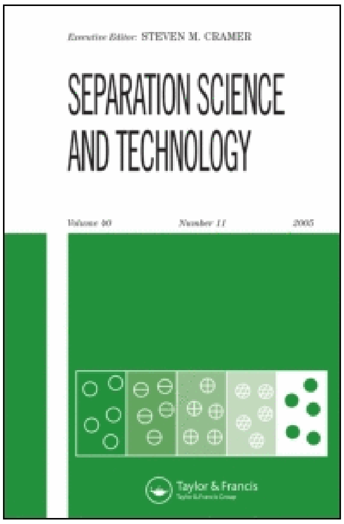

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# Equilibrium and Kinetics of Nickel Extraction with 2-Hydroxy-5-nonylbenzophenone Oxime

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# Equilibrium and Kinetics of Nickel Extraction with 2-Hydroxy-5-nonylbenzophenone Oxime

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## Abstract

The extraction of nickel with 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N; HL) has been studied into chloroform solution. The extracted species was found to be $NiL_2$, and its extraction constant of $10^{-5.90}$ was obtained. The rate of extraction of nickel has been found to be first-order in metal and ligand, and inverse first-order in hydrogen ion. The apparent rate constant of extraction ($k'$) was $10^{-7.40}$. These results support the hypothesis that the formation of the 1:1 complex in the aqueous phase is the rate-determining step. The rate constant of the formation of this complex was evaluated as $10^{5.90}$.

## INTRODUCTION

Considerable attention has been given to the mechanism of extraction of metal ions by the high molecular weight hydroxyoxime extractant 2-hydroxy-5-nonylbenzophenone oxime (LIX 65N) because of the bearing such information has on the design of improved extractants as well as on practical considerations of optimization of extraction conditions for LIX 65N.

A number of extraction kinetics for the Cu(II)–LIX 65N systems have been carried out by different methods (*1–4*) in which mass transfer rate problems complicated the interpretation of the data. Recently, investigation of this system using a high-speed stirring apparatus (5) led to the conclusion that the rate-limiting step involves a homogeneous chemical reaction in the aqueous phase rather than a heretofore hypothesized interfacial reaction (*6*).

The mechanism of the extraction by LIX 65N of nickel(II) represents an

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interesting and logical second phase of our continuing investigation of high molecular weight chelating extractants for a number of reasons. Inasmuch as quantitative description of the reaction of nickel with LIX reagents is sparse (*7, 8*), it would be of considerable interest to obtain fundamental data on both equilibrium and kinetic aspects of nickel extraction by LIX 65N. Will nickel extract as a simple chelate ($NiL_2$) as did copper (*6*) or will an adduct complex be extracted as with nickel and 8-quinolinol? Will the formation of the neutral 1:2 chelate be rate determining as was the case with copper or, as more generally observed, will the formation of the 1:1 chelate be slower?

In order to clarify the extraction mechanism, the present paper deals with the equilibrium and kinetics in the nickel extraction into chloroform by LIX 65N.

## EXPERIMENTAL

### Reagents

2-Hydroxy-5-nonylbenzophenone oxime (LIX 65N) was kindly supplied in its undiluted form by Henkel Corp., and diluted as required in analytical-grade solvents. All other chemicals were of analytical grade. Acetate buffers were used for all the equilibrium and kinetic studies. The ionic strength was kept at 0.1 with sodium perchlorate.

### Apparatus

Most of the apparatus used is essentially the same as that described previously (*5, 6*). The extraction kinetics apparatus consists of a 500-mL Morton flask fitted with a high-speed stirrer (*5*). Nickel analyses were performed on a Varian AA-6 atomic absorption spectrophotometer at 320.0 nm with an air–acetylene flame.

### Extraction Equilibria

An aqueous phase initially containing $10^{-4}$ $M$ nickel was shaken with an equal volume of a chloroform solution of LIX 65N. The equilibrium state was ensured by comparing results from both forward and backward extraction after shaking for 6 h. After centrifugation, the concentration of nickel in the aqueous phase was determined by atomic absorption.

### Extraction Kinetics

The procedure was essentially similar to that described previously (*6*). An aqueous solution containing $10^{-4}$ $M$ $Ni^{2+}$ and an equal volume of reagent solution was poured into the reaction flask, and the reaction was begun by starting a high-speed stirrer. Experiments were carried out in the "plateau" region where an increase in agitation gave no effect on the rate of extraction.

At timed intervals, samples were taken by purging the reaction flask with nitrogen, then immediately centrifuged. The nickel content in the aqueous phase was determined.

All experiments were carried out at 25°C.

## Nickel Extraction Equilibrium

The distribution ratios of nickel, $D_{\mathrm{Ni}}$, the stoichiometric concentration ratio of metal in the two phases, was measured over a range of pH from 4 to 6 and a LIX 65N range from $10^{-2.3}$ to $10^{-1}$ $M$. The $\log D_{\mathrm{Ni}}$ vs $\log [\mathrm{LIX\ 65N}]_0$ plots at a constant pH were linear and exhibited a slope of 2. The analogous $\log D_{\mathrm{Ni}}$ vs pH plots were also linear with a slope of 2. Thus it may be concluded that only a single species, the simple 1:2 chelate, $\mathrm{NiL_2}$, was present in the organic phase. Hence, under the range of conditions studied, Ni appears to have a coordination number of 4 with LIX 65N. The overall extraction reaction can be represented by

$$\mathrm{Ni^{2+}} + 2\mathrm{HL(o)} \overset{K_{ex}}{\rightleftharpoons} \mathrm{NiL_2(o)} + 2\mathrm{H^+} \tag{1}$$

The value of the extraction constant, $K_{ex}$, was found to be $\log K_{ex} = -5.90$.

The extraction constant is a composite of the chelate formation constant $\beta_2$, its distribution constant $K_{DC}$, as well as of the reagent acid dissociation constant $K_a$, and its distribution constant $K_{DR}$:

$$K_{ex} = \beta_2 K_{DC} K_a^2 / K_{DR}^2 \tag{2}$$

The product $\beta_2 K_{DC}$, which corresponds to the heterogeneous equilibrium constant of the reaction

$$\mathrm{Ni^{2+}} + 2\mathrm{L^-} \rightleftharpoons \mathrm{NiL_2(o)} \tag{3}$$

can be evaluated to be $10^{20.70}$, where we employed the values of $pK_a = 8.70$ (*9*) and $\log K_{DR} = 4.6$ (*6*).

The value of $\log \beta_2 K_{DC}$ compares with other nickel chelate as follows: 8-mercaptoquinolinate (25.26) > dibutyldithiocarbamate (24.70) > 8-hydroxyquinolinate (22.6) > dithizonate (20.2) > dimethylglyoximate (19.76) > 1-nitroso-2-naphtholate (16.9) (*10*). A further comparison is the value of $\log \beta_2 K_{DC}$ for Cu-LIX 65N of 26.6, explaining the ease of separation of Cu from Ni with this extractant.

## Extraction Kinetics

If the reaction was assumed to be first order with respect to metal ion, the initial rate of extraction can be given by

$$\ln \frac{[\mathrm{Ni}]_{t=0}}{[\mathrm{Ni}]_t} = k_{\mathrm{obs}}t \tag{4}$$

Plots of ln $([\mathrm{Ni}]_{t=0}/[\mathrm{Ni}]_t)$ were linear against time $t$, then the slopes gave the observed rate of extraction, $k_{\mathrm{obs}}$. This initial rate involves only the forward reaction and is not affected by the reverse reaction because experimental conditions are far from the equilibrium state. Experimental conditions and data obtained are shown in Table 1.

Slope analysis of the plots of log $k_{\mathrm{obs}}$ vs log [HL] and pH indicates first-order dependence with respect to reagent and inverse first-order dependence with respect to hydrogen ion. The constancy of log $k'$ in Table 1 further confirms this. The rate expression is therefore given by

$$-d[\mathrm{Ni}^{2+}]/dt = k'[\mathrm{Ni}^{2+}][\mathrm{HL}]_0/[\mathrm{H}^+] \tag{5}$$

This simple empirical rate expression eliminates all but the formation of the

TABLE 1

Kinetics in the Extraction of Nickel by LIX 65N at 25°C[a]

| log $[\mathrm{HL}]_0$ | pH | log $K_{\mathrm{obs}}$[b] | log $k'$[c] |
|---|---|---|---|
| −1.00 | 5.80 | −2.48 | −7.28 |
| −1.00 | 5.63 | −2.86 | −7.49 |
| −1.00 | 5.03 | −3.33 | −7.36 |
| −1.00 | 4.49 | −3.79 | −7.28 |
| −0.70 | 5.60 | −2.54 | −7.44 |
| −1.40 | 5.58 | −3.23 | −7.41 |
| −1.70 | 5.60 | −3.61 | −7.51 |
| −1.92 | 5.60 | −3.88 | −7.56 |
| −0.56 | 5.00 | −2.96 | −7.38 |
| −0.70 | 5.03 | −2.94 | −7.27 |
| −1.10 | 5.00 | −3.47 | −7.37 |
| | | | Mean −7.40 ± 0.09 |

[a] $[\mathrm{Ni}]_{t=0} = 9.91 \times 10^{-5}\ M$, $10^{-2}\ M$ acetate buffer (I = 0.1 with $\mathrm{NaClO_4}$).
[b] Slope of the plot of $\ln[\mathrm{Ni}^{2+}]_{t=0}/[\mathrm{Ni}^{2+}]$ vs time (s).
[c] $k' = k_{\mathrm{obs}}[\mathrm{H}^+]/[\mathrm{HL}]_0$.

1:1 complex in the aqueous phase as the rate-determining step in the overall extraction process (*11*). Thus

$$\mathrm{Ni}^{2+} + \mathrm{L}^- \xrightarrow{k_1} \mathrm{NiL}^+ \tag{6}$$

whose rate expression is

$$-d[\mathrm{Ni}^{2+}]/dt = k_1[\mathrm{Ni}^{2+}][\mathrm{L}^-] \tag{7}$$

which is seen to be equivalent to Eq. (5) by the substitution of $K_a[\mathrm{HL}]_0/K_{DR}[\mathrm{H}^+]$ for $[\mathrm{L}^-]$, so that

$$k' = k_1 K_a / K_{DR} \tag{8}$$

The $k'$ values obtained are listed in Table 1, and this average of $10^{-7.40}$ leads to a value of the rate constant of $10^{5.90}$ for the formation of $\mathrm{NiL}^+$. This value is somewhat higher than that reported for many nickel chelation reactions, e.g., $10^{3.92}$ for phenanthroline (*12*), but about the same, $10^{5.10}$, for di-*p*-iodophenylthiocarbazone (*13*).

In conclusion, there can be no doubt that the homogeneous chemical mechanism applies to the extraction of Ni as well as to Cu by LIX 65N, rather than the interfacial mechanism (*1–4*). As a consequence, design of improved chelating extraction agents should consider primarily the effect of further molecular weight increase on the distribution constant of the reagent rather than on its effect on interfacial tension. As a corollary, inasmuch as the observed rate of extraction will, in general, decrease with increasing reagent molecular weight, search for suitable extraction catalysts will remain an important aspect of the full exploitation of high molecular weight extractants.

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