

# Kinetics of nickel(II) extraction by 2-ethylhexanal oxime in ammonium nitrate solutions

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## Abstract

Kinetics of nickel(II) extraction by 2-ethylhexanal oxime (EHO) has been investigated in a homothetic cell (Rushton cell) from ammonium solutions. The kinetic study was carried out with a stirring speed fast enough to eliminate the diffusion limitation. The chemical regime can then be assumed and the kinetic result can be used to determine the reaction mechanism. Thus, a kinetic mechanism has been suggested and a limiting step found. Influence of pH and the concentrations of  $\text{NH}_4\text{NO}_3$  and EHO on rate have been investigated and results suggest that the limiting step is an interfacial reaction between a molecule of EHO monomer ( $\text{HOx}$ ) and the adsorbed complex  $\text{Ni}(\text{Ox})(\text{H}_2\text{O})_{5\text{ad}}^+$ .  
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## 1. Introduction

In a previous study [1] the extraction of nickel(II) in ammonium nitrate media was successfully achieved using 2-ethylhexanal oxime (EHO), in dodecane. However the extraction rate was found to be very small. The kinetics of extraction is also important to understand the nature of the process. Knowledge of the extraction mechanism allows predicting a possible inhibition or enhancement of the extraction rate. Therefore, a complete kinetic study should be performed.

Complex studies on the kinetics and the mechanism of copper(II) extraction have been carried out and we considered them as models for the extraction of other metals such as nickel(II) with different reagents. In this case, the main features and relationships between the kinetics and mechanism of extraction are similar [2].

Many papers dealing with the kinetics of copper(II) extraction by oximes [3–5] show that the limiting step always depends on the hydrogen ion concentration. This could also be the case for nickel(II), therefore, the chemical parameters and especially pH must be carefully studied. Indeed, Freiser [6,7] who studied copper(II) extraction by LIX65N (2-

hydroxy-5-nonylbenzophenone oxime) using the highly stirred cell report a first order dependence on both copper ion and ligand concentration while inversely dependent on the hydrogen ion concentration. Freiser used a two-step mechanism to explain the observed kinetics and showed that the limiting step was the cationic exchange reaction in which a second extractant molecule (HL) reacts with  $\text{CuL}^+$  complex:  $\text{CuL}^+ + \text{HL} \rightarrow \text{CuL}_2 + \text{H}^+$ . The kinetic constant of this reaction was determined to be  $k_1 = 2.2 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$ . For the same chemical system using the single drop technique, Komasa et al. explained their result by an interfacial mechanism [3]. Flett et al. [8,9] showed that the extraction of copper(II) with commercial hydroxyoxime is also an interfacial mechanism with two rate limiting steps:  $\text{CuL}_{\text{ad}}^+ + \text{HL}_{\text{int w}} \rightleftharpoons \text{CuL}_{2 \text{ ad}} + \text{H}_{\text{w}}^+$  and  $\text{CuL}_{\text{ad}}^+ + \text{HL}_{\text{ad}} \rightleftharpoons \text{CuL}_{2 \text{ ad}} + \text{H}_{\text{w}}^+$ , where subscripts ‘ad’ and ‘int w’ denote the adsorption layer and the aqueous phase layer close to the interface. In this reaction, the dissociation of the phenolic group of weak acidity was neglected and the direct reactions of copper(II) with nonionized hydroxyoxime molecules were considered.

In aqueous ethanol solvent, Pratt and Tilley [10] discovered a first order dependence on both metal ion and ligand and a mechanism involving the rate determining formation of mono-complex. A similar mechanism was also found by Nicol et al. [11] for the extraction of copper(II) by salicyldoxime using stepped flow in an ethanol–water mixture.

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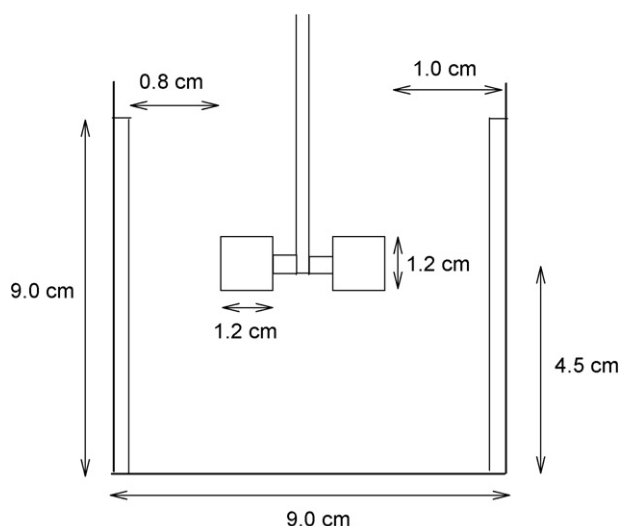


Fig. 1. Diagram of the stirred Rushton homothetic cell used in this study.

Authors who investigated nickel extraction by oxime [1,12] found that the extraction rate was very slow. Since extraction of Ni(II) by EHO is a very slow process [1], our study was conducted using a highly stirred cell as done previously [13]. By increasing the interfacial area which the technique yields, the study of this very slow solvent extraction kinetic can be achieved.

Four internal baffles were used in order to limit the vortex and to control the reproducibility of the interfacial area.

## 2. Experimental

### 2.1. Reagents and solutions

The extractant used was EHO. The oxime was synthesized (98.5% purity) as previously reported [1,14,15].

Dodecane (Aldrich, >99%), an apolar diluent, was selected. Organic solutions of EHO in dodecane were prepared with concentrations up to  $1.18 \text{ mol kg}^{-1}$ . The aqueous solutions were prepared by dissolving nickel nitrate (Fluka, 99%) with ammonium nitrate (Fluka, 99%) in water.

### 2.2. Solvent extraction procedure

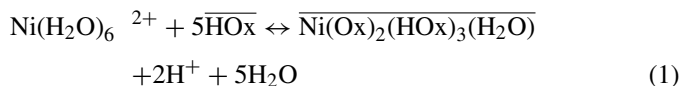
The metal distribution was studied at  $24^\circ\text{C}$ . Equal volumes (150 mL) of aqueous and organic phases were vigorously stirred at 700 rpm in a glass cell. The aqueous phase initially contained  $5 \times 10^{-4} \text{ mol L}^{-1}$  nickel(II) and  $1 \text{ mol L}^{-1} \text{ NH}_4\text{NO}_3$ . After settling, Ni concentrations were measured by atomic absorption spectrometry (A400S Varian), either directly for aqueous solutions or after stripping for organic solutions. Mass balances were always verified with an excellent precision (<2%). UV-vis measurements have been performed with a UV-vis spectrophotometer (Varian Cary 300 scan).

In the rapidly Rushton stirred cell (Fig. 1), the organic and aqueous phases are strongly agitated to eliminate diffusion resistance. Thanks to the great interfacial area, the study of this

slow chemical system can be achieved [16]. The stirrer of the cell rotated at the interface of the aqueous and organic phases. The temperature of the cell is controlled by using a heating or refrigerated bath circulator (Julabo).

## 3. Results and discussion

In ammonium solution, the thermodynamic extraction reaction is as follows:



where HOx represents the EHO monomer calculated from osmometry measurements [1].

### 3.1. Kinetic model

Let us consider the following notations:

- $a$ : interfacial area per volume unit;
- $D$ : distribution coefficient of nickel;
- $N$ : quantity of Ni transferred by time and surface units;
- $X, Y$ : nickel concentrations at time  $t$  in aqueous and organic phases, respectively;
- $X^*$ : aqueous nickel concentration that would be in equilibrium with the instantaneous organic phase at the  $Y$  nickel concentration. Then,  $Y = DX^*$ ;
- $X_\infty, Y_\infty$ : equilibrium concentrations of nickel in the aqueous and organic phases, respectively;
- $k_A^g$ : aqueous global transfer coefficient of nickel;
- $A, S$ : aqueous and organic volume, respectively.

The transfer flux of nickel can be written as

$$N = k_A^g (X - X^*) \quad (2)$$

By using equilibrium and material balance relations, the following equation is obtained:

$$N = k_A^g \left( 1 + \frac{1}{\varepsilon} \right) (X - X_\infty) \quad (3)$$

where  $\varepsilon = DS/A$  is the extraction factor.  $\varepsilon = D$  because in this work  $S = A$ .

A material balance on nickel in the aqueous phase between  $t$  and  $dt$  gives:

$$-A dX = Na dt \quad (4)$$

After integration of the Eq. (4) the following relationship is obtained:

$$\ln \left( \frac{X - X_\infty}{X_0 - X_\infty} \right) = -\alpha t \quad (5)$$

with

$$\alpha = \frac{D + 1}{D} \frac{ak_A^g}{A}$$

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