

# Solvent Extraction Separation Study of Copper (II) , Iron (III) , Nickel (II) , and Cobalt (II) from Aqueous Solution with 2-Hydroxyphenylethylketone Oxime

Takehiro KOJIMA, Shinji UKITA\*, Kazuko HARA\*,  
and Yasumasa SHIGETOMI\*

*Department of Life Science, Faculty of Science, Okayama University of Science,  
1-1, Ridai-cho. Okayama 700-0005, Japan*

*\* Department of Chemistry, Faculty of Science, Okayama University of Science,  
1-1, Ridai-cho, Okayama 700-0005, Japan*

(Received September 29, 2004; accepted November 5, 2004)

Three aliphatic  $\alpha$ -oxime compounds have been prepared and characterized. These reagents are highly selective for the extraction of copper(II) and copper(I) from weakly acidic aqueous solution. Copper(II) is separated from nickel(II), cobalt(II) and iron(III). Iron(III) is reduced to iron(II) by the addition of ascorbic acid or hydroxylamine hydrochloride, and iron(II) was not extracted with the oximes. The extraction behavior of copper(I), copper(II) and iron(III) with these extractants is described in detail.

## 1. Introduction

Solvent extraction systems with  $\alpha$ -oxime compounds, such as Lix-63 and Kelex-100 have been reported in many papers<sup>1-6</sup>. Furthermore, to clarify the mechanism of selective extraction, many fundamental investigations have been done: the competitive extraction of copper(II)<sup>7</sup> and the kinetics of the copper extraction<sup>8,9</sup>. Also,  $\alpha$ -benzoin oxime was introduced in 1923 by Feigl<sup>10-11</sup> and Strebinger<sup>12</sup> for the micro-determination of copper(II) in ammoniacal solution. The use of aliphatic  $\alpha$ -hydroxy oxime compounds for copper(II) was not stressed until 1965, when Swanson reported that these oximes selectively extracted copper(II) from an acidic solution<sup>13</sup>. The development of many oxime extractants has taken place since this report. Also these extractants came to be used as well in the wet refining process of low quality metal resources showing a tendency to be complicated<sup>14</sup>.

In a previous paper<sup>15-16</sup>, we have reported on the separation of copper(II) from sea-water by the adsorption of cellulose-triacetate polymers containing  $\alpha$ -oxime compounds. The object of the present work is to investigate the possibility of the extraction and separation of copper(II) from a solution containing iron(III), nickel(II), and cobalt(II) by  $\alpha$ -oximes in carbon tetrachloride.

## 2. Experimental

### 2.1. Reagents and Apparatus

All the chemicals used were of analytical-reagents grade. A standard copper(II) solution was prepared by dissolving 0.393 g of copper(II) sulphate in 5 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> hydrochloric acid and diluting the

solution with deionized water to exactly 100 cm<sup>3</sup>. The concentration of copper(II) in the solution was standardized

by chelatometric titration by using Murexide as an indicator<sup>17</sup>. Stock solutions of other metal ions (10<sup>-2</sup> mol dm<sup>-3</sup>) were prepared by dissolving appropriate amounts of the salts in 100 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> hydrochloric acid.  $\alpha$ -benzoin oxime (cupron) was purchased from Nacalai tesque, and used without further purification.

Other oximes such as 2-hydroxyphenylethylketone oxime (HPEKO), 2-hydroxyacetophenone oxime (HAPO), and 2-hydroxy-4-octyloxybenzophenone oxime (HOBPO) were prepared in a similar manner<sup>15-16</sup>.

A Hitachi U-2000 spectrophotometer was used for the determination of metals. The pH of the solution was measured with a Hitachi-Horiba M-8 pH meter.

## 2.2. Preparation of $\alpha$ -hydroxy oxime compounds

2-Hydroxyethylketone oxime (HPEKO, C<sub>5</sub>H<sub>11</sub>NO<sub>2</sub>; mp; 94.7-94.8 °C) was prepared according to the procedure of Swanson<sup>14</sup>. Into a 500cm<sup>3</sup> flask equipped with a reflux condenser were charged 25.0 g (0.167 mol) 2-hydroxyamine hydrochloride, 30 cm<sup>3</sup> of pyridine, and 50 cm<sup>3</sup> of absolute ethanol. The reaction mixture was heated to reflux for 3 h, diluted with about 125 cm<sup>3</sup> and extracted with 50 cm<sup>3</sup> of diethyl ether. The aqueous layer was discarded. The ether layer was washed 4 times with water, twice with 3% hydrochloric acid and 4 more times with water. The ether layer was dried over anhydrous sodium sulfate, and after filtration the ether was removed by evaporation. The residue was dissolved in petroleum ether and cooled in an ice-bath. The solid compound had an analysis of C, 65.45%; H, 6.71%; N, 8.35% (calculated C, 65.45%; H, 6.67%; N, 8.45%). Other  $\alpha$ -hydroxy oxime compounds were prepared in a similar manner, as described above. Analyses of these compounds were as follow: 2-hydroxyacetophenone oxime (HAPO, C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>, mp. 115-115.7 °C) C, 63.02%; H, 5.98%; N, 9.25% (cal. C, 63.58%; H, 5.98%; N, 9.27%), 2-hydroxy-4-n-octyloxybenzophenone oxime (HOBPO, C<sub>21</sub>H<sub>27</sub>NO; mp. 80.0-81.7 °C) C, 73.99%; H, 7.92%; N, 3.98% (cal. C, 73.90%; H, 7.92%; N, 4.11%).

## 2.3 Extraction procedure

The extractions were done in stoppered centrifuge tubes using 2.0 cm<sup>3</sup> of organic phase and 5.0 cm<sup>3</sup> of aqueous phase. The aqueous phase, consisting of a solution of metal ions, with concentration (5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) in a buffer of given ionic strength ( $\mu$  = 0.1 mol dm<sup>-3</sup>, with potassium chloride) was shaken with the organic phase in a Test Tube Concentrator (A Taitec TC-10F) for 30 min at 25 °C. The phases were separated after centrifugation. Copper(II) and copper(I) were determined colorimetrically with bathocuproine<sup>18</sup>. Iron(III), nickel(II) and cobalt(II) were determined spectrophotometrically with 1,10-phenanthroline<sup>19</sup>, dimethyl glyoxime, and 2-(2-thiazoylazo)-4-methyl-5-(sulfomethylamine)benzoic acid<sup>20</sup>, respectively. Each distribution experiment was done in triplicate.

## 3. Results and Discussion

### 3.1. Extraction parameters

The reactivities of cupron, HPEKO, HAPO, and HOBPO for eleven metals were examined by the spot test method<sup>15</sup>. A negligible reaction was observed for aluminum(III), zinc(II), tungsten(VI) and molybdenum(VI). The formation of complexes with these oxime compounds were observed for copper(I), manganese(II), cobalt(II), nickel(II) iron(II), (III), and palladium(II). But copper(II), nickel(II), and iron(III) were observed as having a high reactivity. The time required to reach equilibrium at 25 °C was examined by measuring the copper(II) concentration in the aqueous phase after different intervals. Complete extraction was obtained in 10 min, but 30 min was chosen in a Test Tube Concentrator for subsequent experiments. Copper(II), copper(I), nickel(II), and iron(III) were extracted from solution in

the pH range of 2-8 with  $10^{-2}$  mol dm<sup>-3</sup> HPEKO carbon tetrachloride system. The results are shown in Fig.1. Copper(II) and copper(I) were quantitatively extracted from pH 3 to pH 8. The extraction of iron(III) increased with raising pH, and it was quantitatively extracted from above pH 4. Nickel(II) was extracted from pH 5, and the extraction increased with increasing pH. Iron(III) is readily reduced to iron(II) in the presence of ascorbic acid or hydroxylamine hydrochloride, and iron(II) was not extracted over the pH range of 2 to 8. But copper(I) was easily extracted. These results show that copper(II) and copper(I) can be separated from nickel(II) and iron(III).

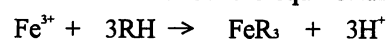
### 3.2. Separation of copper from iron, nickel and cobalt

From the above data, it is clear that copper can be separated from iron, nickel and cobalt with HPEKO in acidic solution. Typical results are shown in Table 1. Fritz et al. have reported<sup>18</sup> on the extraction of copper(II) with 5,8-diethyl-7-hydroxydodecane-6-oxime (DHDO) in toluene solution. That is, a green complex is formed at below 0.1 mol dm<sup>-3</sup> oxime concentration, and a brown complex is produced at higher oxime concentration. In the case of HPEKO, a green complex of copper(II) is produced at below 0.1 mol dm<sup>-3</sup> oxime concentration along with DHDO. Also, a brown complex is formed at higher HPEKO concentration.

### 3.3. Extraction behavior of copper with four kinds of oxime

Extraction of copper(II) from aqueous solution with HPEKO, HAPO, cupron, and HOBPO dissolved in carbon tetrachloride solution produce a brown-greenish complex in the organic phase. A plot of log D as a function of the concentration of oximes results in a straight line with a slope of about 2.0, as shown in Fig. 2. This indicates that 1:2 oxime-copper complex as formed. Also, a plot of log D vs. log hydrogen ion concentration yields a straight line with a slope of about 1.0, representing the loss of protons during the formation of the complex. The results are shown in Fig. 3. An experiment with continuously varying amounts of HPEKO and copper(II), (I) in acidic solution at pH 2 indicated that the extracted complexes had compositions of Cu(II):HPEKO=1:1.9, and Cu(I):HPEKO=1:1.1 from Fig. 4. Therefore, the species extracted in the organic phase were Cu(HPEKO)<sub>2</sub> and Cu(HPEKO). Also, from Fig. 3, The extractability of copper(II) was in the order HPEKO  $\geq$  HAPO > HOBPO > cupron. This tendency is similar to the adsorption of copper(II) by cellulose-triacetate polymer containing  $\alpha$ -oximes(RH) observed previously<sup>16</sup>.

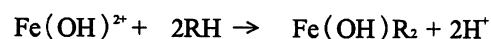
In the case of iron(III), third power dependence on the extraction is generally accepted, in which case the extraction mechanisms should follow the equilibrium.



But the results show that the slopes are +1.9 and +1.3 at pH 2 and pH 4, respectively, and may be considered a second power dependence on the extractant concentration. This value is perhaps due to the hydrolysis of iron(III) in the aqueous solution:



This behavior of iron(III) has been reported by Islam et al<sup>21</sup>. The species Fe(OH)<sup>2+</sup> may then react with  $\alpha$ -oximes as



and for which a slope of +2.0 is expected. A plot of log D as a function of the concentration of HPEKO results in a straight line with a slope of about 1.9, as shown in Fig. 5. The iron complex formed in the organic phase contains Fe(III):HPEKO in the mole ratio 1:2 for pH 2 and 3, indicating the composition of an Fe(OH)(HPEKO)<sub>2</sub> complex, which is in agreement with the finding of Islama et al<sup>21</sup>.

## References

1. H. A. Suter and P. W. West, *Anal. Chim. Acta*, 13 (1955) 501.
2. V. I. Lakshmanan and G. J. Lawson, *J. Inorg. Nucl. Chem.*, 37(1975) 207.
3. T. T. Tammi, *Hydrometallurgy*, 2 (1976/1977) 371.
4. A. W. Ashbrook, *Hydrometallurgy*, 1(1975) 5.
5. A. W. Ashbrook, *Coord. Reviews*, 16(1975) 285.
6. A. W. Ashbrook, *J. Chromatog.*, 105(1975) 141.
7. D. S. Flett, Cox, and J. D. Heels, *J. Inorg. Nucl. Chem.*, 37(1975) 2533.
8. J. D. Miller and R. L. Atwood, *J. Inorg. Nucl. Chem.*, 37(1975) 2539.
9. R. J. Whewell, M. A. Hughes and C. Hanson, *J. Inorg. Nucl. Chem.*, 37(1975) 2303.
10. F. Feigl, *Mikrochemie*, 1(1923) 74.
11. F. Feigl, *Ber.*, 56B(1923) 2083.
12. R. Strebinger, *Mikrochemie*, 1(1923) 72.
13. R. R. Swanson, U. S. Patent, 3,224,837(1965).
14. K. Murayama, *Sekiyu Gatsukaisi*(in Japanese), 20(1977) 608.
15. T. Kojim, N. Ono, Y. Shigetomi and Y. Yamamoto, *Anal. Sci.*, 5(1989) 185.
16. T. Kojima, T. Sowa, S. Kodama, M. Sato, Y. Shigetomi and Y. Yamamoto, *Anal. Chim. Acta*, 264(1992) 59.
17. K. Ueno, "Chelato Tekiteihou (Chelatometric Titration, in Japanese)", Nankodo Press, Tokyo(1972).
18. D. Blair, H. Diehl, *Talanta*, 7(1961) 163.
19. T. Yotsuyanagi, K. Goto, M. Nagayama and K. Aoyama, *Bunseki Kagaku*(in Japanese), 18(1969) 477.
20. Y. Shoji and T. Kakeuchi, *Bunseki Kagaku*(in Japanese), 14(1965) 551.
21. F. Islam, H. Rshman, and M. Ali, *J. Inorg. Nucl. Chem.*, 41(1979) 217.

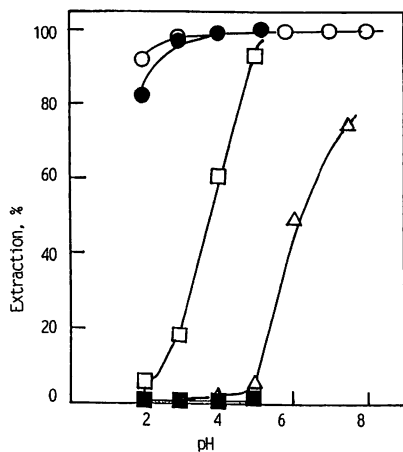


Fig. 1 Relation between pH and extraction of Cu(I), Cu(II), Fe(II), Fe(III), and Ni(II).  
 Metal taken:  $50 \mu\text{g cm}^{-3}$ , HPEKO:  $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  
 Organic phase:  $2.0 \text{ cm}^3$ , Aqueous phase:  $5.0 \text{ cm}^3$   
 ● Cu(I), ○ Cu(II), ■ Fe(II), □ Fe(III),  
 △ Ni(II)

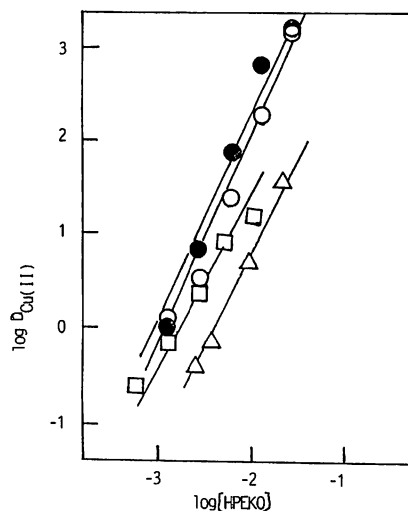


Fig. 2 Effect of concentration of  $\alpha$ -oximes on distribution of Cu(II) at pH 4.8  
 Cu(II) taken:  $50 \mu\text{g cm}^{-3}$ , Organic phase:  $2.0 \text{ cm}^3$ ,  
 Aqueous phase:  $5.0 \text{ cm}^3$ , Shaking time: 30 min  
 ○ HPEKO, ● HAPO, □ HOBPO, △ cupron

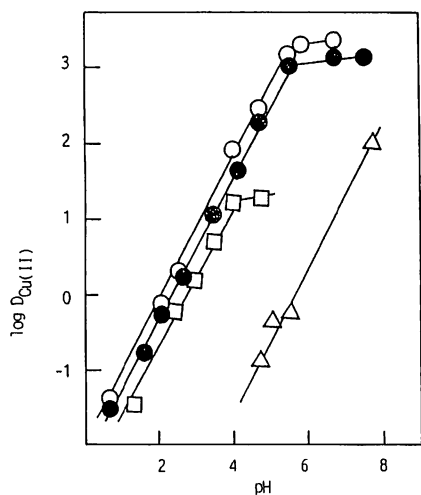


Fig. 3 Effect of pH on distribution of Cu(II) with  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$   $\alpha$ -oximes.  
 Cu(II) taken:  $50 \mu\text{g cm}^{-3}$ , Organic phase:  $2.0 \text{ cm}^3$   
 Aqueous phase:  $5.0 \text{ cm}^3$ , Oxime compounds:  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  
 Shaking time: 30 min.  
 ○ HPEKO, ● HAPO, □ HOBPO, △ cupron

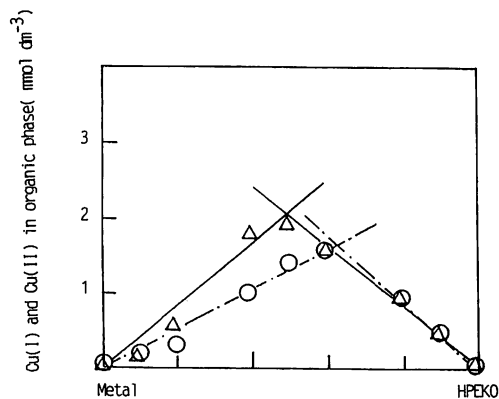


Fig. 4 Application of the method of continuous variations to Cu(II)/HPEKO and Cu(I)/HPEKO systems at pH 2.  
 Organic phase:  $3.0 \text{ cm}^3$  of  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  HPEKO,  
 Aqueous phase:  $3.0 \text{ cm}^3$  of  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  Cu(I) or Cu(II),  
 Shaking time: 30 min.  
 ○ Cu(II)/HPEKO, △ Cu(I)/HPEKO

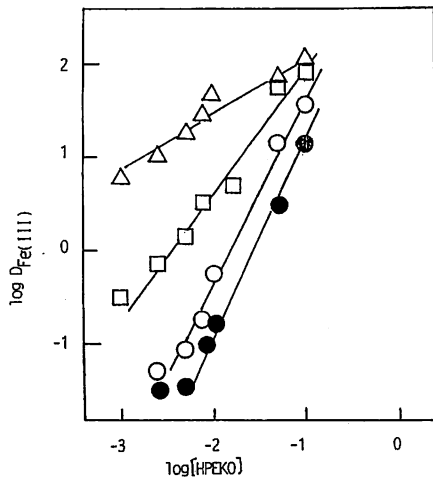


Fig. 5 Effect of pH on distribution of Fe(III).  
 Fe(III) taken:  $20 \mu\text{g cm}^{-3}$ , Aqueous phase:  $5.0 \text{ cm}^3$ ,  
 Organic phase:  $2.0 \text{ cm}^3$ , Shaking time: 30 min.  
 ● pH 2, ○ pH 3, □ pH 4, △ pH 5

Table 1 Separation of copper ( $100 \mu\text{g}$ ) from iron(III), nickel(II) and cobalt(II).

Ion added	Amount added $\mu\text{g}$	Unextracted metal* $\mu\text{g}$	Extracted Cu $\mu\text{g}$
Fe(III)	25.0	24.3	99.4
	50.0	48.7	99.4
	100.0	98.3	98.8
	250.0	244.3	98.7
Ni(II)	25.0	24.7	99.4
	50.0	49.4	99.1
	100.0	98.8	99.4
	250.0	243.0	99.4
Co(II)	25.0	18.6	97.5
	50.0	46.7	99.5
	100.0	96.0	97.8
	250.0	248.0	95.6

\* Amount of metal ions remaining in the aqueous phase.