## Extraction Behavior of Metal Ions Using D2EHPA
## in Cyclopentyl Methyl Ether

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Cyclopentyl methyl ether (CPME) has been developed as a commercially available ethereal solvent for application to various chemical processes. In the present study, the extraction of transition metal ions using di-(2-ethylhexyl) phosphoric acid (D2EHPA) in CPME and dodecane was studied in order to evaluate the potential of CPME as a diluent in the liquid-liquid extraction process. Transition metal ions were extracted by a proton exchange reaction using D2EHPA in CPME. The degree of extraction into CPME was reduced compared with dodecane. The extraction reaction of Cu(II) using D2EHPA in CPME and dodecane was confirmed by slope analysis. A 2 : 1 complex between dimeric D2EHPA and Cu(II) was formed in CPME and dodecane, and the extraction equilibrium constants were determined.

## 1. Introduction

In the liquid-liquid extraction process, extractants are generally diluted in water-immiscible organic solvents to control the concentration and reduce viscosity [1]. Diluents should show high solubility for the extractant and the metal-extractant complex, while simultaneously showing a low solubility in water. Additionally, the boiling point should be high for safety. Generally, aliphatic hydrocarbons such as kerosene are used as diluents. If the solubility of the extractant in aliphatic hydrocarbons is low, aromatics are also employed as diluents. Addition of modifiers such as phenols and alcohols is also performed to improve the solubility and prevent third phase formation.

Oxygen-containing solvents are good diluents for amphiphilic extractants because of their moderate polarity. However, typical ethereal solvents such as diethyl ether ($Et_2O$), tetrahydrofuran (THF), and 1,4-dioxane (DO) are not good as diluents in liquid-liquid extraction because of their low boiling points and high solubility in water. Recently, cyclopentyl methyl ether (CPME, Fig. 1) was developed as a commercially available ethereal solvent. Table 1 summarizes the physical properties of CPME and other organic solvents. CPME is more hydrophobic (logP = 1.59) and less soluble in water (solubility in water =1.1/100g) compared with typical ethereal solvents. Additionally, CPME has a relatively high boiling point, suppressed peroxide formation, stability under acidic and basic conditions, and a narrow explosion range [2]. On the basis of its favorable properties, application of CPME as a process solvent in organic synthesis has been studied [3,4]. However, there has been no study wherein CPME was used as a diluent in liquid-liquid extraction processes for metal ions.
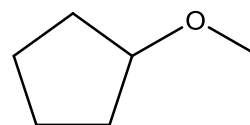


Figure 1. Molecular structure of CPME.

In the present study, the application of CPME as a diluent for liquid-liquid extraction processes was confirmed. The extraction behaviors of transition metal ions using di-2-(ethyl-2-hexyl) phosphoric acid (D2EHPA, Fig. 2) in CPME and dodecane were compared to determine the effect of the diluent on the extraction. D2EHPA is one of the most popular acidic extractants for liquid-liquid extraction processes and has been used in various processes for the purification of metals such as uranium, rare earths, and zinc [5-8]. The extraction reaction for Cu(II) in CPME and dodecane was confirmed and the extraction equilibrium constants were determined.

Table 1. Physical properties of CPME and other organic solvents [2].

| | CPME[*] | THF[*] | Et$_2$O[*] | DO[*] | dodecane | toluene | CHCl$_3$[*] |
|---|---|---|---|---|---|---|---|
| density (20℃) [g/cm$^3$] | 0.86 | 0.89 | 0.71 | 1.03 | 0.75 | 0.86 | 1.48 |
| boiling point [℃] | 106 | 65 | 34.6 | 101 | 216 | 111 | 61 |
| viscosity [cP] | 0.55 | 0.55 | 0.245 | 1.31 | 1.47 | 0.59 | 0.57 |
| dielectric constant [-] | 4.76 [a] | 7.58 [a] | 4.20 [a] | 2.23 [a] | 2.0 [b] | 2.38 [c] | 4.8 [d] |
| solubility in water [g/100g] | 1.1 [c] | ∞ [c] | 6.5 [c] | ∞ [c] | $3.7\times10^{-7}$ [a] | $5.2\times10^{-2}$ [a] | 0.82 [d] |
| log$P$[**] | 1.59 | 0.47 | 0.89 | -0.42 | 6.80 | 2.73 | 1.97 |

a;at 25℃, b; at 30℃, c; at 23℃, d; at 20℃.

*CPME; cyclopentyl methyl ether, THF; tetrahydrofuran, Et$_2$O; diethyl ether, DO; 1,4-dioxane, CHCl$_3$; chroloform.

** the logarithm of the partitioning coefficient between $n$-octanol and water

## 2. Experimental

### 2.1 Materials

Analytical grade iron(III), magnesium(II), calcium(II), manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) chlorides (Wako Pure Chemical Ind. Ltd., Japan) were used to prepare test solutions of the metal ions. Analytical grade D2EHPA (Tokyo Kasei Co., Japan) and CPME (Wako Pure Chemical Ind. Ltd., Japan) for the extraction tests were purchased and used without further purification. All other reagents and solvents were of analytical grade and were used as received.

### 2.2. Extraction of metal ions using D2EHPA in CPME and dodecane

Liquid-liquid extraction tests were conducted by the batchwise method and a typical procedure was as follows: The aqueous solution was prepared by dissolving 0.1 mM metal ions Fe(III), Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cu(II) or Zn(II). The pH of the aqueous solutions was adjusted using 100 mM HEPES (4-(2-hydroxyethyl)-1- piperazineethanesulfonic acid) buffer and a small quantity of HCl or NaOH. Organic solutions were prepared by dissolving 20 mM D2EHPA in CPME or dodecane. Equal volumes (10 cm$^3$) of the aqueous and organic solutions were mixed in a



Figure 2. Molecular structure of D2EHPA.

stoppered Erlenmeyer flask and shaken (120 rpm) in a thermostated water bath at 30 °C. After shaking for 3 h to attain equilibrium, each phase was separated and the equilibrium pH was measured. In a similar
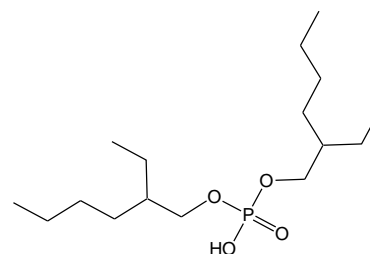
manner, an aqueous solution containing 0.1 mM metal ion was mixed with an organic solution without D2EHPA, followed by shaking and phase separation to determine the initial concentration of metal ions. The initial and equilibrium concentrations of metal ions in the aqueous phases were determined using 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 (1) and (2);

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

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

where $[M]_{aq,init}$ and $[M]_{aq,eq}$ represent the initial and equilibrium concentrations of the metal ions in the aqueous phase. $[M]_{org,eq}$ 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.

## 2.2. Back Extraction of Cu(II)

The forward extraction of 0.1 mM Cu(II) with 20 mM D2EHPA in CPME at pH 6.0 was performed from the aqueous to the organic phase (50 cm$^3$/50 cm$^3$) in a similar manner to that in the above section. The organic phase containing Cu(II) was divided into 10 cm$^3$ portions, and each solution was contacted with a 10 cm$^3$ fresh aqueous solution containing a different mineral acid. Both phases were mixed and shaken at 30°C for 3 h. The stripping solution was separated from the organic phase and the back extraction percentage (B.E. [%]) was calculated according to Eq. (3).

$$B.E.[\%] = \frac{[Cu(II)]_{aq,eq}}{[Cu(II)]_{org,init}} \times 100 \tag{3}$$

where $[Cu(II)]_{org,init}$ represents the initial concentration of the metal ion in the organic phase and $[Cu(II)]_{aq,eq}$ is the total concentration of the metal ion in the aqueous phase after equilibrium. The stripping tests were conducted twice using different mineral acids.

## 3. Results and Discussion

### 3.1 Extraction of metal ions using D2EHPA in CPME

Since CPME is almost immiscible in water as shown in Table 1, the upper CPME organic phase remained separated from lower aqueous phase in the liquid-liquid extraction tests. However, a small quantity of CPME (1.1 g in 100 g water, as shown in Table 1) is dissolved in the aqueous phase.

Figure 3 shows the extraction profiles of the metal ions using D2EHPA in CPME as a function of pH. As the extraction of the metal ions with the acidic extractant D2EHPA proceeds by a proton-exchange reaction, the extraction increased with increasing pH value. Fe(III) was extracted under strong acidic conditions, in the divalent metal ion series, Zn(II) was selectively extracted as shown in previous studies [9, 10]. The order of extraction in CPME was Fe(III) > Zn(II) > Cu(II), Mn(II), Ca(II) > Co(II), Mg(II), Ni(II). The order is comparable with that in kerosene reported in a previous study, however the order was slightly
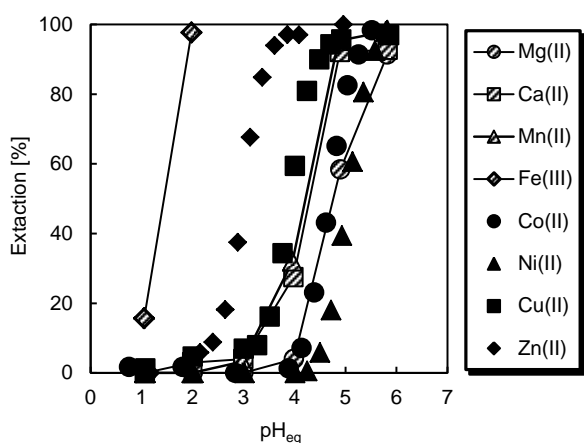
Figure 3. Effect of the equilibrium pH on the extraction of metal ions using D2EHPA in CPME. [D2EHPA]=20 mM, [metal ion]=0.1 mM.
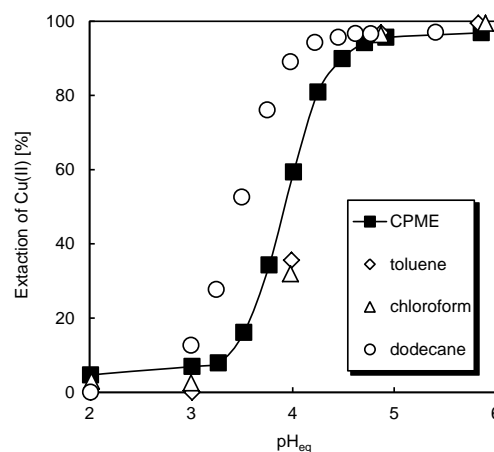
Figure 4. Extraction profiles of Cu(II) using D2EHPA in different diluents as a function of the equilibrium pH. [D2EHPA]=20 mM, [Cu(II)]=0.1 mM.

different; Zn(II) > Ca(II) > Mn(II) > Cu(II) > Co(II) > Ni(II) > Mg(II) [10].

Figure 4 shows extraction profiles of Cu(II) using D2EHPA in different diluents as a function of pH. Cu(II) was quantitatively extracted using D2EHPA in all diluents at pH value greater than 5. In dodecane, Cu(II) was extracted under more acidic conditions compared with other diluents. The extraction of Cu(II) in CPME was slightly higher than for toluene and chloroform. The order of Ni(II) and Co(II) extraction using D2EHPA was reported as follows [11]; *n*-heptane > *n*-butylether > toluene, which is comparable with that in this study; dodecane > CPME > toluene. Additionally, the order of Cu(II) extraction using D2EHPA in dodecane, toluene, and 1-octanol was also reported; dodecane > 1-octanol > toluene [12]. The diluent can interact with the extractant molecules, which affects the activity of the extractant and changes the extraction performance of the extractant, as well as the extracted metal complex, which may change the composition of the complex through coordination and/or substitution of the diluent molecules [11-13]. The polarity of the diluent is suggested to be one of the important parameters that reduces the effectiveness of the extraction [1].

**3.2 Extraction equilibrium of Cu(II) using D2EHPA in CPME**

The extraction reaction for Cu(II) using D2EHPA in CPME and dodecane was investigated using slope analysis. Figure 5 shows the effect of equilibrium pH on the extraction of Co(II), Ni(II), Cu(II) and Zn(II) using D2EHPA. The logarithm of the distribution ratio increased with increasing equilibrium pH. The slope of the relationship between logD versus the equilibrium pH was 2, which indicates that two hydrogen ions were released from the extractant into the aqueous phase.

D2EHPA exists as a dimeric species in various organic solvents. The logarithm of the dimerization constant for D2EHPA in various organic solvents (kerosene, toluene, hexane, isooctane, octane, chloroform, heptane) is in the range of 4.32-5.10 [14-17], suggesting that most D2EHPA molecules are dimerized in the extraction phase. Therefore, the extraction data as a function of the extractant concentration was analyzed using plots of logD versus the logarithm of the equilibrium concentration of the dimeric D2EHPA
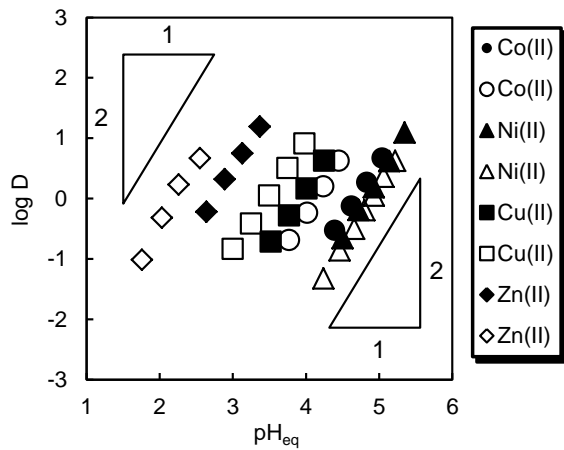
Figure 5. Effect of the equilibrium pH on the distribution ratio of Co(II), Ni(II), Cu(II) and Zn(II) using D2EHPA. Filled keys; in CPME, open keys; in dodecane. [D2EHPA]=20 mM, [metal ion]=0.1 mM.
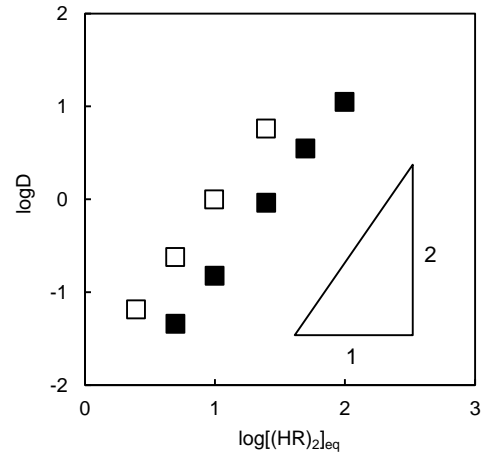
Figure 6. Effect of the dimer concentration of D2EHPA on the distribution ratio of Cu(II). Filled key; in CPME, open key; in dodecane. $pH_{eq}$ 3.5±0.01, [Cu(II)]=0.1 mM.

$((HR)_2)$. Figure 6 shows the effect of the dimer concentration of D2EHPA on the distribution ratio of Cu(II). The slope of the relationship between logD versus the logarithm of the equilibrium concentration of $(HR)_2$ is two, which indicates that two D2EHPA dimers take part in the extraction of Cu(II). The stoichiometry agrees with that reported in previous papers [12, 18, 19].

From the results of slope analysis, the extraction reaction for Cu(II) using D2EHPA can be expressed as in Equation (4);

$$Cu^{2+} + 2\overline{(HR)_2} = \overline{Cu^{2+}(R^-)_2(HR)_2} + 2H^+ \tag{4}$$
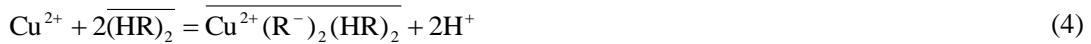
Bars denote the species in the organic phase, and $(HR)_2$ denotes the D2EHPA dimer. The extraction equilibrium constant $K_{ex}$ is given by Eq. (5)

$$K_{ex} = \frac{\overline{[Cu^{2+}(R^-)_2(HR)_2]}[H^+]^2}{[Cu^{2+}][\overline{(HR)_2}]^2} \tag{5}$$

and the distribution ratio of Cu(II) between the organic and aqueous phases is defined as

$$D = \frac{[Cu^{2+}]_{org,eq}}{[Cu^{2+}]_{aq,eq}} = \frac{\overline{[Cu^{2+}(R^-)_2(HR)_2]}}{[Cu^{2+}]} \tag{6}$$

By combining Eqs.(5) and (6), Eq. (7) in its logarithmic form is obtained:

$$logD = 2pH + 2log[\overline{(HR)_2}] + logK_{ex} \tag{7}$$

The experimental logD data for the extraction of Cu(II) using D2EHPA are plotted in Fig. 7. The extraction equilibrium constants $(K_{ex})$ of Cu(II) were evaluated from the intercept of the straight line with the ordinate of Fig. 7 as $2.52 \times 10^{-4}$ [-] in CPME and $1.44 \times 10^{-3}$ [-] in dodecane, respectively. Thus the

extractability of D2EHPA in ethereal solvents is slightly reduced compared with aliphatic solvents as shown in previous reports [11, 12].
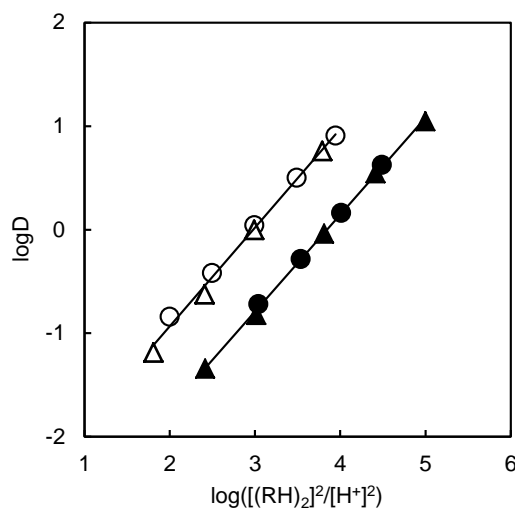


Figure 7. Effect of equilibrium pH and the dimeric concentration of D2EHPA on the distribution ratio of Cu(II). Filled keys; in CPME, open keys; in dodecane, circles; result of pH dependency, triangles; result of D2EHPA concentration dependency.

### 3.3. Back extraction of Cu(II)

Table 2 summarizes the back extraction percentage of Cu(II) from extracting phase using each stripping agent. As shown in Table 2, Cu(II) extracted with D2EHPA was quantitatively stripped into the aqueous phase using mineral acids. There is therefore no obstacle to the use of CPME as the diluent in liquid-liquid extraction processes in view of the stripping of the extracted metal ions.

Table 2 Back extraction of Cu(II).

| Stripping agent | B.E. [%] |
| --- | --- |
| 0.1 M HCl | 100 |
| 1.0 M HCl | 100 |
| 0.05 M $H_2SO_4$ | 100 |
| 0.5 M $H_2SO_4$ | 100 |
| 0.1 M $HNO_3$ | 100 |
| 1.0 M $HNO_3$ | 100 |

### 4. Conclusion

CPME was found to be a potential diluent in liquid-liquid extraction processes. However, a small quantity of CPME is dissolved in the aqueous phase. CPME is manufactured by the methylation of cyclopentanol or the addition of methanol to cyclopentene [4]. If a longer alkyl chain is introduced to the cyclopentane scaffold, the resulting ethereal compound should be less soluble in water. The extraction efficiency in CPME is slightly reduced compared with that in an aliphatic solvent because of polarity. CPME could take part in the octahedral coordination of Ni(II) due to the polarity of the ethereal oxygen [11], however, determination of the extraction reaction of Ni(II) is still under study.

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