Interfacial Kinetics in the Extraction of Copper(II) and Nickel(II) with 2'-Hydroxy-5'-nonylbenzophenone Oxime

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The kinetics of the extractions of copper(II) and nickel(II) with 2'-hydroxy-5'-nonylbenzophenone oxime (HL) in heptane was studied by means of a high-speed stirring apparatus. Linear correlations were established between the initial extraction rate of the metal ions and the amount of HL adsorbed at the liquid-liquid interface. The rate-controlling step was the reaction between L− at the interface and the metal ions in aqueous phase adjacent to the interface. A solvent effect of heptane and chloroform on the interfacial mechanism of the extraction of nickel(II) was also examined.

Keywords Extraction kinetics, interfacial adsorption, interfacial reaction, LIX65N, copper(II), nickel(II)

The kinetic mechanism of the solvent extraction of metal chelates has remained controversial, although many research results have been reported over the last few decades. A major difficulty in the elucidation of the kinetic mechanism is in the experimental technique for the evaluation of the role of the liquid-liquid interface. The importance of the interfacial reaction has been emphasized in the research projects which employ a stirred cell with a stagnant liquid-liquid interface2, a falling (rising) drop method3, or a rotating diffusion cell.4 In these types of apparatus, the mass transfer rates between an interface and an aqueous phase or an organic phase make significant contributions to the overall extraction rates. In order to measure the extraction rate controlled by a chemical reaction, we must minimize the thickness of the diffusion layers and promote solute transfer between the interface and the bulk phases.

The high speed stirring method, which we developed recently5, has some advantages for the purposes of the study of interfacial reactions, since the interfacial amount of a ligand and the extraction rate of a metal ion can be measured under the same experimental conditions of wide interfacial area and rapid mass transfer.

The metal extraction with 2'-hydroxy-5'-nonylbenzophenone oxime, an active component of the commercial extractant LIX65N, is a representative chelate extraction system in which the kinetic mechanism has been widely discussed and the importance of the interfacial reaction has been suggested. However, no report has been available in which the interfacial mechanism was established from the studies conducted under vigorously agitated conditions, except those for the other oximes.6,7

In the present study, in order to confirm the interfacial mechanism under the vigorously agitated conditions, the extraction rates of nickel(II) and copper(II) with 2'-hydroxy-5'-nonylbenzophenone oxime were investigated by means of the high speed stirring technique. The effects of heptane and chloroform on the extraction rate of nickel(II) were also examined.

Experimental

Chemicals

2'-Hydroxy-5'-nonylbenzophenone oxime (LIX65N or HL) was isolated from the commercial extractant LIX65N (Henkel(Japan) Ltd.) in the form of sodium salt and was purified by means of the copper-complex method.8 The stock solutions of nickel(II) and copper(II) were prepared by dissolving nickel powder and copper oxide, both reagent grade, into perchloric acid. The analytical concentration of the metal ions was determined by means of EDTA titration. Heptane (Wako, reagent grade) was purified by distillation after being washed with a mixture of nitric acid and sulfuric acid. Chloroform (Wako, reagent grade) was washed three times with an equal volume of water prior to use. Other reagents used in the present study were all of reagent grade. Water was purified by the use of Millipore, Milli Q-II system. The pH of aqueous solutions was controlled by acetate buffer (0.002 M, 1 M=1 mol/dm3) and perchloric acid or sodium hydroxide. The ionic strength was kept at 0.1 by the addition of sodium perchlorate.

Measurements of extraction rate

The high speed stirring apparatus used was almost the same as the one reported previously.7 Fifty milliliters of
LIX65N in heptane or chloroform and 45 or 48 ml of aqueous buffer solution was agitated in a stir-cell thermostatted at 25±0.1°C at the rate of 1000 – 4700 rpm. Only the organic phase was continuously separated by the aid of a Teflon phase separator; this was circulated at the flow rate of 16 ml/min through the flow cell mounted in a UVIDEC 430A spectrophotometer. Injection of 5 or 2 ml of the metal solution started the extraction. The increase in the absorbance of NiL₂ or CuL₂ in the organic phase, A', was observed at the maximum-absorption wavelength, 397 nm for NiL₂ and 355 nm for CuL₂ in heptane, and recorded in a microcomputer at the acquisition rate of 1 Hz. From the initial stage of the extraction, the observed initial extraction rate defined as \( r_{	ext{obs}} = (dA'/dt)_{t=0} \) was obtained.

Measurements of interfacial adsorption
The amount of LIX65N adsorbed at the interface generated by the agitation was measured by means of the same apparatus as used for the extraction rate measurements. Fifty milliliters of LIX65N in an organic solvent and the same volume of an aqueous buffer solution was stirred at 1000 – 4700 rpm or 200 rpm at which the interface was not disturbed. The absorbance of LIX65N in the organic phase was measured under both the stirring conditions as A' and A, respectively. The wavelength, here, was chosen at the maximum-absorbance of LIX65N, 321 nm in heptane and 319 nm in chloroform. The interfacial amount, \( n \) (mol), was calculated by

\[
 n = ([HL]S) = (A-A')V_0/\varepsilon \ell
\]

where \([HL]\) and \(S\) stand for the interfacial concentration of LIX65N (mol/cm²) and the total interfacial area which was estimated as 2.0×10⁴ cm² in heptane system, \(V_0\) refers to the volume of the organic phase (1) and \(\varepsilon\) to the molar absorptivity of LIX65N in the organic phase and \(\ell\) to the optical length of the cell. By varying the concentration of LIX65N or pH, the change of the interfacial amount was measured at 25±0.1°C.

Results and Discussion

Interfacial adsorption of LIX65N
The stirring effect on the organic phase absorbance was observed in distribution systems employing both heptane and chloroform. In Fig. 1, the interfacial adsorption of LIX65N is shown as the percentage decrease in the organic phase absorbance of LIX65N against pH. Interfacial adsorption in chloroform was less than that in heptane. The preferential adsorption of the dissociated form was indicated from the rapid increase in the adsorptivity at higher pH. The adsorption equilibrium of the neutral form of LIX65N between the organic phase and the interface was analyzed according to the Langmuir isotherm:

\[
 [HL] = \frac{aK'[HL]_0}{a+K'[HL]_0}
\]

where \(a\) refers to the saturated interfacial concentration (mol/cm²) and \(K'\) to the adsorption constant (1/cm²) defined by \(K' = [HL]/[HL]_0\) at infinitely diluted concentration of LIX65N. The experimental results obtained in the two organic solvents followed satisfactorily the next equation derived from Eqs. (1) and (2), as shown in Fig. 2:

\[
 \frac{1}{n} = \frac{1}{K'S[HL]_0} + \frac{1}{aS_i}
\]

The slopes and the intercepts of Fig. 2 afforded the
values of the parameters $a_S$ and $K'S_i$, which are listed in
Table 1 together with those for 2'-hydroxy-5'-nonylacetophenone oxime (SME529) obtained previously.\(^7\) The
interfacial adsorptivity of LIX65N, as compared from
the values of $K'$ in heptane system, is very close to that of
SME529. This can be understood from the fact that
both extractants have the same hydrophilic groups of the
phenolic OH and oxime $\equiv$N-OH which will predominate
the adsorption process from the organic phase to the
interface. On the other hand, a comparison of $K_i$, which
is defined by \[\frac{[L^-]}{[L]}\] shows a great difference between
the two oximes. The lower values of $a_S$ and $K'S_i$ for
LIX65N in chloroform than in heptane suggests the
stronger solvation of chloroform both in the interface
and in the bulk organic phase.

**Kinetic mechanism of nickel(II) extraction**

The extraction rate of nickel(II) with LIX65N was
significantly affected by the solvent used as an organic
phase, as shown in Fig. 3: faster in heptane and slower in
chloroform. The rate of the increase of NiL\(_2\) in the
organic phase obeyed the first-order kinetics. It was
found from the pH dependence of the initial extraction
rate that the reaction order with respect to hydrogen ion
was $-0.94 \pm 0.17$ and $-1.31 \pm 0.16$ for heptane and
chloroform systems, respectively. These results suggested
the rate-controlling process was the formation of
NiL\(^+\) complex.

If the formation of the mono-complex proceeds in the
bulk aqueous phase, the initial extraction rate defined by
$r^0 = \left(\frac{d[NiL_2]}{dt}\right)_{t=0}$ can be represented by

$$r^0 = \frac{k_1 K_a[Ni^{2+}][HL]}{K_D[H^+]}$$

(4)

where $k_1$ refer to the formation rate constant of NiL\(^+\) in
the aqueous phase, $K_a$ to the dissociation constant of
LIX65N in the aqueous phase and $K_D$ to the distribution
constant, respectively. However, the change of the
initial extraction rate with respect to the LIX65N
concentration did not show the first-order dependence
which was expected from Eq. (4) and it was unable to
interpret the experimental results by Eq. (4). Actually,
the negligible contribution of the aqueous reaction could
be demonstrated by a simple calculation using Eq. (4):
for example, and insertion of $k_1=10^{4.3}/M\cdot s$ (the forma-
\tion rate of nickel(II)-glycine complex$^9$), $pK_a=8.70^{10}$,
log $K_D=5.69^{11}$, $[Ni^{2+}]=8.0 \times 10^{-4}$ M, $[HL]=1.96 \times 10^{-4}$ M
and pH 5.13 into Eq. (4) gives $r^0=1.7 \times 10^{-12}$ M/s, which
was only $3 \times 10^{-4}\%$ of the observed value, $r^0=6.3 \times 10^{-12}$
M/s.

The initial extraction rate determined experimentally
was linearly dependent on the interfacial amount of
LIX65N, and suggested that the rate-controlling step
was the reaction between NiL\(^+\) and L\(^-\) at the interface.

Fig. 3 Rate profiles of the extraction of Ni(II) complex in
heptane and chloroform systems. ([LIX65N]=4.0\times10^{-4} M;
[Ni\(^{2+}\)]=8.0\times10^{-4} M, pH=4.87 in heptane system and [Ni\(^{2+}\)]=
1.0\times10^{-3} M, pH=6.53 in chloroform system.

![Fig. 3](image)

Fig. 4 Linear relationship between the initial extraction rate
of Ni(II) or Cu(II) and the interfacial amount of LIX65N in
heptane systems: [Ni\(^{2+}\)]=8.0\times10^{-4} M, [LIX65N]=4.0\times10^{-4} -
7.8\times10^{-4} M, pH=5.05, 4700 rpm and [Cu\(^{2+}\)]=5.0\times10^{-5} M,
[LIX65N]=5.0\times10^{-4} M, pH=2.40, 1180-4700 rpm.

![Fig. 4](image)
The initial extraction rate governed by the interfacial reaction was formulated as
\[ r^o = k_i K_i^* [\text{Ni}^{2+}] [\text{HL}_3] S_i \frac{1}{[H^+] V_o} \]  \tag{5}

where \( k_i \) refers to the formation rate constant of NiL\(^+\) at the interface and \( K_i^* \) to the dissociation constant of LiX65N at the interface, respectively. Figure 4, which shows the linear correlation between \( r^o \) and \([\text{HL}_3] S_i\), is strong evidence supporting the validity of Eq. (5). The slope of the Ni(II) system gave the value of \( 2.76 \times 10^{-4}/s \) as \( k_i^* K_i^* \). If \( K_i^* \) was assumed to have the same value as \( K_a \), \( k_i \) could be estimated as \( 1.38 \times 10^3/M \text{s} \) which was in agreement with the value obtained in SME529 system. The result that the value of \( k_i \) is larger than that of \( k_1 \) for gly system may be due to the favorable orientation of the oxime at the interface.

When chloroform was used as solvent, the contribution of the aqueous phase reaction estimated by Eq. (4) could be neglected. An application of Eq. (5) to the chloroform system gave the values of \( k_i K_i^* \) and \( k_i \) listed in Table 1. Although a significant effect of the organic solvents on the interfacial reaction was recognized from the result that the estimated value of \( k_i = 2.13 \times 10^3/M \text{s} \) was rather smaller than that in heptane, it is concluded that the extraction rate in chloroform was essentially controlled by the interfacial reaction as in heptane. In the chloroform system, the oxime was slightly adsorbable at the interface, so the oxime at the interface may be highly solvated with chloroform and less oriented, resulting in the \( k_i \) being smaller than in the heptane system.

**Kinetic mechanism of Cu(II) extraction**

The extraction rate of Cu(II) with LIX65N was much faster than that of Ni(II), as expected from the rapid-exchange rate of the hydrated water on Cu(II) ion. It was, therefore, necessary to lower the pH in order to measure the extraction rate reliably, unless the LIX65N concentration was lowered. The initial extraction rate depended on the hydrogen ion concentration with the order of \(-0.85 \pm 0.39\) under the conditions of \([\text{Cu}^{2+}] = 5.0 \times 10^{-3} \text{M}, [\text{LiX65N}^+] = 5.0 \times 10^{-4} \text{M}\) in heptane, \( \text{pH}=2.19-2.61 \) and 1950 rpm.

If the extraction rate is controlled by an interfacial reaction, it has to be significantly affected by the interfacial area generated by the stirring. Indeed, the increase of the stirring speed over the range of 1180-4700 rpm caused the increase in both of the interfacial amount of LIX65N and the extraction rate. The relationship between the initial extraction rate and the interfacial amount of LIX65N is shown in Fig. 4, so as to be compared with that of the Ni(II) system. The slope of the linear plots, corresponding to \( k_i K_i^*[\text{Cu}^{2+}]/[H^+] V_o \), allowed us to estimate \( k_i \) as 7.42 \times 10^3/M \text{s}, which is close to 4.0 \times 10^3/M \text{s} reported as the rate constant between Cu(II) and gly. From the above results, we concluded that the rate-controlling reaction in the extraction of Ni(II) and Cu(II) takes place at the interface generated by the vigorous agitation, not in the bulk aqueous phase.

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**References**