Liquid-liquid Extraction of Copper(II), Cadmium(II), Lead(II) and Zinc(II) from Perchlorate and Tartrate Media by Di-2-methylnonylphosphoric Acid into Heptane

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The liquid-liquid extraction equilibrium of Cu(II), Cd(II), Pb(II) and Zn(II) from 0.10 M perchlorate medium by di-2-methylnonylphosphoric acid (DMNPA) as an extractant dissolved in heptane has been investigated. By using a slope analysis of method and the theory of charge balance, the extracted species were found to be $CuA_2 \cdot 3HA$, $CdA_2 \cdot 3HA$, $PbA_2 \cdot 3HA$ and $ZnA_2 \cdot HA$. The metal extractability decreased in the order of Zn(II)>Pb(II)>Cd(II)>Cu(II). The distribution coefficient of Cu(II) was also found to decrease with increasing concentrations of tartrate at a fixed DMNPA concentration. When tartrate was added to perchlorate media, the extracted Cu(II) species was suggested to form a less-extractable one containing dissociated tartrate molecule.

Key Words: Liquid-liquid Extraction, Di-2-methylnonylphosphoric Acid, Heavy Metal Ions, Perchlorate, Tartrate

1. Introduction

Such heavy metal ions as Cu(II), Cd(II), Pb(II) and Zn(II) are biologically important, because a variety of living organisms accumulate them in bodies from the polluted environment and may take any damage and disorders. Being highly toxic, these metal ions in water and soil must be restricted at concentrations as low as possile, although some of them are known as the vital elements to maintain the biological functions [1], [2]. Serious problems arising from aqueous effluents containing these heavy metal ions have still been encountered in the fields of mining industry, waste water treatment, incineration of wasters and spent batteries recycling. A great deal of attention has been paid to advances in the engineering and increasing demands for the process control of such kinds of hazardous metals. The environmental pollution of industrial wastes has greatly been improved except some of developed nations. Although a range of treatment methods have been used for the separation of these heavy metal ions in various matrices [3], [4], the two phases partitions-based separation has still been interested in the fields of inorganic chemistry, separation science and technology, purification and recovery of metal compounds. Being a simple and efficient process, high performance centrifugal partition chromatograph (HPCPC) has been used as one of the separation techniques for desired metal ions from aqueous solutions by using highly selective extractants [5].

We have reported the extraction behavior of transition and rare earth metal ions using bis-2-ethylhexylphosphoric acid, and di-2-methylnonylphosphoric acid (abbreviated as DMNPA) [6]-[9]. Although DMNPA has been found to extract metal ions from highly acidic solution due to high molecular weight and long hydrophobic chains, it is interesting that the separation efficiencies on the extraction of heavy metal ions are expected to be relatively large.

In this paper, we describe the solvent extraction of Cu(II), Cd(II), Pb(II) and Zn(II) from aqueous perchlorate media by DMNPA in heptane. The metal species extracted into the organic solution and their corresponding extraction constants have been discussed by the slope analysis of method. The effect of tartrate concentration on the Cu(II) extraction, further, has been

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studied as a representative among the metal ions.

2. Exparimental

2.1 Reagents

DMNPA (purity≥96%) was kindly supplied by Daihachi Chemical Industries (Osaka, Japan) and used without further purification. Heptane of reagent grade (Wako Pure Chemical Industries, Tokyo, Japan) was used as the organic solvent. Standard solutions of heavy metal ion were prepared by dissolving the corresponding metal perchlorates in perchlorate or tartrate media before extraction.

All other chemicals were of analytical reagent grade and used without further purification. All standard solutions and buffers were prepared with distilled water.

2.2 Apparatus

An Iwaki Model V-S KM shaker was used to equilibrate the aqueous and organic phase. A TOA-DKK Model IM-55G Ion Meter equipped with a Model GST-5721C glass electrode (TOA-DKK Electronics Co. Ltd., Tokyo, Japan) was used to measure pH of the aqueous phase. An APEL spectrophotometer (Model PD-303) was used for determination of metal ions in the aqueous phase after complexation with 4-(2-pyridylazo) resorcinol (PAR).

2.3 Procedures

Extraction experiments were carried out at 298±1 K by shaking both aliquots of 10.0 cm³ of the aqueous and organic phases in a 50-cm³ separation funnel using a mechanical shaker. The initial concentration of metal ions was 5.0×10^{-4} M, and the ionic strength of the aqueous phase was maintained at 0.10 with sodium perchlorate or with tatarate. The concentration of DMNPA in the heptane phase was varied in the range of 0.012~0.24 M. The distribution coefficient (D) was obtained as a function of pH. The pH of aqueous phase was adjusted by addition of NaOH or $HClO_4$. A shaking time of 30 minutes was enough to get the extraction equilibrium. After the two phases were allowed to separate completely, the equilibrium pH was measured with the pH meter. The concentration of metal ions in the aqueous phase was determined by the following two methods: one was the titration using 5.0×10^{-4} M EDTA standard solution with 1-(2-pyridylazo)-2-naphthol (PAN)

as the indicator for Cu and Cu-PAN for other metal ions, and another was the spectrophotometric determination of the metal ions using PAR. The concentration of the metal ion in the organic phase was calculated as the difference between the initial and equilibrium concentrations of the aqueous phase. By the slope analysis and the non-linear least square analysis of methods, the composition of the extracted species and the extraction equilibrium constant were estimated.

3. Results and discussion

3.1 Extraction of Cu(II), Cd(II), Pb(II) and Zn(II) complexes with DMNPA from perchlorate medium

Fig.1 shows the relationship between log$D$ and pH for the four metal ions with DMNPA in heptane as the organic phase. The D values all increased with increasing pH of the aqueous phase. All the slopes of the lines shown in Fig.1 were about 2, suggesting that the extracted metal species were neutral and inner complexes. The extractability decreased in the order of Zn(II)>Pb(II)>Cd(II)>Cu(II).

If a x-merized divalent metal complex with DMNPA, $M_xA_{2x}(HA)_n$, is extracted in heptane, the extraction equilibrium between the metal ion (M^{2+}) and extractant (HA) can be written as:

$$x M_{aq}^{2+} + \frac{2x+n}{2}(H_2A_2)_{org} \longrightarrow M_xA_{2x}\cdot(HA)_{n,org} + 2xH_{aq}^{+} \quad (1)$$

where the subscripts "aq" and "org" refer to the aqueous and organic phase, respectively. The n value denotes the number of DMNPA molecule involved in the extracted metal species. Assuming that all chemical species are present at very low concentrations in both phases, the extraction equilibrium constant (K_{ex}) of the metal complex may be expressed as:

$$K_{ex} = \frac{[M_x A_{2x}(HA)_n]_{org}[H^+]_{aq}^{2x}}{[M^{2+}]_{aq}^x[HA]_{2,org}^{(2x+n)/2}} \quad (2)$$

The total concentration of the metal complex in the organic phase is written as follow:

$$[M_xA_{2x}(HA)_{n,org}] =$$
$$\sum_x \sum_n K_{ex}[M^{2+}]^x[H_2A_2]^{(2x+n)/2}[H^+]^{2x} \quad (3)$$

$$\log[M_xA_{2x}(HA)_n]_{org} = (2pH + \log[M^{2+}]_{aq} +$$
$$\log[H_2A_2]_{org})x + \frac{n}{2}\log[H_2A_2]_{org} + \log K_{ex} \quad (4)$$
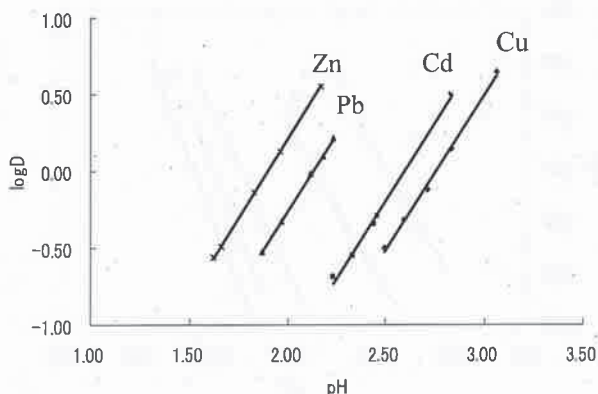
Fig. 1　Effect of pH on the distribution ratio of metal ions by DMNPA in heptane
Concentration of metal ion in aqueous phase: 5.0×10^{-4} M; organic phase: 0.048 M DMNPA/heptane; aqueous phase: 0.10 M perchlorate.

According to Eq.(4), the degree of polymerization of the extracted species (x) can be found from the plot of $\log[M_xA_{2x}(HA)_n]_{org}$ against ($2pH + \log[M^{2+}]_{aq} + \log[H_2A_2]_{org}$) at constant $[H_2A_2]_{org}$ in heptane. The plot should be a straight line with a slope of x. The slope analysis of method has been used to ensure the degree of polymerization of the extracted species in the organic phase. Table 1 summarizes the results obtained for the extraction of Cu(II), Cd(II), Pb(II) and Zn(II) by using linear regression analyses. The straight lines with slopes close to unity were obtained for the four heavy metal ions (Table 1), indicating that only monomeric species were extracted in heptane when 5.0×10^{-4} M each metal ion was initially taken.

The following equation can be derived from Eq.(4):

$$\log D - 2xpH = \frac{n+2x}{2}\log[H_2A_2]_{org} + \log K_{ex} \qquad (5)$$

The number (n) of DMNPA molecule involved in the monomeric species can be determined from the slope ($\frac{n+2x}{2}$) of the plots of ($\log D - 2xpH$) against $\log[H_2A_2]_{org}$. As shown in Fig.2, the slopes of the straight lines obtained for Cu(II), Cd(II), Pb(II) and Zn(II) were found to be 2.50, 2.52, 2.53 and 1.5, respectively. The intercepts of the lines correspond to $\log K_{ex}$ values. Table 2 summarizes the results obtained for the extracted species, extraction equilibria and their constants.

Table 1 Results of linear regression analyses for the determination of x-values in the extraction of heavy metal ions by DMNPA

Ions	0.012 M			0.024 M		
	a	b	r^2	a	b	r^2
Cu(II)	1.00	-4.97	0.994	0.99	-4.59	0.995
Cd(II)	0.96	-4.51	0.998	1.02	-4.01	0.987
Pb(II)	1.04	-3.42	0.990	1.04	-3.06	0.998
Zn(II)	0.94	-2.40	0.996	1.00	-2.26	0.996

Ions	0.036 M			0.048 M		
	a	b	r^2	a	b	r^2
Cu(II)	0.97	4.32	0.977	0.98	-3.88	0.983
Cd(II)	0.96	-3.85	0.998	1.00	-3.50	0.981
Pb(II)	1.06	-2.81	0.998	1.04	-2.60	0.998
Zn(II)	1.04	-2.20	1.000	1.04	-2.11	0.999

Ions	0.12 M			0.24 M		
	a	b	r^2	a	b	r^2
Cu(II)	0.97	-3.56	0.978	0.93	-3.02	0.992
Cd(II)	1.02	-2.91	0.998	1.00	-2.59	0.994
Pb(II)	1.01	-1.95	0.999	0.97	-1.51	0.995
Zn(II)	1.00	-1.90	1.000	1.00	-1.74	0.986

a = intercept, b = slope and r^2 = correlation coefficient for the regression equations.

3.2 Extraction of Cu(II), Cd(II), Pb(II) and Zn(II) complexes with DMNPA from tartrate medium

The half-extraction pH values of the metal extraction from both perchlorate and tartrate media were determined using 0.12 M DMNPA in heptane. The results shown in Table 3 indicate that the Cu(II) extraction had a serious influence by the presence of tartrate, being apart from the other three metals. Therefore, the extraction equilibrium of Cu(II) from tartrate medium was investigated. The relationships between log D and pH were investigated at different concentrations of DMNPA in heptane while the tartarate (H_2L) concentration was kept at 0.05 M. The linear plots were obtained at all DMNPA concentrations investigated, as shown in Fig.3. The slopes of the lines shown in Fig.3 were about 1.0 and 1.5 at relatively high concentrations of DMNPA (0.12 M and 0.06 M) and at lower concentrations of 0.036 M and 0.024 M, respectively. This suggests that two kinds of the Cu(II) species were extracted into the heptane phase in the region of slope 1.5. In the region where the hydrogen ion dependency is unity, on the other hand, the dissociated tartrate ion seems to take part in the

extraction followed by formation of less-extractable metal species; tartaric acid has the two pKa values 3.04 and 4.37. We presume that judging from the slope analysis and the charge balance theory, the following two equations can be expressed in the tartrate extraction system:
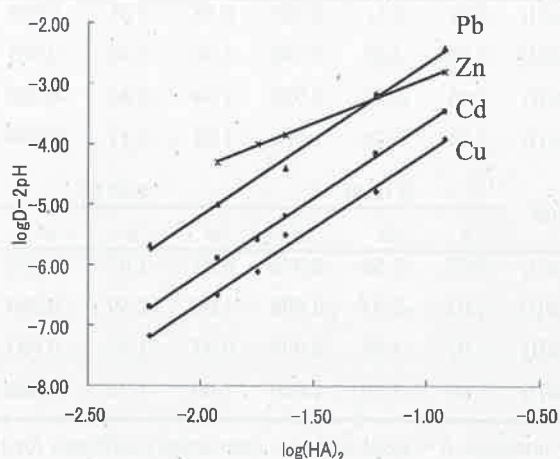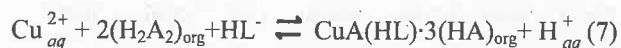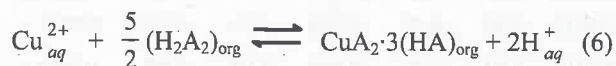
$$Cu_{aq}^{2+} + \frac{5}{2}(H_2A_2)_{org} \rightleftharpoons CuA_2 \cdot 3(HA)_{org} + 2H_{aq}^+ \quad (6)$$

$$Cu_{aq}^{2+} + 2(H_2A_2)_{org} + HL^- \rightleftharpoons CuA(HL) \cdot 3(HA)_{org} + H_{aq}^+ \quad (7)$$

Fig. 2 Determination of the number of DMNPA molecule involved in the monomeric species in heptane
Concentration of metal ion in aqueous phase: 5.0×10^{-4} M; organic phase: 0.012~0.24 M DMNPA/heptane; aqueous phase: 0.1 M perchlorate.

Table 2 Extraction species and conditional extraction constants of Cu(II), Cd(II), Pb(II) and Zn(II) with DMNPA in heptane at 298 K

Extracted species	$\log K_{ex}$	Extraction equilibrium
$CuA_2 \cdot 3HA$	-1.63	$Cu^{2+} + 5/2(H_2A_2) = CuA_2 \cdot 3HA + 2H^+$
$CdA_2 \cdot 3HA$	-1.11	$Cd^{2+} + 5/2(H_2A_2) = CdA_2 \cdot 3HA + 2H^+$
$PbA_2 \cdot 3HA$	-0.12	$Pb^{2+} + 5/2(H_2A_2) = PbA_2 \cdot 3HA + 2H^+$
$Zn A_2 \cdot HA$	-1.38	$Zn^{2+} + 3/2(H_2A_2) = ZnA_2 \cdot HA + 2H^+$

Table 3 Half-extraction pH values of heavy metal ions in different aqueous media with 0.12 M DMNPA in heptane at 298K

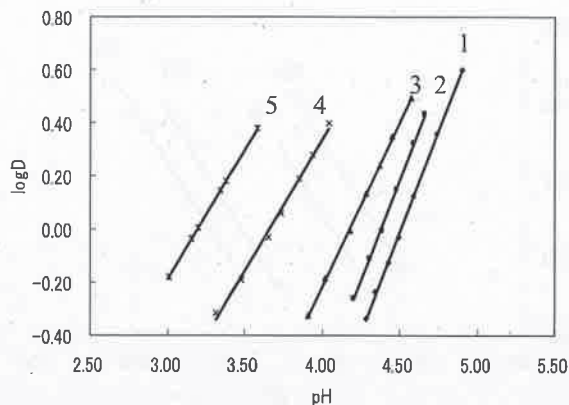|	Cu(II)	Cd(II)	Pb(II)	Zn(II)
0.10 M tartrate	3.54	2.03	1.63	1.56
0.10 M perchlorate	2.39	2.07	1.60	1.53

Fig. 3 Effect of pH on the distribution ratio of metal ions by DMNPA in heptane
Concentration of metal ion in aqueous phase: 5.0×10^{-4} M; organic phase: 1: 0.12 M DMNPA/heptane;
         2: 0.060 M DMNPA/heptane;
         3: 0.048 M DMNPA/heptane;
         4: 0.036 M DMNPA/heptane;
         5: 0.024 M DMNPA/heptane;
aqueous phase: 0.05 M perchlorate+0.05 M tartrate.

Effect of the tartrate concentration in the aqueous phase on distribution coefficient was investigated at different DMNPA concentrations. Fig.4 shows plots of $\log D$ against logarithm of tartrate concentration at pH 4.0. It was found that the distribution coefficient of Cu(II) decreased with increasing tartrate concentration when the initial Cu(II), DMNPA and H^+ concentrations were kept at certain values. The curves shown in Fig.4 also indicate that the slopes of 0 and -2 were obtained for the relationships between distribution coefficient and tartrate concentration when a non-linear square method was adopted. The following empirical equations can be expressed mathematically:

$$\log D = \log K_{ex} [H_2A_2]^2[H^+]^{-1} - \log(1 + K_{H_2L}[L^{2-}]) \quad (8)$$

In Eqs.(8), K_{H_2L} is a proportionality constant and the value was determined to be 9.1 by the curve-fitting method under the experimental conditions. The empirical equations were obtained for 0.024, 0.036, 0.048, 0.060, 0.12 M DMNPA, respectively.

$$\log D = 0.25 - \log(1 + 9.1[H_2L] \quad (9)$$
$$\log D = 0.45 - \log(1 + 9.1[H_2L]) \quad (10)$$
$$\log D = 0.8 - \log(1 + 9.1[H_2L]) \quad (11)$$
$$\log D = 1.25 - \log(1 + 9.1[H_2L]) \quad (12)$$
$$\log D = 1.8 - \log(1 + 9.1[H_2L]) \quad (13)$$

Using the equations described above, the log D values were calculated from any tartaric acid concentration in the aqueous phase and were then drawn as the solid lines shown in Fig.4. Obviously, the distribution coefficient of Cu(II) decreased with increasing tartaric ion concentration. The results suggest that at higher tartaric ion concentrations, the Cu(II) species forms a non-extractable CuL or $Cu(HL)_2$ in aqueous solution at pH between pKa_1 and pKa_2, and then less-extractable species [Cu(HL)A·3HA] with release of one hydrogen ion. At higher pH values than pKa_2 and low tartrate in concentrations, an extractable species [CuA_2·3HA] prevails. The extracted metal species, thus, is assumed to vary with the ratio of H_2L and HA concentration.
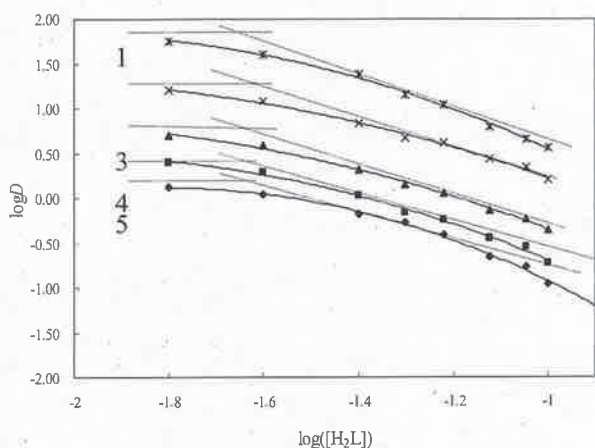

Fig. 4   Dependence of distribution ratio on tartaric
   acid concentration in aqueous phase
Cu(II) concentration in aqueous phase: 5.0×10^{-4} M;
Organic phase: 1: 0.12 M DMNPA/heptane;
                    2: 0.060 M DMNPA/heptane;
                    3: 0.048 M DMNPA/heptane;
                    4: 0.036 M DMNPA/heptane;
                    5: 0.024 M DMNPA/heptane;
ion strength of aqueous phase: 0.10;
tartrate concentration in aqueous phase: 0.01~0.09 M.

4. Conclusions

The results obtained in this work suggest that DMNPA can be used as an effective ligand for the extractant of heavy metal ions from perchlorate medium. The extracted metal species are all monomer when the concentration of metal ions is relatively low. The metal extractability is in the order of Zn(II)>Pb(II)>Cd(II)>Cu(II). The extracted species are CuA_2·3HA, CdA_2·3HA, PbA_2·3HA and ZnA_2·HA. In the tartrate system, the extracted species is assumed to form a mixed-ligand metal complex with DMNPA and tartrate.

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