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Kinetics of the Complexation of Nickel (II) with 8-Hydroxyquinoline in Aqueous Solution

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KINETICS OF THE COMPLEXATION OF NICKEL (II) WITH 8-HYDROXYQUINOLINE IN AQUEOUS SOLUTION

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ABSTRACT

The complexation of nickel ion (II) with 8-Hydroxyquinoline were studied in aqueous solution for the pH range from 4.6 to 5.4 and the temperature range from 15°C to 50°C. The reactions were found to be first-order for the nickel ion concentration and inverse first-order for the hydrogen ion concentration. The formula of the observed rate constant may be expressed as

$$k_{obs} = k_{+1}K_{H1}\ [N_i^{++}]/[H^+] + k_{-1}$$

where k_{+1} and k_{-1} represent the forward and the backward step reaction rate constant, and K_{H1} is the equilibrium constant for 8-hydroxyquinoline in aqueous solution. Both k_{+1} and k_{-1} follow Arrhenius equation behavior and the activation energy is calculated as 8.9 Kcal/g-mole for the forward reaction and 10.63 Kcal/g-mole for the backward reaction.

INTRODUCTION

The kinetics of complexation between Ni (II) and 8-Hydroxyquinoline (oxine) has been studied in a solvent extraction system (1, 2, 3, 4) for the pH range of 4.6 to

5.4 at various ionic strengths. Although the reaction has been reported as first order in nickel ion concentration, the reactions were complicated by mass transfer process. The kinetic rate constant measured may be distorted by diffusion resistance.

In this study, a stopped-flow spectrophotometer is used to eliminate the diffusion resistance. This equipment has been found to be successful in the measurement of the true reaction rate constant (5) between Fe (III) and oxine. The findings of this study can be used for further understanding of reactions occurring in the industrial extraction of nickel.

EXPERIMENTS

The experimental work was performed with a Durrum-Gibson Model D-110 Stopped-Flow Spectrophotometer at the wavelength of 255 nm. Temperature control was provided by a Rosemont temperature controller (within ±0.1°C). Kinetic data were recorded using a Soltec 310 strip-chart recorder.

All the chemical reagents used here were ACS grade. Ionic strengths were adjusted to 0.2 M by adding sodium perchlorate. Acidity of the reaction solution was controlled with a buffered solution of potassium hydrogen phthalate and sodium hydroxide. During all the reactions, nickel ion concentrations were in large excess so that pseudo-first-order reaction analysis could be used.

EQUILIBRIUM ANALYSIS

In an aqueous solution containing nickel ions and oxine, the following equilibria can be recognized,

$$HOx = H^+ + Ox^- \tag{1}$$

$$H_2Ox^+ = HOx + H^+ \tag{2}$$

$$NiOx^+ = Ni^{++} + Ox^- \tag{3}$$

$$NiOx_2 = NiOx^+ + Ox^- \tag{4}$$

where the equilibrium constants are defined as

$$K_{H1} = \frac{[H^+]\ [Ox^-\ ]}{[HOx]} \tag{5}$$

$$K_{H2} = \frac{[HOx]\ [H^+]}{[H_2Ox^+]} \tag{6}$$

$$K_1 = \frac{[Ni^{++}]\ [Ox^-]}{[NiOx^+]} \tag{7}$$

$$K_2 = \frac{[NiOx^+]\ [Ox^-]}{[NiOx_2]} \tag{8}$$

Some representative pK values for these constants can be found in the literature and are listed in Table 1. For this study, the pK values are therefore taken as $pK_{H1}=10$, $pK_{H2}=5$, $pK_1=10$ and $pK_2=9$.

An over-all oxine mass balance for the system gives

$$[HOx] + [H_2Ox^+] + [NiOx^+] + 2[NiOx_2] + [Ox^-] = [HOx]_0 \tag{9}$$

Equations (5) through (9) can be combined to give

$$\left\{\frac{[H^+]}{10^{-10}} + \frac{[H^+]^2}{10^{-15}} + \frac{[Ni^{++}]}{10^{-10}} + 1\right\} [Ox^-] + \left\{\frac{2[Ni++]}{10^{-19}}\right\}[Ox^-]^2 = [HOx]_0 \tag{10}$$

Since the pH and nickel concentrations are known, this equation can be solved for oxine anion concentrations in the system. And therefore, the other species concentrations can be computed and are shown in Table 2 for the extreme pH values and nickel ion concentrations used in this study.

It may be concluded that $NiOx^+$ is the predominant product of the reaction. The amount of $NiOx_2$ present is about two orders-of-magnitude less and therefore is negligible. Although this finding is contradictory with that reported by Haraguchi et al. (2), it is supported by a stability study (7) of Ni^{++} and oxine complexation.

KINETIC ANALYSIS

The equilibrium analysis indicated that under the conditions used in this study, nickel and oxine react to produce the complex $NiOx^+$. Reasonable reaction steps for

Table 1. Representative Values of the Equilibrium Constants for the Nickel-Oxine System.

Equilibrium	Value	Conditions		Reference
pK_1	10.03	$\mu=0.0$	T=25°C	Vasilev(7)
pK_1	9.55	$\mu=0.2(KNO_3)$	T=25°C	"
pK_1	9.9	$\mu=0.1(ClO_4^-)$	T=20°C	Sillen(6)
pK_2	8.8	$\mu=0.1(ClO_4^-)$	T=20°C	"
pK_1	9.27	$\mu=0.0$	T=25°C	"
pK_{H1}	9.90	$\mu=0.0$	T=20°C	"
pK_{H2}	5.01	$\mu=0.0$	T=20°C	"
pK_{H1}	9.81	$\mu=0.0$	T=25°C	"
pK_{H2}	4.91	$\mu=0.0$	T=25°C	"
pK_{H1}	9.89	$\mu=0.01$	T=20°C	"
pK_{H2}	5.13	$\mu=0.01$	T=20°C	"
pK_{H1}	9.66	$\mu=0.1$	T=25°C	"
pK_{H1}	9.86	$\mu=0.085$	T=25°C	"
pK_{H2}	5.01	$\mu=0.085$	T=25°C	"

Table 2. Equilibrium Concentrations for the Nickel-Oxine System at the Extremes of the pH and Nickel Concentrations used in this Study.

pH	$[Ni^{++}]$ M $x10^3$	$[Ox^-]$ M $x10^{12}$	$[HOx]$ M $x10^8$	$[H_2Ox^+]$ M $x10^8$	$[NiOx^+]$ M $x10^5$	$[NiOx_2]$ M $x10^7$
4.60	0.502	9.31	234.	587.	4.67	4.35
	2.509	2.14	53.8	135.	5.37	1.15
5.40	0.502	11.6	46.1	18.3	5.81	6.72
	2.508	2.38	9.47	3.77	5.97	1.42

this complexation reaction may start with the equilibrium dissociation of oxine, as shown in Equation (1), following a reaction between nickel ions and the oxinate ions,

$$Ni^{++} + Ox^{-} \underset{k_{-1}}{\overset{k_{+1}}{=}} NiOx+. \tag{11}$$

The above reaction steps produce the following rate law equation,

$$\frac{d[NiOx^{+}]}{dt} = k_{+1}[Ni^{++}]^{a}[Ox^{-}]^{b} - k_{-1}[NiOx^{+}]^{c}. \tag{12}$$

By using the equilibrium constant K_{H1}, Equation (5), Equation (12) can be converted into,

$$\frac{d[NiOx^{+}]}{dt} = k' \; [HOx]^{b} - k_{-1}[NiOx^{+}]^{c}, \tag{13}$$

where

$$k' = K_{H1}{}^{b}k_{+1} \frac{[Ni^{++}]^{a}}{[H^{+}]^{b}} \tag{14}$$

Since the nickel and hydrogen ion concentrations are maintained as constants during the reactions, they have been combined with the other constants for ease in manipulation. Making the assumption that the equation is first-order in oxine and nickel mono-oxinate and using the equation for oxine mass balance,

$$[HOx] = [HOx]_{o} - [NiOx^{+}], \tag{15}$$

equation (13) produces

$$\frac{d[NiOx^{+}]}{dt} = k' \; [HOx]_{o} - (k' + k_{-1}) \; [NiOx^{+}]. \tag{16}$$

At equilibrium the initial oxine concentration can be solved to produce

$$[HOx]_{o} = (1 + (k_{-1}/k')) \; [NiOx^{+}]_{\infty} \tag{17}$$

Equation (17) is then substituted back into equation (16) and the result simplified to produce

$$\frac{d[\mathrm{NiOx}^+]}{dt} = k_{obs} \{ [\mathrm{NiOx}^+]_\infty - [\mathrm{NiOx}^+]\}, \tag{18}$$

where

$$k_{obs} = k' + k_{-1} = K_{H1}k_{+1} \frac{[\mathrm{Ni}^{++}]^a}{[\mathrm{H}^+]^b} + k_{-1}. \tag{19}$$

Integrating equation (18) produces the following basic kinetic equation;

$$\ln \{\frac{[\mathrm{NiOx}^+]_\infty - [\mathrm{NiOx}^+]}{[\mathrm{NiOx}^+]_\infty - [\mathrm{NiOx}^+]_o}\} = k_{obs}t. \tag{20}$$

KINETIC EQUATION IN OPTICAL FORMULA

The basic expression relating concentration and optical absorbance is the Beer's Law which can be written as

$$A = \varepsilon bc, \tag{21}$$

where A is the absorbance, ε is the absorbtivity, b is the path length, and c is the molar concentration of the absorbing species. For this study, the path length is constant and can be combined with the absorbtivity. The total absorbance for any solution is the sum of the absorbances of each of the individual species involved. Therefore,

$$A_0 = \varepsilon_1[\mathrm{Ni}^{++}]_0 + \varepsilon_2[\mathrm{HOx}]_0, \tag{22}$$

$$A = \varepsilon_1[\mathrm{Ni}^{++}] + \varepsilon_2[\mathrm{HOx}] + \varepsilon_3[\mathrm{NiOx}^+], \tag{23}$$

and

$$A_\infty = \varepsilon_1[\mathrm{Ni}^{++}]_\infty + \varepsilon_2[\mathrm{HOx}]_\infty + \varepsilon_3[\mathrm{NiOx}^+]_\infty \tag{24}$$

These equations are written for the initial conditions, the intermediate reaction, and at equilibrium respectively.

In accordance with the pseudo-first-order kinetics of this study, the nickel ion is present in large excess. In essence, this means that the nickel ion concentration is effectively constant, or

$$[\mathrm{Ni}^{++}]0 = [\mathrm{Ni}^{++}] = [\mathrm{Ni}^{++}]_\infty \tag{25}$$

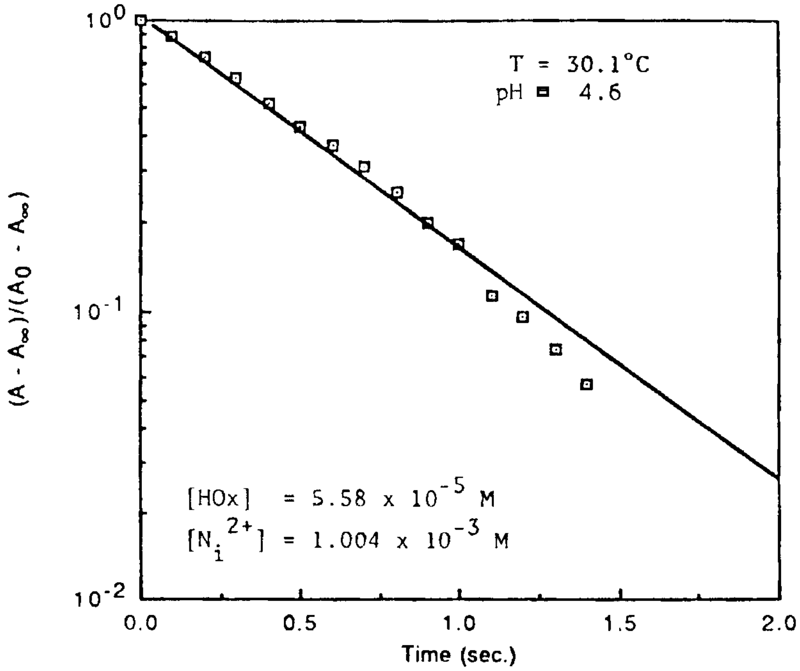

Figure 1. Example of Optical Data versus Time Plot Used to Obtain the Observed Rate Constant.

With the help of Equations (23) through (25), the kinetic equation (20) can be converted into an optical density formula,

$$\ln \left\{\frac{A - A_\infty}{A_0 - A_\infty}\right\} = k_{obs}t. \qquad (26)$$

EXPERIMENTAL RESULTS

As may be seen from Figure 1, a plot of $(A-A_\infty)/(A_0-A_\infty)$ versus reaction time on a semi-logarithmic scale gives a straight line. The experimental data follow

Table 3. Experimental Conditions and the Observed Rate Constants for the Nickel-Oxine System used for Rate Law Development.

pH	Temp. °C	Ionic Strength M	Oxine $M\times10^5$	Nickel $M\times10^3$	K_{obs} Run A	K_{obs} Run B	K_{obs} Run C
4.60	30.1	0.2063	5.58	0.502	1.357	1.473	1.481
				1.004	1.833	1.674	1.651
				1.506	2.193	1.769	2.150
				2.007	2.167	2.375	2.421
				2.509	2.455	2.571	2.540
4.68	29.8	0.2057	6.17	0.502	1.249	1.275	1.241
				1.004	1.756	1.733	1.798
				1.506	2.062	2.045	2.072
				2.007	2.358	2.602	2.507
				2.509	2.671	2.854	2.639
4.93	30.2	0.2056	6.37	0.502	1.826	1.570	1.603
				1.003	1.982	1.942	1.897
				1.505	3.294	2.736	2.210
				2.006	3.052	2.929	2.878
				2.508	3.130	2.884	3.692
5.09	30.0			0.501	3.357	2.983	3.076
				1.003	5.041	5.890	5.275
				1.504	6.070	5.879	5.336
				2.005	6.610	7.189	9.812
				2.507	7.329	7.481	7.894
5.40	29.9	0.2055	6.01	0.502	1.632	1.760	1.503
				1.003	2.762	2.964	3.063
				1.505	4.653	4.403	5.194
				2.006	5.272	5.343	4.632
				2.508	7.405	6.251	8.428

the straight line quite well for the reaction time covering more than twice of the half life. This indicates that the reaction is first-order in oxine for forward and first-order in nickel mono-oxinate for backward reaction. The observed rate constant can be obtained from the slope of the straight line. They are presented in Table 3 for the reaction conditions at 30°C and 0.2 M of ionic strength and for different pH values.

A plot of the observed rate constants versus nickel ion concentration at constant pH value showed a straight line

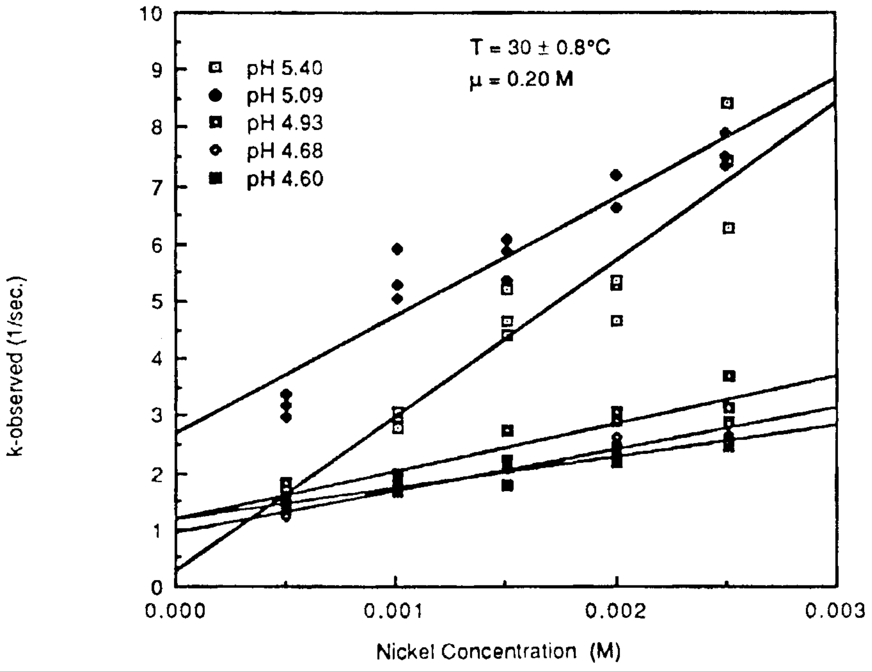

Figure 2. Effect of Nickel Ion Concentration on the Observed-Rate Constant.

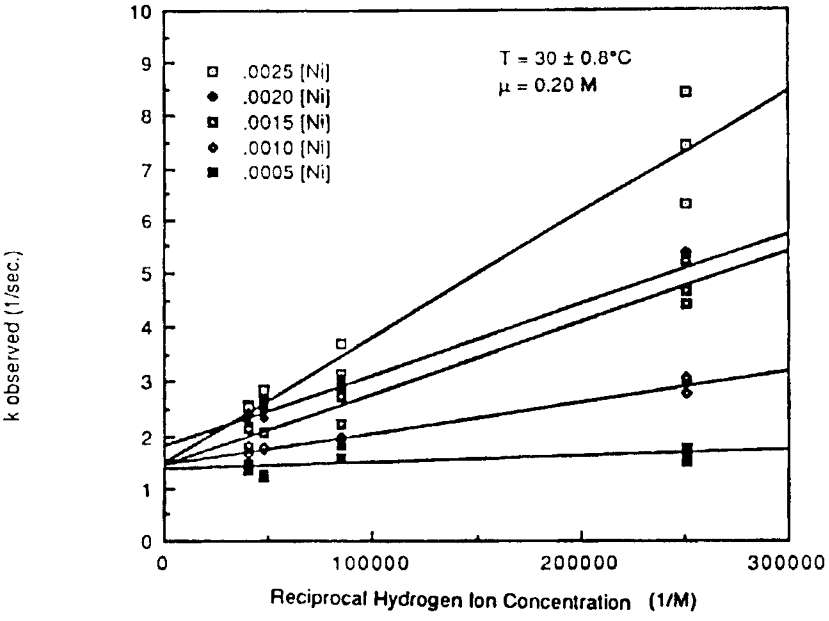

Figure 3. Effect of Hydrogen Ion Concentration on the Observed Rate Constant.

Table 4. Rate Constants Determined from the Data in Figures 2 and 3.

$[Ni^{++}]$ M	k_{-1} sec^{-1}	k_{+1} sec^{-1}	pH	k_{-1} sec^{-1}	k_{+1} sec^{-1}
0.0005	1.37	2.32×10^7	4.60	1.18	1.39×10^8
0.0010	1.48	5.75×10^7	4.68	0.96	1.52×10^8
0.0015	1.45	8.70×10^7	4.93	1.21	9.73×10^7
0.0020	1.84	6.44×10^7	5.09	2.69	1.66×10^8
0.0025	1.51	9.22×10^7	5.40	0.27	1.08×10^8

Table 5. Experimental Conditions and the Observed Rate Constants for the Nickel-Oxine System at Different Temperatures.

pH	Temp. °C	Ionic Strength M	Oxine $Mx10^5$	Nickel $Mx10^3$	K_{obs} Run A	K_{obs} Run B	K_{obs} Run C
4.60	20.9	0.2063	5.58	1.004	0.610	0.588	0.570
	29.6				1.266	1.328	1.447
	40.3				3.757	3.727	2.623
4.93	15.7	0.2056	6.37	1.003	0.697	0.733	0.674
	21.2				0.652	0.705	0.727
	30.5				1.555	1.565	1.543
	40.0				2.571	3.265	2.828
	49.7				3.757	3.591	3.141
5.09	24.7	0.2057	4.86	1.003	1.401	1.637	1.466
	30.8				1.921	1.709	1.916
	35.9				2.660	3.100	3.459
	41.6				4.496	3.633	4.039
5.40	15.2	0.2055	6.01	1.003	1.446	1.113	0.929
	21.1				1.386	1.235	1.266
	30.0				1.798	1.934	2.160
	39.8				4.178	4.857	5.879
	50.7				5.781	5.781	5.781

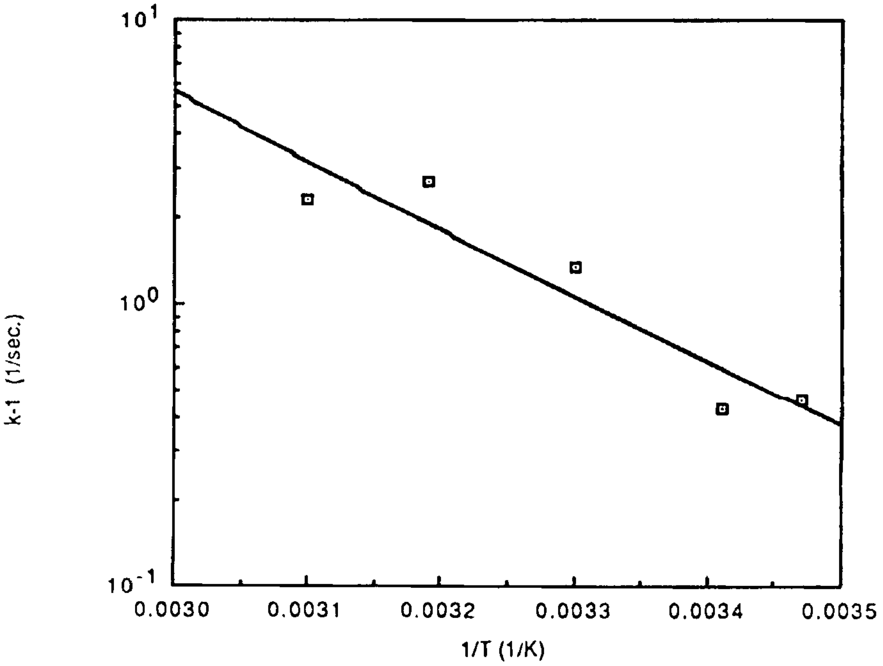

Figure 4. Effect of Temperature on the Reverse Rate Constant.

with a positive slope as can be seen from Figure 2. This indicates that the reaction is first-order with respect to nickel ion concentration. Another plot of the observed rate constants versus the inverse of the hydrogen ion concentration also gives a straight line as shown in Figure 3. This is an indication of an inverse first-order reaction with respect to the hydrogen ion concentration. Therefore, the observed rate constant ; Equation (19) can be written as

$$k_{obs} = K_{H1}k_{+1}\frac{[Ni^{++}]}{[H^+]} + k_{-1}. \tag{27}$$

Taking the pK_{H1} value as 10, the forward constant, k_{+1}, and the backward rate constant, k_{-1}, can then be computed from the sloped and the intercepts of these straight lines.

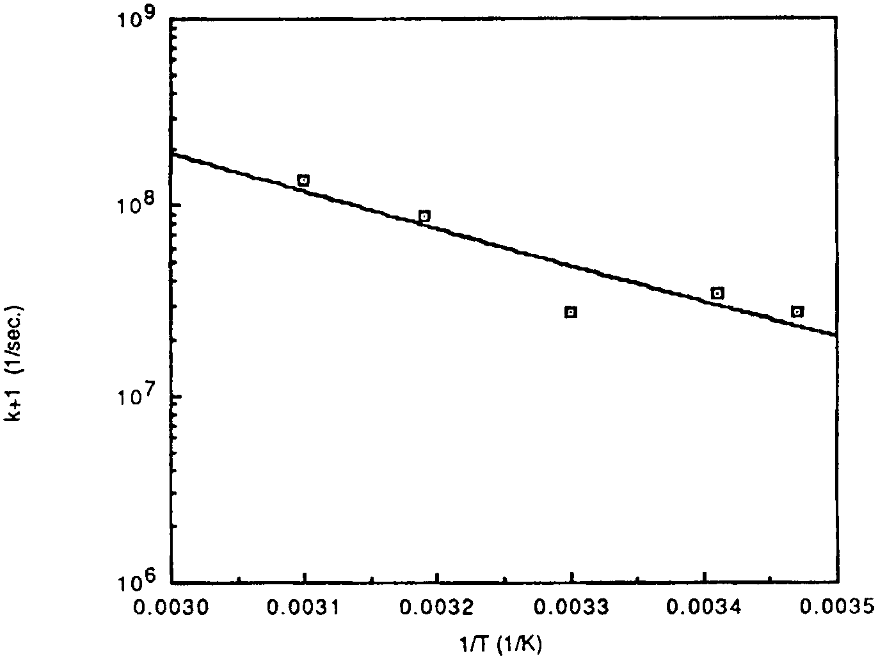

Figure 5. Effect of Temperature on the Forward Rate Constant.

They are listed in Table 4. The average value of k_{+1} is 1.23 ± 0.42 sec^{-1}, and the average reverse rate constant is $8.90 \pm 0.90 \times 10^7$ sec^{-1}. With these kinetic rate constants, the K_I value can be estimated as 10^{-8} (at 30^oC).

THE TEMPERATURE EFFECT

The observed rate constants, k_{obs}, at different temperature are measured and are listed in Table 5. Using the same procedures as mentioned in the above the rate constants, k_{+1} and k_{-1} at different temperatures can be estimated. The plots of rate constants versus 1/T on a semi-logrithmic scale indicate that both reaction rate constants follow the Arrhenius equation quite well as may be seen from Figures 4 and 5. The activation energy, Ea, and the frequency factor in the Arrhenius equation can then be calculated and are shown in Table 6.

Table 6. Activation Parameters for the Nickel-Oxine System.

	k sec^{-1}	A sec^{-1}	Ea $\frac{cal}{gmol}$	ΔH $\frac{cal}{gmol}$	ΔS $\frac{cal}{gmol\ K}$	ΔG $\frac{cal}{gmol}$
k_{+1}	3.76×10^{7}	1.25×10^{14}	8900	8300	3.98	7120
k_{-1}	7.81×10^{-1}	4.87×10^{7}	10630	10000	10.3	6970

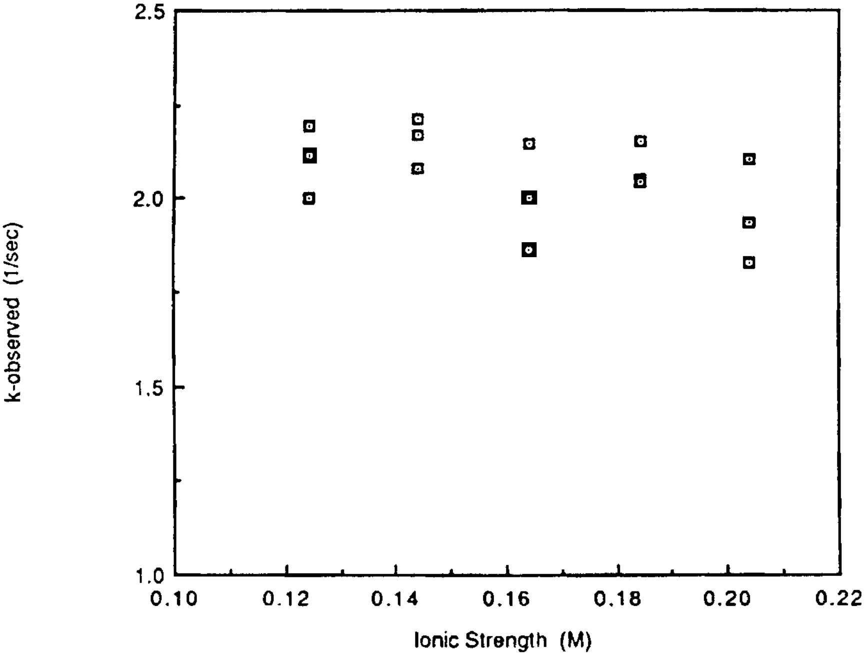

Figure 6. Effect of the Ionic Strength on the Observed Rate Constant.

The enthalpy of activation at 25°C can be calculated by

$$\Delta H = Ea - RT. \tag{28}$$

The entropy and the free energy of activation can then be computed by

$$\Delta S = R \ln \left(\frac{N_o h}{RT} k \exp(\Delta H / RT)\right) , \tag{29}$$

and

$$\Delta G = \Delta H - T\Delta S . \tag{30}$$

These activation parameters at 25°C are also listed in Table 6.

The relatively small entropy of activation indicates that the entropy barrier is not predominant during the activation of this complexation reaction. And therefore it may be considered that the enthalpy of activation is the controlling factor for this complexation reaction.

IONIC STRENGTH EFFECT

Ionic strength was varied from 0.124 M to 0.204 M, with the temperature, pH, and nickel concentration held constant. Lower ionic strengths were not studied to be sure that the ionic strength did not change during the reaction. The buffer solution also limit the ionic strength to go any higher. Within this narrow ionic strength range, as may be seen from Figure 6, the ionic strength effect is not significant.

CONCLUSION

The kinetics of the reaction between nickel and oxine are first-order with respect to both nickel and oxine. The reaction is inverse-first-order with respect to hydrogen ion concentration from pH 4.60 to 5.40. The activation of this complexation reaction is enthalpy controlling rather than entropy controlling. The ionic strength effect is not significant for the condition of this study.

NOMENCLATURE

Symbol	Description
A	- (1) Optical absorbance - (2) Frequency factor in the Arrhenius Law
b	- Optical path length

c - Concentration
Ea - Activation energy
ΔG - Free energy of activation
ΔH_0 - Standard enthalpy of reaction
ΔH - Enthalpy of activation
h - Planck's constant
K - Equilibrium constant
k - Rate constant
k_{+1} - Forward rate constant
k_{-1} - Reverse rate constant
N_o - Avagadro's number
R - Gas constant
ΔS - Entropy of activation
t - Time
ε - Molar absorbtivity in Beer's Law
μ - Ionic strength

Subscripts

0 - Initial value
obs - Observed value
∞ - Equilibrium value

Superscripts

a,b,c,d - Reaction orders in rate laws

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