EXTRACTION RATE OF NICKEL IN AQUEOUS AMMONIUM SULFATE SOLUTION WITH 5-DODECYLSALICYLALDOXIME IN KEROSENE

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ABSTRACT

In order to clarify the adsorption equilibrium for the species of the extractant and the extraction complex, the interfacial tensions between the aqueous and the organic solutions were investigated, using equilibrated kerosene solution in the presence of 5-dodecylsalicylaldoxime (LIX® 860-IC) and aqueous solution in the presence and absence of nickel ion. The interfacial tensions decreased with increasing in the concentration of LIX® 860-IC. Experimental results of the interfacial tension were analyzed by Gibb’s adsorption isotherm. The adsorption equilibrium constant and the interfacial area for the extractant and the extraction complex were determined.

The extraction rate of nickel from the aqueous ammonium sulfate solution with LIX® 860-IC in kerosene was investigated using a Lewis-type transfer cell. The concentration effects of extractant, nickel, and hydrogen ion on the extraction rate were examined. The extraction rate increased with increasing in the concentrations of nickel and the extractant, and approached to constant values depending on the extractant concentration at a high concentration of nickel. The rate increased with decreasing in the concentration of hydrogen ion, and approached to constant values depending on the extractant concentration. These results were analysed based on an interfacial reaction model in which the reaction proceeds between an extractant species adsorbed at the interface and nickel ion in the aqueous solution. The extraction rate is interpreted based on the rate equation in which the interfacial reaction between a 1:1 nickel chelate complex species adsorbed at the interface and the extractant in the organic solution is the rate-determining step. The reaction rate constants and equilibrium constants were determined.

Keywords: nickel, 5-dodecylsalicylaldoxime, extraction rate, interfacial reaction, Lewis type transfer cell
INTRODUCTION

The process of electroless plating of waste water has become a problematic with the increased demand for electroless plating of waste water. Due to the complex composition of waste water to be subjected to electroless plating, a successful waste water treatment method [1,2,3] has not yet been established. Recently, from the viewpoint of the resource recycling [4], it has been important to recover useful materials from waste water. The solvent extraction method, which has received favorable consideration as a closed system based on the zero-emissions concept, is useful for small amounts of waste for disposal, and has the advantages of continuous operation [5,6,7], and recycling of the extractant [8,7]. In order to design an extraction process for use with the solvent extraction method, it is first necessary to clarify the extraction equilibrium, interfacial adsorption, and extraction rate. In this study, the extraction rate of nickel in an aqueous ammonium sulfate solution with 5-dodecylsalicylaldoxime (LIX® 860-IC) in kerosene was investigated in a Lewis-type transfer cell. The interfacial adsorption of LIX® 860-IC and the extraction complex were investigated by measurement of the interfacial tension. The experimental results of the extraction rate were analysed based on an interfacial reaction model in which the reaction proceeds between LIX® 860-IC species adsorbed at the interface and nickel ion in the aqueous solution.

EXPERIMENTAL

Materials, Method and Procedures

LIX® 860-IC as an extractant was purchased from Henkel Hakusui Co. and used without further purification. Guaranteed grade reagents of kerosene, NiSO₄, NH₄OH, and H₂SO₄ were purchased from Wako Pure Chemicals Co. and used without further purification. The organic solution was prepared by dissolving LIX® 860-IC into kerosene. The aqueous solution was prepared by dissolving nickel sulfate into an aqueous ammonium sulfate solution and adjusting the pH value by addition of concentrated sulfuric acid or 25% aqueous ammonia solution. pH values were measured by pH meter (Horiba Co. F-12 pH meter). The concentrations of nickel in the aqueous solution were measured by atomic adsorption spectrophotometry (Hitachi Co. Z-8000 type). The nickel concentrations in the organic solution were calculated from the mass balances of nickel in the aqueous solutions. The mass balances of nickel were checked by the back-extractions of nickel from the organic solution into 6.1×10⁻³ mol/m³ of sulfuric acid solution, and were found to be satisfactory.
Measurement of interfacial tension for the extraction equilibrium system

The interfacial tensions between the organic and aqueous solutions after the equilibration were measured using the Wilhelmy's vertical plate method (Kyowa Interfacial Science Co.; automatic surface tensiometer CBVP-Z type) to clarify adsorption equilibrium constants for the extractant, HR, and the complex, NiR$_2$ at 303 K.

Measurement of the extraction rate

The extraction rates of nickel in the aqueous solutions with LIX$^\text{®}$ 860-IC in kerosene were measured in a Lewis-type transfer cell as shown in Fig.1 at 303 K.

The cell consisted of two compartments of equal volume (about 1.5×10$^{-4}$ m$^3$). The disk block was settled at the interface, which arrangement improves the mixing of both solutions. The net interfacial area between the aqueous and the organic solutions was 1.1×10$^{-3}$ m$^2$. The aqueous and organic solutions were maintained beforehand in each bullet at 303 K. The aqueous solution was poured first, into the lower compartment, and the organic solution into the upper one. Once the organic solution had covered the surface of the aqueous solution, which occurred with immediacy the flat blade was settled in each solution and stirring commenced at 80 rpm. The solutions in the cell were stirred in opposite directions. Samples of the organic solution were taken out at intervals. After the stripping with 6×10$^{-3}$ mol/m$^3$ aqueous sulfuric acid solution, the nickel concentration in the aqueous solution was determined by the method above mentioned. Under various experimental conditions, the initial extraction rates of nickel were determined from the concentration changes of nickel complex in the organic solution at various extraction times.
RESULTS AND DISCUSSION

In our previous paper [9], the overall reaction for the extraction of nickel in aqueous ammonium sulfate solution with LIX® 860-IC in kerosene was expressed by the following reaction:

\[
\text{Ni}^{2+} + 2\text{HR} \rightleftharpoons \text{NiR}_2^2 + 2\text{H}^+ \quad K_{ex}
\]

The equilibrium constant, \( K_{ex} \), of the system was determined as:

\[
K_{ex} = \frac{[\text{NiR}_2^2][\text{H}^+]^2}{[\text{Ni}^{2+}][\text{HR}]^2} = 7.2 \times 10^{-6} \quad [-]
\]

**Interfacial adsorption equilibrium of LIX860 and the extraction complex**

The interfacial tensions between the aqueous and organic solutions were measured equilibrated organic solution in the presence or absence of extractant and in the aqueous solution in the presence or absence of nickel ion. In equilibrated kerosene containing extractant, HR, and the aqueous solution in the absence of nickel the interfacial tensions are plotted against the initial concentrations of HR in the kerosene solution for each pH in Fig. 2-a. The interfacial tension decreases with increasing the concentration of HR in the organic solution, independent of the pH value in the aqueous solution.

The organic solution containing HR was equilibrated with the aqueous solution containing excess nickel concentration. Under these conditions, all molecules of HR in the organic solution are converted to the complex NiR\(_2^2\), at the extraction equilibrium [9]. The interfacial tensions in the system are plotted against one-half of the initial concentrations of HR in the organic solution for each pH in Fig. 2-b. The interfacial tension decreases with increasing the concentration of HR in the organic solution, independent of the pH value in the aqueous solution.

In both cases, the interfacial tension decreased with an increasing in the concentration of HR in the organic solution. These decreases of the interfacial tension are shown in Fig. 2.

![Fig. 2. Relationship between the interfacial tension and the concentration of HR.](image-url)
interfacial tension show that HR and NiR₂ species are adsorbed at the interface, and that the adsorptions of these species are not affected by the pH value in the aqueous solution. The adsorption equilibrium of HR and NiR₂ species to the interface are expressed as follows:

\[ \text{HR}_{\text{org}} + \theta_v \rightarrow \theta_{\text{HR}} ; K_{\text{HR}} \]

\[ \text{NiR}_{2,\text{org}} + \theta_v \rightarrow \theta_{\text{NiR}2} ; K_{\text{NiR}2} \]

where \( K_{\text{HR}} \) and \( K_{\text{NiR}2} \) are the adsorption equilibrium constants of HR and NiR₂, and subscripts org and v denote the organic solution and the vacant site at the interface, respectively. Assuming Gibb’s adsorption isotherm, the relationship between the interfacial tension and the equilibrium concentration of HR is expressed as follows:

\[ \gamma = \gamma_0 - \left( \frac{RT}{S_{\text{HR}}} \right) \ln(1 + K_{\text{HR}}[\text{HR}]) \]  

(5)

where \( \gamma_0 \) is the interfacial tension between kerosene and water and \( S_{\text{HR}} \) is the interfacial area occupied by one mole of HR. Analysing the experimental results using Eq. (5), the values of \( K_{\text{HR}} \) and \( S_{\text{HR}} \) were determined using nonlinear least square method as shown in Table 1. The solid lines in Fig.2-a are the calculation results by Eq. (5) with the constant values obtained. The values of \( K_{\text{NiR}2} \) and \( S_{\text{NiR}2} \) were also obtained by the experimental result for interfacial adsorption of NiR₂ species as shown in Table 1.

Tab. 1. Various of constants for nickel extraction.

<table>
<thead>
<tr>
<th>( K_\text{ex} )</th>
<th>7.2 × 10⁶ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{HR}} )</td>
<td>9.9 × 10⁷ [m³ / mol]</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>10 × 10⁷ [-]</td>
</tr>
<tr>
<td>( K_3 )</td>
<td>1.3 × 10⁹ [-]</td>
</tr>
<tr>
<td>( K_{\text{NiR}2} )</td>
<td>5.3 × 10⁴ [m³ / mol]</td>
</tr>
<tr>
<td>( 1/K_{\text{NiR}2} )</td>
<td>1.9 [mol / m³]</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>9.5 × 10⁷ [m / sec]</td>
</tr>
<tr>
<td>( S_{\text{HR}} )</td>
<td>2.7 × 10⁵ [m² / mol]</td>
</tr>
<tr>
<td>( S_{\text{NiR}2} )</td>
<td>3.2 × 10⁵ [m² / mol]</td>
</tr>
</tbody>
</table>

The calculated results agreed well with the experimental results. The adsorption behaviors of HR and NiR₂ species were interpreted by Gibb’s adsorption isotherm with values of \( K \) and \( S \).

**Extraction rate of nickel**

It was clarified that the extraction rates of nickel at the same concentration condition were independent of the stirring speed of the blades and the volume of the organic solution. These results show that the reaction between the extractant and nickel proceeded at the interface, and that the extraction rates depended on the interfacial reaction rates.
The effect of nickel concentration on the extraction rate is shown in Fig. 3. The extraction rate increases with increasing of the nickel concentration, and approaches the constant values depending on the extractant concentration.

Fig. 3. Effect of nickel concentration on initial extraction rate.

Fig. 4. Effect of extractant concentration on initial extraction rate.

Fig. 5. Effect of hydrogen ion concentration on initial extraction rate.

The effect of the extractant concentration on the extraction rate is shown in Fig. 4. The rate increases with the extractant concentration. The effect of
hydrogen ion concentration on the extraction rate is shown in Fig.5. The rate increases with decreasing of the concentration of hydrogen ion, and approaches the constant values depending on the extractant concentration. These results suggested that the extraction rates are dependent on the concentrations of extractant in the organic solution, and on nickel and hydrogen ions in the aqueous solution.

**Extraction mechanism of nickel with LIX® 860-IC**

In the based on the reaction, Eq.(1) and equilibrium constant, Eq.(2), the reaction was assumed to consist of the following consecutive steps:

\[
\begin{align*}
\text{HR}_{\text{org}} + \theta_v &= \theta_{HR} ; \quad K_{HR} \quad (2) \\
\text{Ni}^{2+}_{\text{aq}} + \theta_{HR} &= \theta_{\text{NiR}^+} + H^+_{\text{aq}} ; \quad K_2 \quad (6) \\
\theta_{\text{NiR}^+} + \text{HR}_{\text{org}} &= \theta_{\text{NiR}_2} + H^+_{\text{aq}} ; \quad K_3 \quad (7) \\
\theta_{\text{NiR}_2} &= \text{NiR}_{2\text{org}} + \theta_v ; \quad 1/K_{\text{NiR}_2} \quad (8)
\end{align*}
\]

Step (2) is the adsorption of HR into the interface. Steps (6) and (7) are reactions on the interface between the adsorbed species and the species in the bulk solution. Step (8) is desorption of the formed complex into the organic solution. Equilibrium constants for Eqs. (2) and (8) have already been estimated. Assuming that any reaction in Eqs. (2), (6), or (8) is the rate-determining step, the rate equation derived from each assumption cannot satisfy the experimental results of the extraction rate of nickel for all systems. Assuming that the step of Eq. (7) is the rate-determining step, the initial reaction rate, \( r_0 \), is derived as follows:

\[
r_0 = k_3[\theta_{\text{NiR}^+}][\text{HR}]_{\text{org}} - k_3[\theta_{\text{NiR}_2}][H^+]_{\text{aq}} \quad (9)
\]

where \( k_3 \) and \( k_3 \) are the rate constants for forward and reverse reactions in Eq.(7), respectively. At the initial stage, the fraction occupied by \( \text{NiR}_2 \) species at the interface is assumed to be negligibly small compared with those of HR and \( \text{NiR}^+ \) species. The rate of reverse reaction of Eq.(7) is neglected, and the rate equation is expressed as follows:

\[
r_0 = \frac{k_3K_{HR}K_2[\text{HR}]_0[\text{Ni}^{2+}]_0}{[H^+]_0 + K_{HR}[\text{HR}]_0[H^+]_0 + K_2[\text{Ni}^{2+}]_0[\text{HR}]_0} \quad (10)
\]

By the reciprocal of Eq.(10), the following equation is derived:

\[
\frac{1}{r_0} = \frac{(1 + K_{HR}[\text{HR}]_0)[H^+]_0}{k_3K_2K_{HR}[\text{HR}]_0^2}[\text{Ni}^{2+}]_0 + \frac{1}{k_3[\text{HR}]_0} \quad (11)
\]

At constant concentrations of the extractant and hydrogen ions for the experimental results, \( 1/r_0 \) was plotted against \( 1/[\text{Ni}^{2+}]_0 \) in Fig. 6. All
Experimental results are plotted on straight lines that have different slopes for each extractant and hydrogen ion concentration. These plots show that the results are expressed by Eq. (11). The combined parameter $k_3K_2$ is determined as $1.6 \times 10^{-8}$ m/s using the values of the slope in Fig. 6.

Transforming Eq. (11), the following equation is obtained:

$$\frac{[HR]_0^2}{r_0} = \frac{[H^+]_0 + K_2[Ni^{2+}]_0 \times [HR]_0}{k_3K_2[H][Ni^{2+}]_0} + \frac{[H^+]_0}{k_3K_2[H][Ni^{2+}]_0} \times \frac{[HR]_0^2}{r_0} \quad (12)$$

At constant concentrations of nickel and hydrogen ions for the experimental results, $[HR]_0^2/r_0$ was plotted against $[HR]_0$ in Fig. 7. All results are plotted on straight lines that have different slopes for each nickel and hydrogen ion concentration. The values of $K_2$ and $k_3$ are determined as $1.0 \times 10^{-7}$ and $9.5 \times 10^{-7}$ m/s, respectively, using the values of the slope in Fig. 7 and $k_3K_2$ value obtained. Solid lines in Figs. 3, 4, and 5 are the calculation results by Eq. (10) with the equilibrium and rate constants shown in Table 1. The calculated results agreed well with the experimental results. The initial extraction rate of nickel in the Lewis-type transfer cell is interpreted by the interfacial reaction rate, in which the reaction between adsorbed NiR* species at the interface and HR in the organic solution is the rate-determining step.
CONCLUSION

The interfacial tensions for the extraction equilibrium were investigated for various concentrations. The dependency of concentration on the interfacial tension was analyzed by Gibb’s adsorption isotherm. The interfacial adsorption constants and the interfacial area for LIX® 860-IC and its nickel complex NiR₂ species were determined. The extraction rate of nickel from aqueous ammonium sulfate solution with LIX® 860-IC in kerosene was investigated using a Lewis-type transfer cell. The experimental results were analyzed based on an interfacial reaction model in which LIX® 860-IC, HR species adsorbed on the interface reacts with nickel in the aqueous solution to form the complex species NiR⁺. The NiR⁺ species further reacts with HR to form 1:2 complex species, NiR₂. NiR₂ species on the interface is desorbed into the organic solution. The extraction rate of nickel is controlled by the reaction in which the 1:1 complex adsorbed on the interface reacts with the extractant in the organic solution to form the 1:2 complex NiR₂. The rate constant for each interfacial reaction and the equilibrium constants were determined.

List of symbols and abbreviations

\( K_{HR} \) adsorption equilibrium constant of extractant [mol/m³]
\( K_2 \) equilibrium constant of Eq.(6) [-]
\( K_3 \) equilibrium constant of Eq.(7) [-]
\( K_{NiR_2} \) adsorption equilibrium constant of nickel complex [mol/m³]
\( K_{ex} \) equilibrium constant of nickel extraction [-]
\( k_3 \) forward reaction rate constant of Eq.(7) [m³/s]
\( R \) gas constant [N m/(mol/K)]
\( r \) reaction rate [mol/(m²s)]
\( S_{HR} \) interfacial area occupied by one mole of HR [m²/mol]
\( S_{NiR_2} \) interfacial area occupied by one mole of NiR₂ [m²/mol]
\( T \) temperature [K]
\( \gamma \) interfacial tension [N/m]
\( \theta \) fraction of active site at interface [-]

Subscripts

aq aqueous solution
H⁺ hydrogen ion
HR extractant
org organic solution
Ni²⁺ nickel
NiR₂ nickel complex
V vacant site
0 initial value

REFERENCES


