

**EXTRACTION EQUILIBRIUM OF NICKEL FROM  
AQUEOUS AMMONIUM SULFATE SOLUTION  
WITH 5-DODECYLSALICYLALDOXIME  
IN KEROSENE**

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Extraction equilibrium of nickel from 0.5 kmol/m<sup>3</sup> aqueous ammonium sulfate solution by 5-dodecylsalicylaldoxime (LIX860-I) as an extractant in kerosene was studied at 303 K. The effects of pH in the aqueous phase and the concentration of the extractant in the organic phase on the extraction were examined. The extraction of nickel with the extractant was effectively observed at pH higher than 3. The fractional extraction of nickel increased with increasing equilibrium pH and the concentration of the extractant. The experimental results of the extraction equilibrium were analyzed by the reaction model. The overall extraction equilibrium of nickel in this system was expressed by the following reaction and the equilibrium constant of the reaction was determined as follows:



All experimental results could be explained well by this reaction model.

### 1. Introduction

Recently, factory wastes from production process have caused several problems such as pollution of water and air, their disposition. The wastes should, however, be necessary to be reconsidered as a resources because the wastes are containing various useful materials, especially various metals. There are very important subjects to construct separation and recycle processes of these metals from the wastes.

Solvent extraction method is one of useful methods for selective separation of metals from waste waters containing various impurities and has a high potential to solve several problems in conventional disposed type processes. Solvent extraction method is considered to close to zero-emission concept, because small amounts of

wastes for disposal, ability of continuous operations<sup>1, 2)</sup>, recycle of extractant<sup>3)</sup>, easy concentration of metal in back extraction<sup>4)</sup> are provided.

Hydroxyoximes which are one of useful extractants have ability to extract many metals which are sometimes cause environmental pollution<sup>5, 6)</sup>. Aqueous solubility of oxime type extractants has been discussed from spectroscopic properties<sup>7)</sup>. Some papers have reported hydroxyoximes are polymerized in low dielectric solvent<sup>6, 8, 9)</sup>. Another papers have, however, reported that polymerization of hydroxyoximes is not always required to consider extraction equilibrium of metals<sup>10, 11)</sup>. 5-Dodecylsalicylaldoxime (here after called LIX860-I) and its mixture products are sometimes called as a hydroxyoximes of second generation<sup>13)</sup>, because LIX860-I type extractants are provide a high extraction and back-extraction yields of metals compared with conventional hydroxyoximes, for example LIX63, LIX65 and LIX70. The extraction process using LIX860-I type extractants are, therefore, expected to reduce a number of treatment in operations compared with that using the conventional hydroxyoximes<sup>9)</sup>.

In this paper, in order to obtain fundamental information to construct nickel separation process from an aqueous ammonium sulfate solution, solvent extraction of nickel ion with LIX860-I in kerosene was quantitatively investigated. The effects of pH in the aqueous phase and the concentration of the extractant in the organic phase on the extraction were investigated. The extraction equilibrium was discussed on the basis of the reaction model between LIX860-I and nickel.

## 2. Experimental

5-Dodecylsalicylaldoxime, (LIX860-I, diluted by kerosene at 65 %, Henkel Hokusui Co.), as an extractant was used without further purification. No other impurities was almost observed by NMR analysis of the extractant solution. Kerosene, Ni<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>OH and H<sub>2</sub>SO<sub>4</sub> of guaranteed grade reagents were purchased from Wako Chemicals Co. and were used without further purification.

The organic phase was prepared by dissolving LIX860-I in kerosene from  $3.95 \times 10^{-3}$  to  $1.00 \times 10^{-1}$  kmol/m<sup>3</sup>. The initial concentration of LIX860-I in the organic phase was calculated from weight of the LIX860-I added in kerosene.

The aqueous phase was prepared by dissolving nickel sulfate in 0.5 kmol/m<sup>3</sup> ammonium sulfate aqueous solution at  $4.00 \times 10^{-3}$  kmol/m<sup>3</sup>. Furthermore, small amounts of concentrated sulfuric acid or 25 % ammonia aqueous solution was added to adjust pH values in the aqueous phase.

Equal volumes of the aqueous and the organic phase at  $3.00 \times 10^{-5}$  m<sup>3</sup> were put into a  $1.1 \times 10^{-4}$  m<sup>3</sup> volumes sample phial with stopper. The sample phials were mechanically shaken to attain equilibrium state in water bath at 303 K for one week.

This period was determined by preliminary experiments that were required for 5 days to attain equilibrium. After equilibrium, both phases were leaved for at least 30 min, and then separated completely to each phase. The values of equilibrium pH were measured using pH meter (Horiba Co. F-12 pH meter). The concentrations of nickel in the aqueous phase were measured by atomic adsorption spectrophotometry (Hitachi Co. Z-8000 type). The nickel concentration in the organic phase was calculated by mass balance from the aqueous nickel concentrations before and after equilibrium. Further, mass balance of nickel was checked by back-extraction from the organic phase with 24 kmol/m<sup>3</sup> sulfuric acid solution and was found to be appropriate.

### 3. Results and Discussion

Effect of equilibrium pH on the extraction of nickel was investigated at various initial concentrations of LIX860-I. The fractional equilibrium of nickel,  $E (=100 \times [Ni^{2+}]_{org} / ([Ni^{2+}]_{aq} + [Ni^{2+}]_{org}))$  were plotted against equilibrium pH in Fig. 1.  $E$  increases steeply with increasing pH value in the region of higher than pH 3. As an increasing in LIX860-I concentration, an increase in  $E$  is tended to shift toward to more acidic pH range.

The overall reaction of extraction of nickel with LIX860-I is assumed as follows;



It is known that hydroxyoximes partly exist as dimeric species in nonpolar organic phases. Yoshizuka *et al.* have been measured the apparent molecular weights of LIX860-I in the various nonpolar organic phases by means of vapor-phase osmometry<sup>13)</sup>. As the measurement of the molecular weights are in good agreement with the calculated a monomeric species, it is concluded that LIX860-I exists as a monomeric species in the various nonpolar organic phases. Therefore, the association of LIX860-I in the organic phase is also ignored in our model.

The equilibrium constant,  $K$  for Eq. (1) is written as follows;

$$K = \frac{[NiR_m] \cdot [H^+]^z}{[Ni^{2+}] \cdot [HR]^m} \quad (2)$$

Substituting the distribution coefficient,  $D (= [Ni^{2+}]_{org} / [Ni^{2+}]_{aq})$ , into Eq. (2) and taking logarithms, the following equation is obtained;

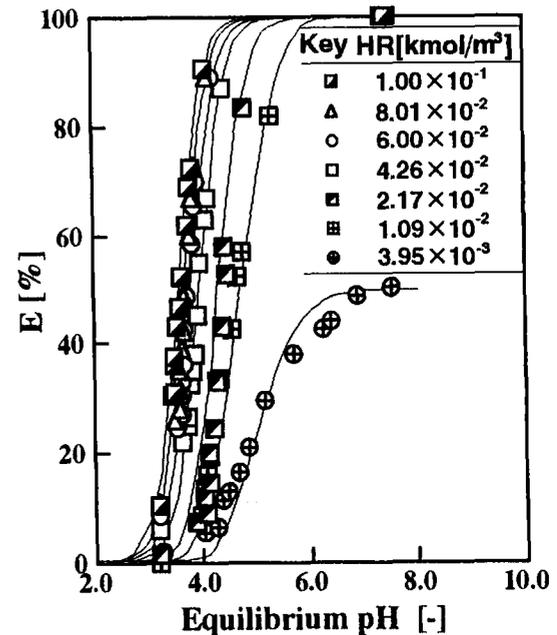


Fig. 1 Effect of equilibrium pH on the extraction of nickel at various concentrations of LIX860-I

$$\log D = z \text{ pH} + m \log [\text{HR}] + \log K \quad (3)$$

Inoue *et al.* have reported that the dissolving hydroxyoxime concentrations in the aqueous phase at acidic pH region are a slight amount for the initial hydroxyoxime in the organic phase<sup>12, 13</sup>. Therefore, dissolution of LIX860-I into the aqueous phase was ignored in this analysis.

When initial LIX860-I concentration is excess for initial concentration of nickel,  $[\text{Ni}]_0 \ll [\text{HR}]_0$ , LIX860-I concentration after extraction equilibrium can be approximated as follows;

$$[\text{HR}] \cong [\text{HR}]_0 \quad (4)$$

Consequently, Eq. (3) is rewritten as follows;

$$\log D = z \text{ pH} + m \log [\text{HR}]_0 + \log K \quad (5)$$

In the first step analysis, experimental results at high initial LIX860-I concentration, which were ten times higher than that of nickel, were used for the analysis. On the basis Eq. (5), the distribution coefficient at various LIX860-I concentrations was plotted against equilibrium pH in Fig. 2. The experimental results are plotted on the straight lines having a slope of 2.0 at each extractant concentration. This means the experimental results at high initial LIX860-I concentration range are expressed by Eq. (5). Hence, the value of  $z$  is determined as 2.0.

The intercept of straight line in Fig. 2,  $I$ , has following relationship from the definition of Eq. (5);

$$I = m \log [\text{HR}]_0 + \log K \quad (6)$$

On the basis of Eq. (6), the intercepts of the straight line in Fig. 2 were plotted against initial LIX860-I concentrations in the organic phase in Fig. 3. The plotted points in Fig. 3 lie on a straight line having a slope of 2.0. Hence, the value of  $m$  was

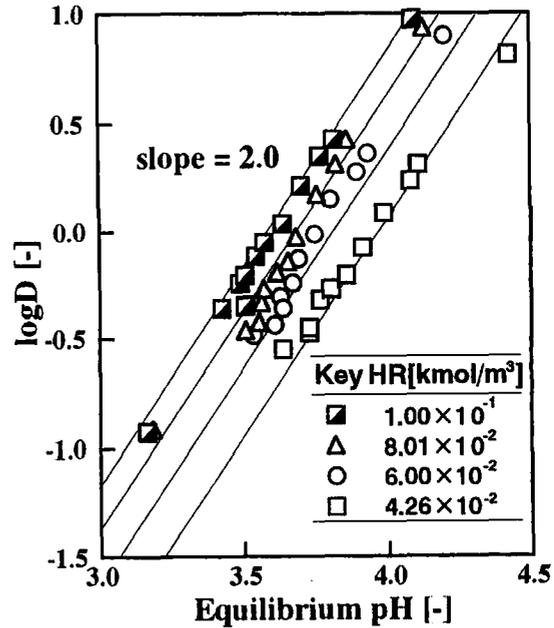


Fig. 2 Relationship between  $\log D$  and equilibrium pH at various concentrations of LIX860-I

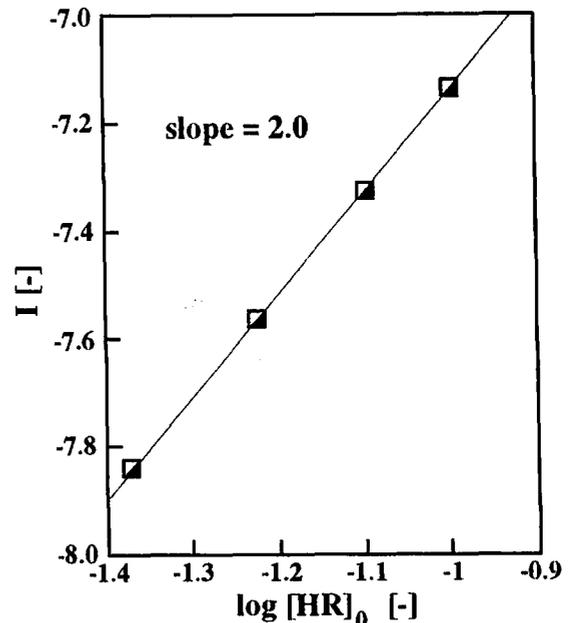


Fig. 3 Relationship between the intercept values of the straight lines in Fig. 2 and the initial concentrations of LIX860-I

determined as 2.0.

Mass balances of LIX860-I and nickel are expressed by following equations;

$$[\text{HR}]_0 = [\text{HR}] + 2 [\text{Ni}]_{\text{org}} \quad (7)$$

$$[\text{Ni}]_0 = [\text{Ni}]_{\text{aq}} + [\text{Ni}]_{\text{org}} \quad (8)$$

Introducing distribution coefficient,  $D$ , and rearranging Eqs. (7) and (8) give following equation;

$$[\text{HR}] = [\text{HR}]_0 - 2 \{D [\text{Ni}]_0 / (D + 1)\} \quad (9)$$

The equilibrium concentrations of LIX860-I in all experimental conditions were calculated using initial LIX860-I concentrations, initial concentration of nickel and distribution coefficient.

Substituting the values of  $m$  and  $z$  into Eq. (3) and rearranging, the following equation is obtained;

$$\log (D / [\text{HR}]^2) = 2 \text{pH} + \log K \quad (10)$$

$\log (D / [\text{HR}]^2)$  plotted against equilibrium pH at all LIX860-I concentrations were shown in **Fig. 4**. The plotted points in Fig. 4 lie on a straight line having a slope of 2.0. This result suggests the values of  $m$  and  $z$  are appropriate values. From the intercept of the line, the apparent equilibrium constant,  $K$  is determined as  $7.2 \times 10^{-6}$  [-].

Consequently, overall reaction of nickel extraction with LIX860-I was represented following equation;

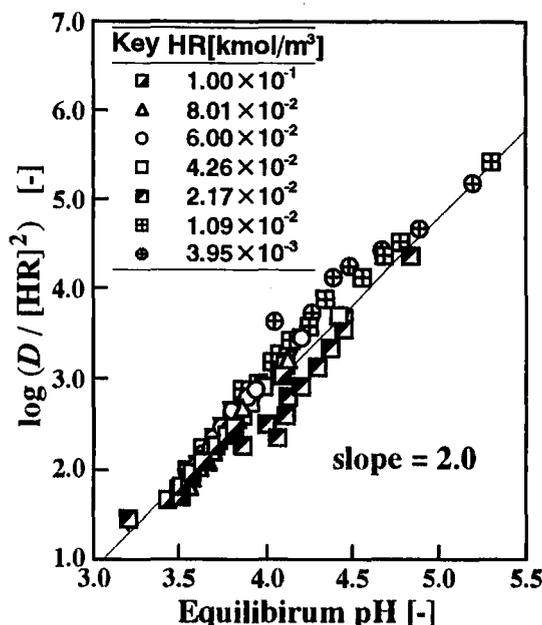


One molecule of nickel ion reacts with two molecules of LIX860-I. The extracted complex is  $\text{NiR}_2$  type. Furthermore, the electric charge of the reaction is satisfactory.

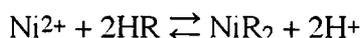
The solid lines in Fig. 1 are the results calculated by Eqs. (3) and (9) using equilibrium constant evaluated in this paper. The calculated results are agreed well with the experimental results.

#### 4. Conclusion

The extraction equilibrium of nickel from  $0.5 \text{ kmol/m}^3$  aqueous ammonium sulfate solution with 5-dodecylsalicylaldoxime in kerosene was investigated at 303 K. The effects of pH in the aqueous phase and the concentration of LIX860-I in the organic phase on the extraction were examined. The experimental results were analyzed on the basis of the reaction model. The overall extraction reaction was expressed by following reaction;



**Fig. 4** Plot of  $\log(D / [\text{HR}]^2)$  against the equilibrium pH at various LIX860-I concentrations



The extraction equilibrium constant of above reaction was evaluated as follows:

$$K=7.2 \times 10^{-6} [-]$$

### Nomenclature

<i>D</i> = distribution coefficient of nickel	[-]
<i>E</i> = the fractional equilibrium of nickel	[%]
<i>I</i> = the intercept of straight line in Fig.2	[-]
<i>K</i> = equilibrium constant for reaction	[-]
HR = LIX860-I	[-]
NiR <sub>2</sub> = the extracted species	[-]
<subscripts>	
aq = aqueous phase	
org = organic phase	
0 = initial state	

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