# Solvent extraction equilibria of nickel from ammonium nitrate solution with LIX84I

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## ABSTRACT

The equilibrium distribution ratios of nickel(II) ion between LIX84I (active component 2-hydroxy-5-nonylacetophenone oxime (HNAPO)), dissolved in a non-polar diluent and 3 kmol m$^{-3}$ ammonium nitrate solution are measured in the pH range 2–10 at 298 K. The effect of pH on the distribution ratio of nickel is analyzed based on the extraction equilibrium model assuming that the extracted complex has the stoichiometry of 1:2 (Ni:HNAPO). The successive aggregation of HNAPO in the organic phase and the nickel-ammine complex formation in the aqueous phase are considered, where the acid dissociation constant of ammonium ion, measured by the half-neutralization method, is used. The equilibrium constants for the extraction, successive aggregation, and distribution of the nickel extractant complex between the aqueous and organic phases are determined to be $4.90 \times 10^{-5}$, 9.9 (kmol m$^{-3}$)$^{-1}$ and $1 \times 10^{-4}$, respectively. These constants reproduce the experimental distribution data with good accuracy.

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## 1. Introduction

Hydrometallurgical recovery of nickel has been in use for a long time, but its full potential has not yet been reached due to technological constraints. Active research is being carried out to make the process more efficient and environmentally friendly. Recently Vale Inco completed their demonstration plant study on a hydrometallurgical pressure oxidative acid leach process to produce high-quality electro-nickel from Voisey's Bay nickel concentrate (Stevens et al., 2009). Ammoniacal leaching is also used in nickel metallurgy as ammonia is a highly selective complexant for nickel, copper and cobalt ions. For example, the Sherritt International Corporation employs an ammoniacal solution in their nickel/cobalt refinery at Fort Saskatchewan, and recently developed a new process for improved recovery of nickel and cobalt in their hexamine leach process (Budac et al., 2009). Many other researchers are also developing new processes to leach nickel using ammoniacal alkaline solutions (Senaputra et al., 2008; Fischmann and Dixon, 2009).

Solvent extraction now plays a very important role in hydrometallurgy, and its applications to the separation and recovery of metals from low-grade ores, complex ores and metallic wastes are many and varied (Ritcey and Ashbrook, 1979, 1984; Sole et al., 2005). Many extractants have been proposed for solvent extraction in hydrometallurgical processes. Among these, β-hydroxyoxime extractants such as LIX65N and LIX84I are known to extract copper and nickel from not only acidic solutions but also from ammoniacal alkaline solutions.

Processes for separating and recovering copper and/or nickel with hydroxyoximes from the ammoniacal solutions have been studied by many researchers (Merigold et al., 1971; Travkin et al., 1984; Sarma et al., 1987; Nilsen et al., 1988; Nathsarma and Sarma, 1993; Alguacil and Cobo, 1998a,b; Parija et al., 1998; Parija and Sarma, 2000; Alguacil, 1999; Brown et al., 1977; Pandey et al., 1989; Kumar et al., 1991; Rokukawa, 1993; Inoue and Kawahara, 1998; Virning et al., 2001; Mackenzie and Virning, 2004). Accordingly, many basic studies were carried out on the extraction equilibrium of copper and nickel with hydroxyoximes from ammoniacal solutions (Rice et al., 1978; Inoue and Tsunomachi, 1984; Cooper and Mak, 1984; Shibata et al., 1987; Russell et al., 1991; Pazos et al., 1991). However, the effect of pH on the extraction behavior is not completely clarified, or the correlation of the experimental data by the model is not sufficient, particularly in non-ideal high ionic strength solutions.

The present study aims at clarifying the effect of pH on the extraction behavior of nickel from 3 kmol m$^{-3}$ ammonium nitrate solutions with LIX84I and establishing the extraction equilibrium model for the quantitative prediction of the nickel distribution ratios. The model will consider the successive aggregation of the hydroxyoxime in the organic phase using IR spectra, as well as the complex formation of nickel with ammonia to determine the relevant equilibrium constants. Due to the lack of literature data for the equilibrium constant necessary for the data analysis, the acid dissociation constant of ammonium ion is measured by the half-neutralization method as a function of ammonium nitrate molarity. The reason for using nitrate system is that nitrate ion does not form a complex with nickel(II) ion and thus we can regard the system as a fundamental one. The model established can be applied to more

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practical systems such as sulfate system if the appropriate complex formation of nickel(II) with the counter anion is considered.

## 2. Experimental

### 2.1. Reagents and solution preparation

The chemicals used in this study were all reagent grade except the extractant and diluent. An 8 kmol m$^{-3}$ standardized ammonium nitrate solution was appropriately mixed with 8 kmol m$^{-3}$ standard sodium hydroxide solution and diluted with water in order to prepare $i$ kmol m$^{-3}$ ammonium nitrate–$i$/2 kmol m$^{-3}$ sodium hydroxide solution ($i = 0.5, 1, 2, 3, 4, 5$). This mixed solution was submitted for the measurement of the acid dissociation constant ($K_a$) of ammonium ion.

LIX84I (Henkel, Lot No. 4841042) was used as an extractant without further purification. The active component of LIX84I is 2-hydroxy-5-nonylacetophenone oxime (HNAPO). The concentration of HNAPO in LIX84I was determined to be 1.72 mmol g$^{-1}$ by the ultimate loading of copper(II) ion. Shellsol D70 (Shell Chemicals, Lot No. 80203) was used as the diluent without further purification. Shellsol D70 is an industrial organic solvent consisting of 55 mass% of C$_{11+}$ paraffins and 45 mass% of naphthenics. A solution containing 0.0625 kmol m$^{-3}$ Ni(NO$_3$)$_2$–3.75 kmol m$^{-3}$ NH$_4$NO$_3$ was prepared as the initial aqueous phase. Various concentrations of sodium hydroxide solution, nitric acid solution and water were used as the pH adjusting reagents.

### 2.2. Extraction of nickel

The initial organic and aqueous phases and the pH adjusting reagent were poured into a 50-cm$^3$ conical flask at the volume ratio of 5:4:1 and shaken in a water bath kept at 298 ± 0.1 K for a sufficient period to attain equilibrium. This procedure is equivalent to mixing the equal volumes of the aqueous phase of 0.05 kmol m$^{-3}$ Ni(NO$_3$)$_2$–3 kmol m$^{-3}$ NH$_4$NO$_3$ having various pH values and the initial organic phase.

After shaking, the mixture was centrifuged at 2000 rpm for 10 min. For the aqueous phase, the pH was measured by a pH meter (TOA HM-50AT) at 298 K. The nickel concentration was determined by EDTA titration using Murexide as an indicator, when it was relatively high. An automatic titrator (TOA AUT-1) installed with an optical titration probe (TOA FUT-1) was used to detect the end point. When the nickel concentration was relatively low, it was determined by an atomic absorption spectrometer (Hitachi 180-50) using a wavelength of 232 nm or 231 nm.

Nickel concentration in the organic phase was determined based on the difference in the nickel concentrations before and after the extraction, when the distribution coefficient *(D)* was larger than unity. When *D* was less than unity, nickel in the organic phase was stripped by the excess volume of 2 kmol m$^{-3}$ HCl, and the nickel concentration in the obtained aqueous solution was analyzed by the atomic absorption spectrometer.

### 2.3. Infrared absorption spectra

Infrared absorption spectra of LIX84I in Shellsol D70 were measured by an FT-IR spectrometer (Nicolet Magna-IR System 750). The transmission method using a 10-mm sodium chloride cell was applied using Shellsol D70 as blank.

## 3. Results and discussion

### 3.1. Dependency of pK$_a$ of NH$_4^+$ on the concentration of ammonium nitrate

In the mixed solution described in Section 2.1, the ammonium ion is half-neutralized by sodium hydroxide. Under this condition, $C(NH_3)$
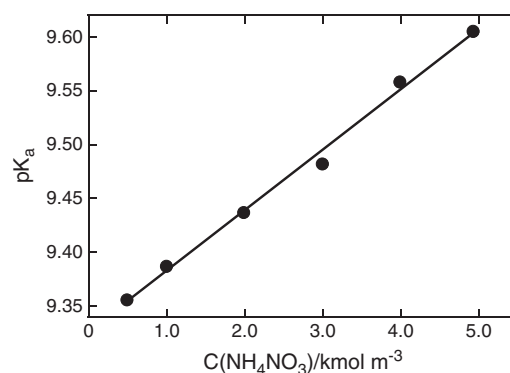


**Fig. 1.** The pK$_a$ values of ammonium ion in the ammonium nitrate solutions determined by the half-neutralization method as a function of ammonium nitrate concentration.

and $C(NH_4^+)$ values are equal and thus pK$_a$ = pH. Fig. 1 shows the pK$_a$ values of NH$_4^+$ in the ammonium nitrate solutions as a function of ammonium nitrate concentration. The straight line in Fig. 1 is drawn by the least squares method and expressed by

$$pK_a = 0.0562C(NH_4NO_3) + 9.33 \tag{1}$$

where the correlation coefficient was 0.9974. From Eq. (1), the pK$_a$ value in the present extraction experiment ($C(NH_4NO_3) = 3$ kmol m$^{-3}$) is 9.50.

### 3.2. Relationship between log D and pH

Fig. 2 shows the log *D* vs. pH diagram at equilibrium. The extraction behavior is described in each pH region as follows.

(i) Region where the pH is less than 4

The experimental data lie on straight lines of slope = 2 when the total hydroxyoxime concentration, $C_{BO}$, is constant. In this pH region, ammonium ions do not dissociate; thus, nickel in the aqueous phase exists as free nickel(II) ion and extraction proceeds via ion-exchange of a nickel(II) ion with two hydrogen ions.

(ii) Region where the pH is between 5 and 8

When $C_{BO}$ values are 0.040 and 0.078 kmol m$^{-3}$, the log *D* values are constant at −0.19 and 0.57, respectively, and the organic phases are saturated with nickel. In this situation, $C_{BO}/2 < C(Ni)_{init}$ at the phase ratio of unity and the ratio of $C(Ni)$ to $C_{BO}$ in the organic phase was 1:2. Again, nickel ion is extracted by proton exchange to form the NiR$_2$ oxime complex using caustic solution addition to adjust the pH. Many researchers agree with this stoichiometry for the solvent extraction of nickel with hydroxyoximes (Rice et al., 1978; Inoue and Tsunomachi, 1984; Shibata et al., 1987; Pazos et al., 1991).
On the other hand, when $C_{BO}$ values are 0.16 and 0.31 kmol m$^{-3}$ (i.e., $C_{BO}/2 > C(Ni)_{init}$), log *D* is constant at 4 in the pH range between 6 and 7.8. Under this condition, the predominant nickel species in the aqueous phase is thought to be NiR$_2$ which is in equilibrium with NiR$_2$ in the organic phase.

(iii) Region where the pH is larger than 8

When the organic phase is saturated, with $C_{BO}$ values of 0.040 and 0.078 kmol m$^{-3}$, the log *D* values hardly differ from those found in pH 4–8 solutions. However, for higher organic concentrations, log *D* is monotonically decreased with increasing pH due to the formation of nickel-ammine complexes and decreased concentration of free nickel(II) ion.