 are insoluble (10 mM) in CPME. CPME cannot be used as a solvent for these macrocyclic compounds.

HQ is soluble (100 mM) in CPME. Table 1 summarizes the solubility of 10 mM HQ in each solvent as well as the HSP values of the solvents. HQ is insoluble in aliphatic solvents such as dodecane and isoctane.

Figure 2. Extractants which are soluble (100 mM) in CPME.
Table 1. Hansen solubility parameters of HQ and various solvents and the solubility of HQ in each solvent.

| Extractant and Solvents | HSP$^1$ | Ra between HQ and each solvent | Solubility of HQ$^2$ |
|-------------------------|---------|-------------------------------|---------------------|
| HQ                      | ΔD 20.5 | ΔP 5.6 | ΔH 5.7 | - | - | soluble |
| acetone                 | 15.5    | 10.4 | 7.0 | 11.2 | soluble |
| chloroform              | 17.8    | 3.1 | 5.7 | 6.0 | soluble |
| tetrahydrofuran (THF)   | 16.8    | 10.4 | 21.3 | 17.9 | soluble |
| toluene                 | 18      | 1.4 | 2.0 | 7.5 | soluble |
| 1-octanol               | 16      | 5 | 11.2 | 10.6 | soluble |
| CPME                    | 16.7    | 4.3 | 4.3 | 7.8 | soluble |
| water                   | 15.5    | 16 | 42.3 | 39.3 | insoluble |
| hexane                  | 14.9    | 0.0 | 0.0 | 13.8 | insoluble |
| dodecane                | 16.0    | 0 | 0 | 12.0 | insoluble |
| cyclohexane             | 16.8    | 0 | 0.2 | 10.8 | insoluble |
| 1,2-propanediol         | 16.8    | 10.4 | 21.3 | 17.9 | insoluble |
| isoctane                | 14.1    | 0 | 0 | 15.1 | insoluble |

1 HSPs ($\delta_D, \delta_P, \delta_H$) [M Pa$^{1/2}$] values were introduced from HSPiP software ver.5. [26]

2 Solubility of 68.9 mM (10.0 g/dm$^3$) HQ

Aromatic compounds such as toluene and diphenyl ether are good solvents for HQ. Chloroform is also a very good solvent for HQ. A variety of research work on solvent extraction of metal ions using HQ has been conducted in chloroform [1, 14-21]. As shown in Table 1, HSP values of CPME are relatively close to those for chloroform. CPME shows moderate polar and hydrogen bonding parameters compared with aliphatic solvents, which is favorable for the dissolution of many extractants bearing both polar and nonpolar groups.

The Hansen solubility parameters (HSPs) are plotted in a three dimensional space known as the Hansen sphere [26-28]. Solvents that show HSP values located in the sphere are good solvents. The Hansen sphere for 68.9 mM (10.0 g/dm$^3$) HQ was investigated by solubility tests using 30 solvents (Figure 3). HQ was insoluble in water, 1,2-propanediol, and all aliphatic hydrocarbons. Other relatively polar organic solvents including CPME can dissolve HQ. A solvent which shows a smaller Ra value (the Figure 3. 3D HSP diagrams of HQ and 30 solvents with a solubility limit of 68.9 mM (10.0 g/dm$^3$) HQ (sphere). Blue keys correspond to solvents that are inside the sphere and red keys to those that are external.)
HSP distance between two materials) to HQ should be a good solvent. In 30 solvents, only 5 solvents (1,4-dioxane (7.83), diphenyl ether (3.55), chloroform (5.95), toluene (7.51), pyridine (4.39)) showed smaller Ra values than CPME (7.84). Hence CPME must be a potential solvent in solvent extraction systems.

3.2 Extraction behavior of metal ions using HQ

As the extraction of metal cations using HQ proceeds via a proton-exchange reaction, the extraction reaction is fast [19, 23]. The authors also confirmed that In(III) was quantitatively extracted using HQ in CPME within 5 minutes. For operational convenience, the extraction experiments in this study were conducted by contacting both phases for 24 h. Figure 4 shows the extraction profiles of the metal ions using HQ in CPME as a function of pH. As the extraction of the metal ions proceeds by a proton-exchange reaction, the degree of extraction increased with increasing pH value. Trivalent cations Ga(III) and Fe(III), as well as Cu(II) were extracted at lower pH values. The order of extraction for first-row transition metal ions in CPME was Cu(II) > Ni(II) > Zn(II), Co(II) > Mn(II), which agrees with that of the Irving-Williams series. Additionally, the order of the extraction for trivalent metal ions in CPME partly agrees with the order of extraction constants ($K_{ex}$) in chloroform reported in previous papers; Fe(III) ($\log K_{ex} = 4.11$), Ga(III) ($\log K_{ex} = 3.72$) > In(III) ($\log K_{ex} = 0.89$) [24,30].

Figure 5 shows the extraction behavior of In(III) using CPME in different diluents as a function of the equilibrium pH. [HQ]=50 mM, [In(III)]=1 mM.
behavior of In(III) using HQ in different diluents as a function of the equilibrium pH. In(III) was quantitatively extracted using HQ in all diluents at a pH value greater than 3. The order of In(III) extraction in each solvent was chloroform > 1-octanol > toluene > CPME. The order does not correlate with the hydrophobicity of the solvents; chloroform ($\log P = 1.97$), 1-octanol ($\log P = 2.70$), toluene ($\log P = 2.57$), CPME ($\log P = 1.65$). Additionally, the order is quite different to that for Cu(II) extraction using D2EHPA in our previous study [9]; dodecane > CPME > toluene, chloroform. In chloroform, In(III) was extracted using HQ under lower pH conditions compared with other diluents. Mottola and Freiser [30] suggested that the distribution constant value for HQ between chloroform and water is higher than that of other halogenated hydrocarbons due to its hydrogen-bonding ability. Probably CPME does not stabilize the chelating complex between HQ and metal cation, resulting in lower extractability.

The pH for 50% extraction of metal ions ($\text{pH}_{50}$) using HQ in CPME and toluene was determined to compare the extractabilities (Table 2). As the extraction using HQ proceeds via proton exchange, a lower $\text{pH}_{50}$ value means higher extractability. The $\text{pH}_{50}$ values for each metal ion in the CPME system is almost similar to that in toluene. As the order of metal extraction in CPME also agrees with that in chloroform [24,30], the selectivity of metal ions in the CPME system is similar to that in the conventional solvent system.

| Solvent | Fe(III) | Ga(III) | In(III) | Mn(II) | Co(II) | Ni(II) | Cu(II) | Zn(II) | Cd(II) |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| CPME    | 2.60   | 2.51   | 2.81   | 6.13   | 4.23   | 3.67   | 2.28   | 4.00   | 5.03   |
| toluene | 2.81   | 2.17   | 2.68   | 6.57   | 4.19   | 3.48   | 2.24   | 3.97   | 5.21   |

3.3 Extraction equilibrium of In(III) using HQ in CPME

In order to study the extraction mechanism in CPME, the extraction reaction for In(III) using HQ in CPME and toluene was investigated using slope analysis. Figure 6 shows the effect of the equilibrium pH on the distribution ratio of In(III) using HQ in CPME. The slope of the relationship between log$D$ versus the equilibrium pH was 3, which suggests that three hydrogen ions were released from HQ into the aqueous phase.

Figure 7 shows the effect of the equilibrium concentration of HQ on the distribution ratio of In(III) in CPME. The slope of the relationship between log$D$ versus the logarithm of the equilibrium concentration of HQ was 3, which indicates that three HQ molecules take part in the extraction of In(III).

From the results of the slope analysis in Figures 6 and 7, the extraction reaction for In(III) using HQ can be expressed as in Equation (5);

$$\text{In}^{3+} + 3\text{HQ} = \text{In}^{3+}(\text{Q}^-)_3 + 3\text{H}^+$$  \hspace{1cm} (5)

Bars denote the species in the organic phase. The extraction reaction agrees with that of In(III) using HQ in chloroform as reported in a previous paper [1,24]. The extraction equilibrium constant $K_{ex}$ is given by Eq. (6)
and the distribution ratio of In(III) between the organic and aqueous phases is defined as

\[
D = \frac{[\text{In}^{3+}_{\text{org}, \text{eq}}]}{[\text{In}^{3+}_{\text{aq}, \text{eq}}]} = \frac{[\text{In}^{3+}(Q\_3)]}{[\text{In}^{3+}]} \quad \text{(7)}
\]

By combining Eqs.(6) and (7), Eq. (8) and expressing in its logarithmic form the following equation is obtained:

\[
\log D = 3\text{pH} + 3\log[\text{HQ}] + \log K_{\text{ex}} \quad \text{(8)}
\]

The experimental logD data for the extraction of In(III) using HQ as a function of equilibrium pH and HQ concentration are plotted in Figure 8. The logarithm of the extraction equilibrium constant (log\(K_{\text{ex}}\)) of In(III) in CPME was evaluated from the intercept of the straight line with the ordinate in Figure 8 as −3.25, which is smaller than that in chloroform (log\(K_{\text{ex}}\) =0.89) [1,24].

Figure 6. Effect of the equilibrium pH on the distribution ratio of In(III) using HQ in CPME. [HQ] = 50 mM, [In(III)] = 1.0 mM.

\[
K_{\text{ex}} = \frac{[\text{In}^{3+}(Q\_3)]}{[\text{In}^{3+}][\text{HQ}]} \quad \text{(6)}
\]

Figure 7. Effect of the equilibrium concentration of HQ on the distribution ratio of In(III) in CPME. pH\text{eq} 2.70 ± 0.07, [In(III)] = 1.0 mM.

Figure 8. Effect of the equilibrium pH and the concentration of HQ on the distribution ratio of In(III). circles; result of pH dependency, diamonds; result of HQ concentration dependency.
3.4. Back extraction of In(III)

As the extraction using HQ proceeds via proton exchange reaction, back extraction tests were conducted using mineral acids. Table 3 shows the back extraction percentage of In(III) extracted using HQ into CPME using each mineral acid. From the results, In(III), extracted using HQ, was quantitatively recovered from the CPME phase into the aqueous phase using any of the mineral acids.

| mineral acid | B.E. [%] |
|--------------|----------|
| 0.1 M HNO₃  | 98.8     |
| 0.3 M HNO₃  | 100      |
| 1.0 M HNO₃  | 100      |
| 3.0 M HNO₃  | 100      |
| 8.0 M HNO₃  | 100      |
| 1.0 M HCl   | 97.2     |
| 0.05 M H₂SO₄| 100      |

4. Conclusion

CPME was found to be a good solvent for various chelating extractants in solvent extraction systems. In the present study, the extraction behavior of metal ions using HQ in CPME was studied. The degree of extraction of HQ in CPME for In(III) is lower than that in chloroform, and is comparable to that in toluene. HQ in CPME enables quantitative transfer of In(III) through a proton-exchange reaction, which is the identical extraction mechanism to the chloroform system. From the results, CPME can be used as a solvent for chelating extractants which are not soluble in aliphatic solvents. For chelating extractants dissolved in toxic solvents such as chloroform, CPME would be an alternative solvent.

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