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1976

EXTRACTION RATE STUDY OF Ni(II) OXINATE AND SEPARATION OF Cu(II) AND Ni(II) WITH OXINE BASED ON DIFFERENCES IN RATES OF EXTRACTION

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of the Requirements for the Degree
Master of Science

by
Somchai Taichilassunthorn
August 1976

EXTRACTION RATE STUDY OF Ni(II) OXINATE AND SEPARATION OF Cu(II) AND Ni(II) WITH OXINE BASED ON DIFFERENCES IN RATES OF EXTRACTION

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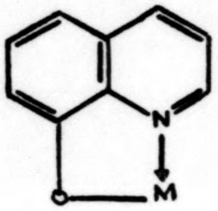
I. INTRODUCTION

In the solvent extraction of metal ions, 8-hydroxyquinoline (mol. wt. 145.15, mp, 75-76°C) which has the trivial name "oxine" (HOx) is well known as a sensitive organic analytical extractant. It acts as a bidentate ligand to form a five-membered chelate ring with many different metal ions, in the manner illustrated below:



Most studies on oxine as an analytical extractant have been aimed at the development of efficient separation under equilibrium conditions. (1)

A. HISTORICAL

Honaker and Freiser (2) pointed out that in favorable cases, solvent extraction techniques can be used to study the rate of fast chelation reactions occurring in aqueous solution. Many authors (3-10) have studied the rates of solvent extraction using numerous organic ligands. These studies have been of a theoretical nature and have determined rate laws, rate constants and postulated mechanisms for these extractions. As a consequence of these fundamental rate studies, the suggestion has been made (11) that knowledge of the rate controlling factor could be used to effect more selective separation. That is, by optimizing the parameters controlling the rate of extraction, it should be possible to separate two metals from each other that would not be separable under equilibrium conditions.

One rate study of interest to this work was done by McClellan and Freiser (12). They compared relative rates of formation of metal chelates at room temperature in the aqueous phase. Differences in the rates of extraction of aqueous solutions of Ni(II), Co(II), Zn(II), and Cd(II) with dithizone were reported. A recent extraction rate study has been reported by Colovos, Yokoyama and Freiser (13). By varying ratios of Ni(II) and ligand concentration, rate constants in aqueous solution of each stepwise chelation of Ni-phenanthroline and Ni-5-nitrophenanthroline were determined. For the system of Ni-5-nitrophenanthroline, it was found that the first stepwise rate constant obtained by the extraction technique proved to be in fair agreement with the result using the stopped-flow method.

The first practical application of extraction rate differences was by Irving, Andrew and Risdon (11). These authors used the difference in extraction rates in chloroform to separate the rapidly extracted Hg(II) dithizonate from the slowly extracted Cu(II) dithizonate. In 1950, Bolomey and Wish (14) used the marked difference in the rate of extraction to separate Fe(III) from Be(II) with a very dilute solution of thenoyltrifluoroacetone in benzene. McKavney and Freiser found Cr(III) extracted extremely slowly with acetylacetone except at relatively high pH values (15). Numerous metals, including Fe(III) and Al(III), were found to form stable chelates much more rapidly at lower pH values (11) and could be separated from Cr(III). McClellan and Freiser (16) developed a scheme of separation of metal ions based on the relative rates of extraction. The separations of Zn(II)-Ni(II), Zn(II)-Co(II), and Co(II)-Ni(II) by optimizing the rate-controlling parameters were reported. At a pH value of 1, Hines used the extraction rate differences to successfully separate Ag(I) from Cu(II) with dithizone in chloroform (17).

B. STATEMENT OF PURPOSE

This study was conducted with metal ion concentrations in the range of parts per million and used batch extraction techniques to study the non-equilibrium extraction of Cu(II) and Ni(II) oxinates. Contrary to other authors, atomic absorption was used exclusively for the analysis of phases.

The two main areas of investigation in this study were:

1. Kinetics study of extraction of Ni(II) oxinate.
2. Separation of Cu(II) and Ni(II) with oxine based on differences in rates of extraction.

It was the purpose of this work to study the extraction of Cu(II) and Ni(II) with oxine in chloroform. This particular pair of elements was chosen for study for several reasons. One prominent reason was that these metals form stable complexes with oxine which remain stable upon extraction with various organic solvents. The extraction curves (pH versus percent extraction) were found to lie very close together making it impossible to separate one from the other without the use of masking agents. Another factor which was important to the undertaking of this extraction rate study was the fact that the equilibrium behavior of metal oxinates (and of oxine) distributed between water and various organic solvents had been previously studied in detail. Fianlly, it was believed that it should be possible to separate the Cu(II) and Ni(II) ions (and perhaps other as well) by a non-equilibrium method even though it was not possible to separate these same two ions by an equilibrium extraction. The present work was aimed at determining the optimum conditions of pH, oxine concentration, shaking time and solvent used for the maximum separation of the ion pair, Cu(II)-Ni(II).

II. EXPERIMENTAL

A. MATERIALS

All materials were of analytical reagent grade and were used without further purification unless otherwise noted.

Solvents

Water used in this study was initially deionized by a Barnsted deionizer (Barnsted Co., Boston, Mass.). It is known that water from local water systems contains organic species (18) not removed by deionizers (19). Also, the deionizing process may introduce some organic impurities (20). Organic compounds, used as a resin in the deionizer, contain donor atoms such as N, O, P or S which are capable of coordination with transition metals. Because the metal ions used in this study were present in trace concentrations, removal of these organic species, even though they were present in only trace quantities, was deemed imperative to prevent possible interference. The strong oxidizing media of acidic permanganate was found suitable for digesting organic matter and converting it to carbon dioxide and water and possible non-volatile ash. The deionized water was further purified by distillation from an acidic $KMnO_4$ solution. Each charge of the distillation apparatus contained 5 grams $KMnO_4$ solution and 15 ml. concentrated H_2SO_4 in approximately 1.7 l. of water. The distilling apparatus used was constructed of Pyrex glass which was acid washed (conc. HCl) and leached before use. Ground glass connections were ungreased and an electric mantle was used for heating. To prevent ebullient entrainment and "carry over" of solids, a column packed with pieces of glass tubing was positioned directly above the still pot. As the water was distilled and collected, the still pot was regularly refilled to the 1.7 l. volume with boiling deionized water. The $KMnO_4$ was normally expended after 4 to 5 refills of the still pot. After the $KMnO_4$ was expended, indicated by the loss of the purple color of the solution, the still pot was cleaned with conc. HCl and recharged.

The distilled water was collected at a rate of 350 to 400 ml. per hour in a pre-treated Pyrex vessel and stored in Nalgene polyethylene containers. Atomic absorption was used regularly to test for the presence of Mn contamination. Such contamination also would have been indicative of solids "carry over". This uncontaminated deionized-purified water was used for all aqueous solutions and for rinsing glassware.

Chloroform, A.C.S. Reagent Grade from J. T. Baker Chemical Co., was used as supplied except for a reductant wash of hydroxylamine hydrochloride. For economic reasons and to prevent the emptying of quantities of the chlorinated hydrocarbon into the local water supply, chloroform, after use, was stored and later purified as needed. Used chloroform solutions were further purified and recovered as recommended by Moeller (21) and Bambach and Burkey (22).

The "used" chloroform solutions were stored in amber bottles. To stabilize the chloroform, to each storage vessel was added, at the outset of collection, a volume of undenatured ethanol equal to 0.5% of the total volume of the vessel. No effort was made at the time of storage to separate either colloidal water droplets in chloroform-oxine solutions or excess aqueous phase from extraction samples. A mechanical separation of the aqueous and organic layers constituted the initial step of the purification procedure. About one liter of the separated chloroform was then washed with 200 ml. of water in 2,000 ml. separatory funnel. This chloroform, in turn, was washed twice with 100 ml. portions of concentrated sulfuric acid. If coloration persisted in the chloroform layer, it was washed with 100 ml. of 1.3 M. aqueous ammonia and then with concentrated sulfuric acid. The final purification step consisted of a wash with a 0.5% hydroxylamine hydrochloride solution which had been made alkaline to phenol red with ammonia. After separation from the aqueous phase, the chloroform, stabilized with 5 ml. of 95% undenatured ethanol, was stored overnight over calcium oxide powder. Purified chloroform was obtained by decanting and distilling through an all-glass still. The first portion of the distillation, about 150 ml., was thrown away and the pure chloroform was collected at a temperature of 61.5°C. in an amber bottle containing a volume of absolute undenatured ethanol equivalent to 1% of the capacity of the bottle. The "used-and-purified" chloroform and reagent grade chloroform were both further purified just prior to the preparation of all oxine solutions.

Carbon tetrachloride, A.C.S. Reagent Grade from J.T. Baker Chemical Co., was further purified by the distillation through an all-glass still. The first portion of about 150 ml. of the distillation was thrown away and the pure carbon tetrachloride was collected at the temperature of 76.5°C. in an amber bottle.

8-Hydroxyquinoline

Reagent, A.C.S. grade, 8-hydroxyquinoline, as supplied by Matheson Coleman & Bell was recrystallized from boiling absolute undenatured ethanol (23). The reagent purity was checked by means of its melting point. The melting point of the recrystallized product, after overnight vacuum drying in a desiccator, was 72°C.

8-Hydroxyquinoline solutions

The oxine-chloroform solutions were prepared by dissolving the exact amount of purified oxine in chloroform. The solutions were freshly prepared before use.

Metal ion solutions

The aqueous metal ion stock solutions were prepared from the hydrated metal perchlorates. The copper perchlorate ($Cu(ClO_4)_2 \cdot 6H_2O$) and the nickel perchlorate ($Ni(ClO_4)_2 \cdot 6H_2O$) were supplied by Alfa Inorganics, Inc., Mass. Stock solutions were prepared in the range of 10^{-2}M. in the respective metal ions by dissolving the desired amount of the reagent in 500 ml. of water. By means of atomic absorption spectrophotometry techniques, these stock solutions were then standardized with metal standard solutions supplied by Fisher Scientific Co., Inc. Concentrations used in these studies containing both metal ions were also prepared by dilution from these stock solutions.

B. APPARATUS

Water bath shaker

All extractions were performed in 250 ml. glass bottle having a polyethylene cap and polyethylene liner. The samples were agitated on a mechanical water bath shaker purchased by Eberbach Corp., Ann Arbor, Mich. The shaker consists of an internal thermostatted heater for controlling of higher than ambient temperatures. An external electric mantle was used to stabilize the water bath temperature. The shaker speed can be adjusted up to about 260 shakes/minute with an 0.5 inch amplitude.

pH meter

A Corning pH meter model 7 was used for pH measurements. This meter was standardized against reference buffer solutions pH 7 and pH 10 before each set of measurements.

Atomic Absorption Spectrophotometer

A Perkin-Elmer model 303 atomic absorption spectrophotometer was used as well as the necessary hollow cathode tubes which were purchased from the Perkin-Elmer Corp.

C. EXPERIMENTAL

The extremely low concentrations (parts per million) of metal ion and chelating agent used in the study were cause for concern in obtaining reproducible data. The extraction was performed in a 250 ml. glass bottle having a polyethylene cap and polyethylene liner. This bottle size was chosen to fit the shaker stand of the water bath shaker. All extractions in the study were with phases of equal volume of aqueous and organic solutions and a total volume per batch extraction of 50 ml. The buffer solution containing the ion or ions to be investigated was prepared by the addition of KH_2PO_4, 1.70 grams in 500 ml. metal ion solution. The pH of the aqueous phase was adjusted to the desired value by the addition of NaOH and/or $HClO_4$ solution. The ionic strength(I) was kept constant at 0.05M by adding a sufficient amount of sodium perchlorate.

A 25 ml. amount of aqueous solution was pipetted into the extraction vessel and thermally equilibrated in the water bath for 15 minutes. A 25 ml. volumetric flask, containing the oxine solution of the desired concentration was equilibrated at the same time. To begin an extraction, the sample extraction vessel and the respective volumetric flask of oxine were taken from the thermostatted bath. The oxine solution was poured into the extraction vessel containing the aqueous solution. The extraction vessel was immediately placed in the shaker stand and the shaker started. The shaker was set at the highest speed of shaking (260 shakes/minute) for all runs except for those runs used to determine the effect of shaking on rate of extraction. From the start to the stop of shaking, time was noted. When it was stopped, the extraction vessel was allowed to stand 5 minutes to ensure complete phase separation. The phase or phases to be analyzed were separated by using clean, dry 25 ml. pipets to draw off approximately 15 ml. of the desired layer. The samples were delivered into clean, dry 40 ml. glass bottles fitted with polyethylene cap and liner. The samples were then analyzed by means of atomic absorption spectrophotometry techniques.

In the extraction rate portion of the study, batch extraction was also used. A separate batch extraction was used for each time interval in the same manner as reported by other researchers. All reaction rate measurements were taken at 25°C. except for those extraction experiments used to determine the temperature effect.

To determine the extraction order, non-stoichiometric batch extractions were run over a short period of time. Concentrations of oxine and nickel were separately varied. One concentration was held constant while the other was varied. The extractions were allowed to proceed to about 20% completion for obtaining initial rate data.

Additional data for the determination of extraction rate constants were obtained with the reactants in stoichiometric proportion:

$$[\mathrm{HOX}] = 2[\mathrm{Ni}^{+2}]$$

(1) and the concentration of the metal ion was followed with respect to time. The pH dependence of the extraction was studied by holding initial concentrations of the metal and ligand constant while varying the pH.

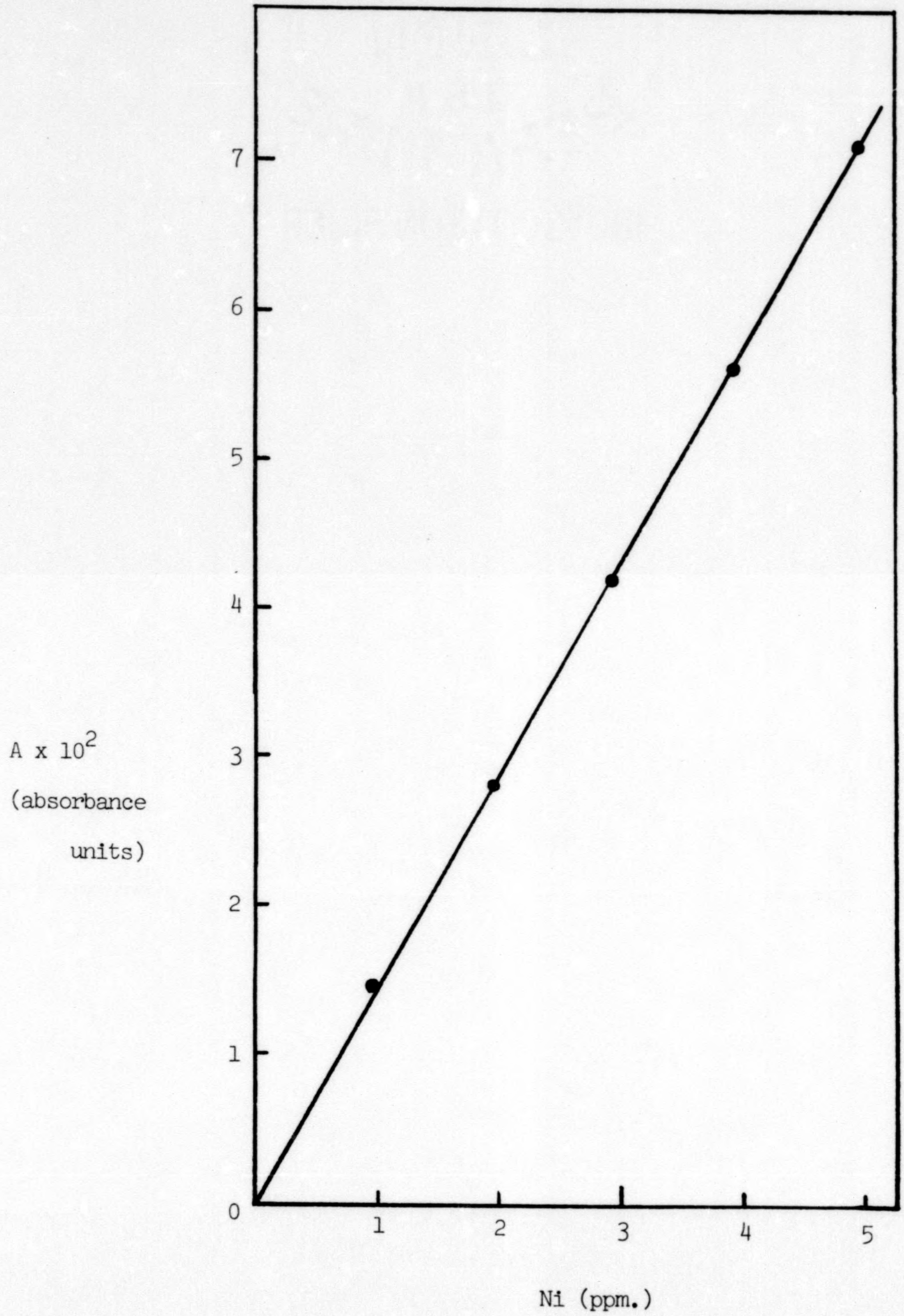
D. ANALYSIS OF SAMPLES

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer with appropriate hollow cathode tubes was used throughout the study for analysis of both aqueous and organic layers of the extraction systems. The trace concentrations employed in the study demanded high precision and sensitivity for the analysis. The required sensitivity was achieved by use of the most sensitive spectral lines for the elements studied. Instrumental parameters such as lamp current, burner height, slit width, fuel and oxidant ratio and aspiration rate were adjusted for each element to give maximum sensitivity. Copper and nickel standards were prepared from Certified Atomic Absorption Standard as supplied by Fisher Scientific Co. The detection limit of both copper and nickel in aqueous solution was 0.1 ppm.

The working standards were prepared to contain the amount of buffer components identical to the sample being analyzed. This was done to ensure that bulk matrix effects of buffer components would not affect the analyses (24). For the analysis of an extraction phase, approximately 15 ml. of phase to be analyzed was taken as a sample. Samples of standard concentrations inclusive of those anticipated in the samples were aspirated into the flame and the percentage absorption recorded for each. Each sample was then aspirated and the percentage absorption recorded. The percentage absorption of the standards was determined again to check the reproducibility of the readings. To correct for instrumental drift, the instrument was zeroed between each standard and sample with a metal free solution, which was identical to standards and samples in other respects.

The percentages of absorption for standards and samples were converted to absorbance readings by reference to a standard table. The percentages of absorption for the standards were averaged for three replicate samples prior to conversion to absorbance. The absorbances of the standards were then graphed versus the known concentrations of the standards to prepare the calibration curve. The curve thus obtained was used to read directly the concentration of the analyzed samples. A typical calibration curve is shown in Figure 1.

Fig. 1. Typical atomic absorption calibration curve



7
6
5
4
3
2
1
0
A x 10²
(absorbance units)
1
2
3
4
5
Ni (ppm.)

Problems arose in the analysis of the chloroform phase with atomic absorption. Several authors have pointed out the reasons for not using chloroform in atomic absorption, reasons such as the formation of poisonous combustion products and incomplete combustion in the flame. (25,26,27). Rains (28), however, claimed chloroform is a satisfactory solvent for use in atomic absorption. It is the experience of this author that chloroform is indeed undesirable for use in atomic absorption. The aspiration into the flame produced a highly unstable flame with intense background radiation. Consequently, no reproducible analyses could be performed using chloroform as solvent.

The problems encountered with chloroform as a solvent were circumvented by a scheme to use a more suitable solvent in the actual analysis. Standards were prepared by evaporating 25 ml. of pure oxine solution (identical solution to that used in the extraction experiment) just to dryness in a 50 ml. volumetric flask. The evaporation of the chloroform from the oxine solution was realized by drawing laboratory air through the flask while heating the flask with water bath setting of approximately 60°C. The residue was taken up in a small amount of distilled reagent acetone and the appropriate volumes of aqueous metal standard solutions were added to yield the desired concentrations. Water was added to those standards containing lesser amounts of the aqueous method standard so that all standards had the same percentage water (8% volume-volume) and would have identical bulk matrix and burning qualities. The standards were then diluted to the mark with acetone. Samples were prepared by taking exactly 5 ml. of the organic layer to be analyzed and transfering it to a 10 ml. volumetric flask. The chloroform was evaporated and the residue taken up with acetone as described above for standards. The loss of nickel by volatilization of their oxinates was assumed to be negligible (29,30). Water was added to match the percentage water of the standards and the flasks were filled to the mark with acetone. This substitution of acetone for chloroform gave a stable flame and allowed the reproducible analysis of organic phase samples.

Replicate samples provided the main criteria for judgement of the reliability of all analysis. Most analyses were done only on the aqueous layer. However, in the organic phase analysis described above, both phases were analyzed. The total concentration of nickel added in the aqueous layer at the outset of one extraction was 2.0 ppm. At the completion of the extraction, an average of 2.02 ppm. nickel was found in the organic layer and undetectable nickel was found in the aqueous layer. The total of 2.02 ppm. was within experimental error. A further experiment was run in which the extraction was less than 100% complete. As before, the total concentration of nickel at the outset of extraction was made 2.0 ppm. After the extraction was run to a state of partial completion, the average concentration found in a aqueous layer and organic respectively was found to be 1.26 ppm. and 0.70 ppm. The total of 1.96 ppm. was also within experimental error. This provided an additional assurance of the reliability of the analyses.

Since concentrations of copper in the aqueous phase often ranged from "nondetectable" to just above the detection limit, it seemed desirable to check the sensitivity and ability of the instrument to differentiate between very low concentrations of Cu(II). Concentrations of 0.05 ppm. and 0.1 ppm. were found to be distinguishable from each other.

III. RESULTS AND DISCUSSION

A. PRELIMINARY EXPERIMENTS

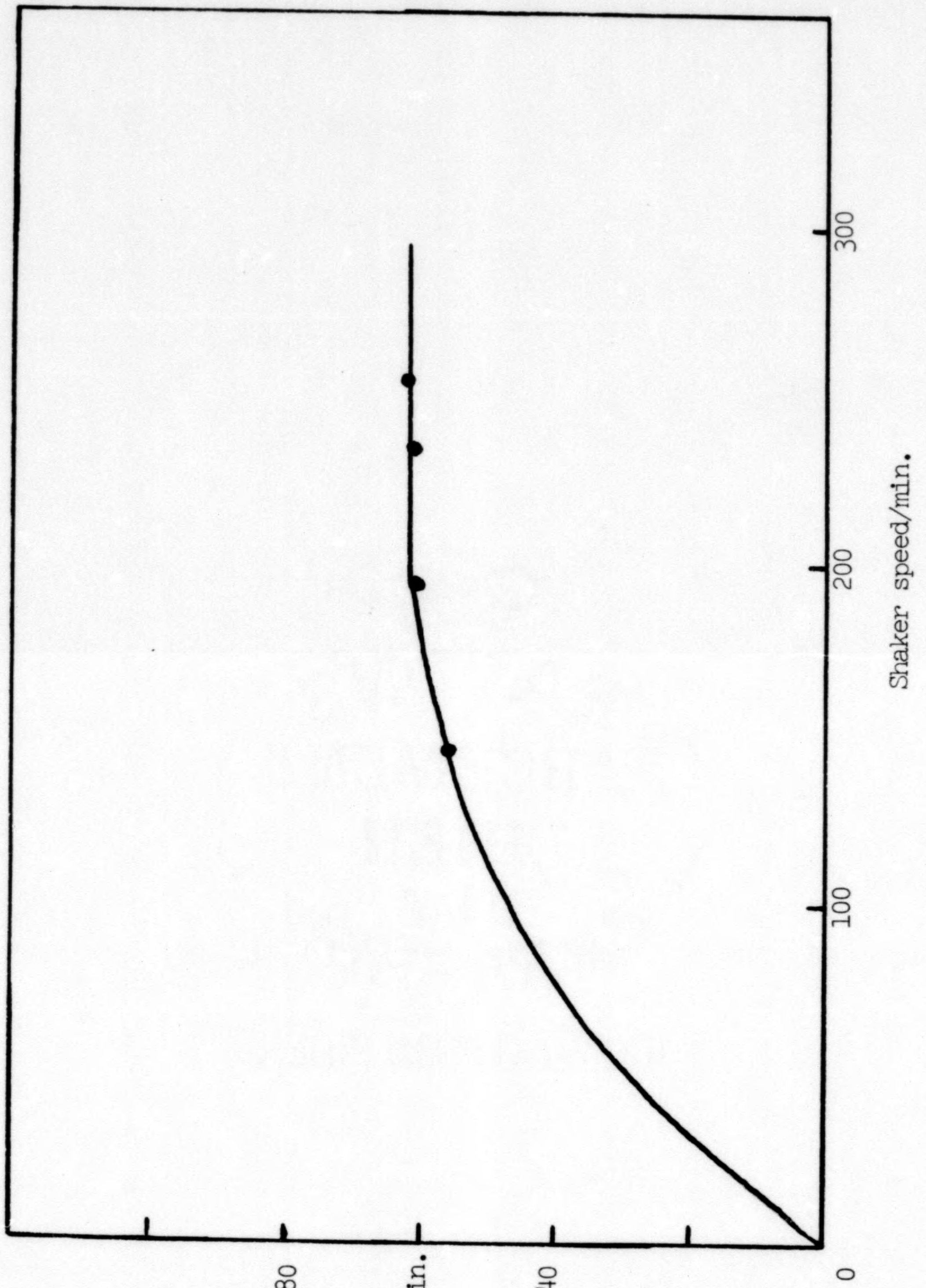
Morrison and Freiser (31) reported that the rate of achievement of equilibrium in solvent extraction depends on two factors:

1. The rate of transfer of the various species from one phase to the other.
2. The rate of formation of the extractable species.

Early attempts to obtain reliable kinetic data without maintaining a constant rate of shaker speed failed. The kinetic results could not be reproduced and the rate of extraction somehow appeared to increase as the shaker speed increased. Honaker and Freiser (2) found that the rate of extraction increased quite rapidly as the shaker speed was increased, up to a maximum value beyond which the increase in agitation had no significant effect on the rate of extraction.

A preliminary series of experiments was performed to determine the effect on the rate of extraction of varying the shaker speed. (see Fig.2) Alimarin, Zolotov and Bodnya(32) suggested that the extraction of lower rate of phase mixing could be controlled by "diffusion" or "transfer" process. When the rate of diffusion exceeds the rate of the chemical reaction occurring, then the extraction rate is controlled by the rate of formation of the extractable species. The extraction rate data is said to be in the "kinetic" region. In this study, to ensure that the rate of phase mixing reached the "kinetic" region, the agitation rate, controlled by the shaker speed, was increased until the corresponding

Fig. 2. Determination of the effect of shaker speed on rate of extraction


%Ext./10 min.
80
40
0
100
200
300
Shaker speed/min.

rate of extraction reached a constant maximum value (a plateau region - see Fig. 2). All subsequent experiments were performed under conditions of agitation rate at this corresponding plateau region. These results obtained for the shaker speed influence on extraction rate are similar to those obtained by Honaker and Freiser in another extraction rate study.

It was believed that standing time after agitation might affect the results of the kinetic study. Preliminary experiments were conducted and the results showed that no extraction occurred during the standing periods of 5, 10, and 15 minutes. All the kinetic data obtained in this study were taken using 5 minues standing time upon extraction.

B. THE EXTRACTION RATE STUDY OF NICKEL OXINATE

To collect extraction rate data for the determination of the rate law, a stoichiometric proportion of oxine and nickel ion concentrations was used in all runs (initial oxine concentration is twice nickel ion conc.). Initial concentrations were chosen (while maintaining this two to one ratio) so as to ensure the formation of extractable nickel oxinate would proceed up to at least 70% completion in a resonable period of time. Extraction rate data obtained at temperature 25°C. and 6.0 pH value are shown in Table 1.

It was found by Stary (1) that nickel ion is extracted into chloroform layer in the oxinate form of $NiOx_2$. The overall stoichiometry of this chelation can be represented as:

$$A + 2B \longrightarrow C$$

Table 2 contains rate equations which were derived based on stoichiometric proportions of oxine and nickel ion concentration.

TABLE 1

EXTRACTION DATA FOR NICKEL[a] WITH OXINE IN CHLOROFORM AT 25°C. AND I = 0.05

Time (hrs.)	Run 1		Run 2	
	Aqueous	Organic[b]	Aqueous	Organic
0.0	14.7 ppm.	0.00 ppm.	15.0 ppm.	0.00 ppm.
0.5	10.1	4.60	12.9	2.10
1.0	9.54	5.16	13.5	1.50
2.0	6.57	8.13	10.1	4.90
3.0	5.18	9.52	7.04	7.96
4.0	4.68	10.0	6.60	8.40
5.0	3.46	11.2	4.74	10.3

Time (hrs.)	Run 3		Run 4	
	Aqueous	Organic	Aqueous	Organic
0.0	15.0 ppm.	0.00 ppm.	14.3 ppm.	0.00 ppm.
0.5	13.4	1.60	11.2	3.10
1.0	11.5	3.50	8.55	5.75
2.0	9.70	5.30	7.32	6.98
3.0	7.20	7.80	5.40	8.90
4.0	5.36	9.64	5.13	9.17
5.0	4.94	10.7	4.15	10.2

[a] One ppm nickel 1.70×10^{-5}M.

[b] Obtained by subtracting aqueous concentration from initial aqueous concentration.

TABLE 2

RATE LAW AND RATE EQUATIONS

Overall reaction rate order	Differential Form	Integrated Form
1	$-\frac{d(A)}{dt} = K_1(A)$	$\ln\frac{(A)_o}{(A)_t} = K_1 t$
2	$-\frac{d(A)}{dt} = K_2(A)(B)$ $= 2K_2(A)^2$	$\frac{1}{(A)_t} - \frac{1}{(A)_o} = 2K_2 t$
3	$-\frac{d(A)}{dt} = K_3(A)(B)^2$ $= 8K_3(A)^3$	$\frac{1}{(A)_t^2} - \frac{1}{(A)_o^2} = 8K_3 t$

$(A)_t$ and $(A)_o$ are the concentrations at time (t) and the initial concentrations respectively.

The extraction rate data were interpreted by graphical means. A straight line fit was obtained by plotting the reciprocal of the concentration versus time, indicative of overall second order reaction. (see Fig. 3, 4, 5 and 6). The calculated extraction rate constant ($k_{ext.}$) which is equal to half of the slope is shown in Table 3. The method of least squares fit was used in all runs. The t = 0 point, considered to be the most reliable, was in reasonable agreement with the calculated intercept.

TABLE 3

CALCULATED EXTRACTION RATE CONSTANT OF NICKEL WITH OXINE IN CHLOROFORM AT 25°C., pH 6.0 and I = 0.05

RUN	SLOPE($l.M.^{-1}min.^{-1}$)	$k_{ext.}$($l.M.^{-1}min.^{-1}$)
1	36.1	18.1
2	27.0	13.5
3	28.2	14.1
4	31.9	16.0

Average $k_{ext.}$ = 15.4 $l.M^{-1}min.^{-1}$

Standard Deviation = 1.8 $l.M.^{-1}min.^{-1}$

To determine reaction order with respect to substances, non-stoichiometric batch extractions were run over a short period of time. Concentrations of oxine and nickel were separately varied. One concentration was held constant while the other was varied. The initial extraction rate data are contained in Table 4. The reaction order was calculated by means of the

Van't Hoff equation (33)

$$n_a = \frac{\log(dx/dt)_1 - \log(dx/dt)_2}{\log(A)_1 - \log(A)_2}$$

where $(A)_1$ and $(A)_2$ are two different initial concentrations of one component and dx/dt is the change of corresponding concentration with respect to time. The average calculated "n" values of oxine and nickel ion concentration are equal to 1.1 and 0.8 respectively and allow one to conclude that the extraction is first order with respect to the oxine concentration and first order with respect to the nickel ion concentration.

TABLE 4

NON-STOICHIOMETRIC EXTRACTION RATE DATA FOR NICKEL WITH OXINE IN CHLOROFORM AT TEMP. 25°C.

Run[a]	Initial (Ni^{+2})	Initial (HOx)	Ave. (Ni^{+2}) extracted	
			30 min.	60 min.
1	$6.4\text{x}10^{-5}$M.	$5.0\text{x}10^{-4}$M.	1.07 ppm.	1.03 ppm.
2	$1.3\text{x}10^{-4}$M.	$5.0\text{x}10^{-4}$M.	1.90 ppm.	2.10 ppm.
3	$2.5\text{x}10^{-4}$M.	$5.0\text{x}10^{-4}$M.	3.10 ppm.	4.22 ppm.
4	$2.5\text{x}10^{-4}$M.	$1.0\text{x}10^{-3}$M.	6.50 ppm.	7.30 ppm.

[a] All extractions at pH = 6.0 and I = 0.05

One ppm. nickel = $1.7\text{x}10^{-5}$M.

Fig. 3. Reciprocal concentration versus time graph for Run 1

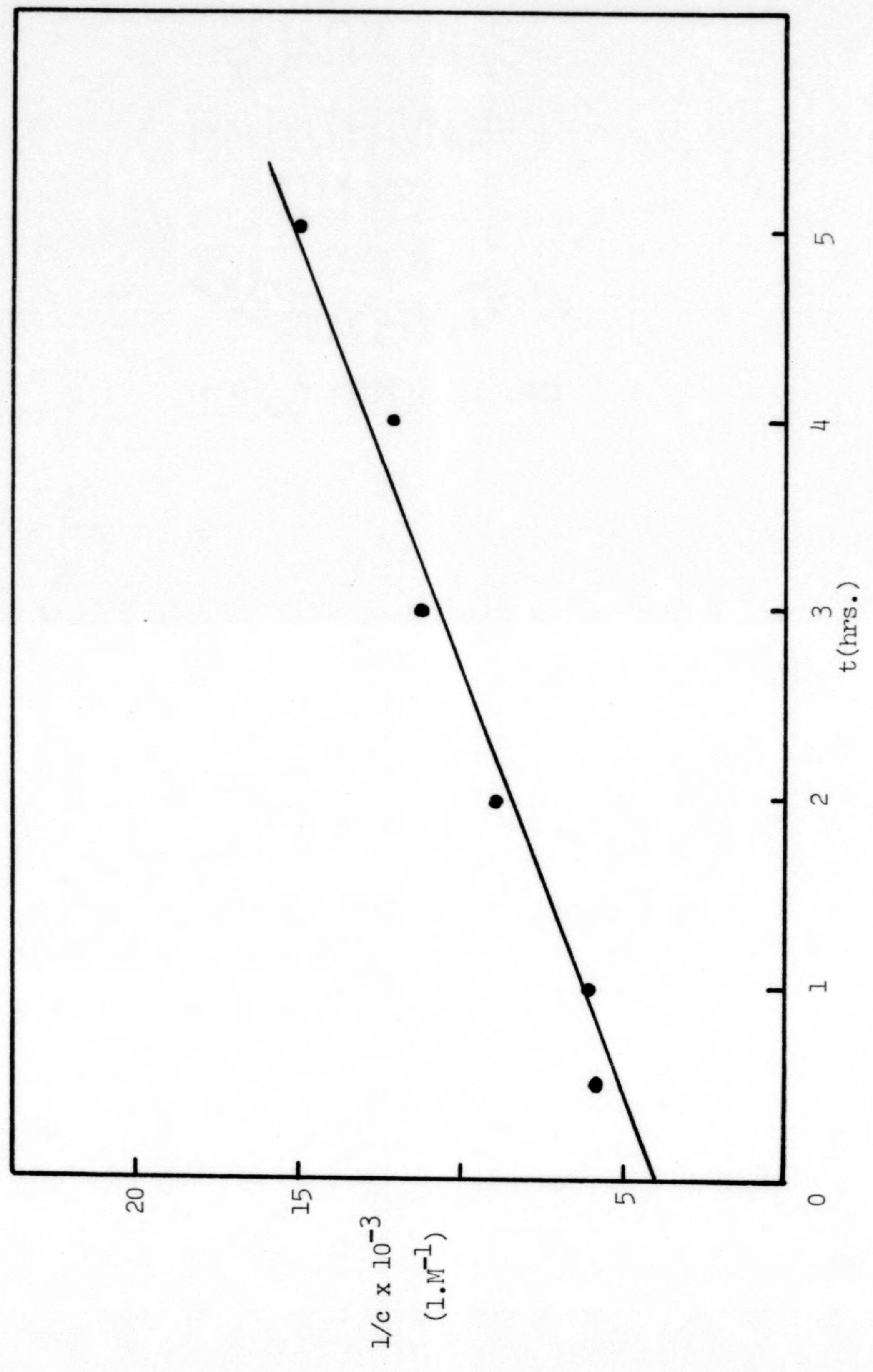

1/c x 10^{-3}
(l.M^{-1})
20
15
5
0
1
2
3
4
5
t(hrs.)

Fig. 4. Reciprocal concentration versus time graph for Run 2

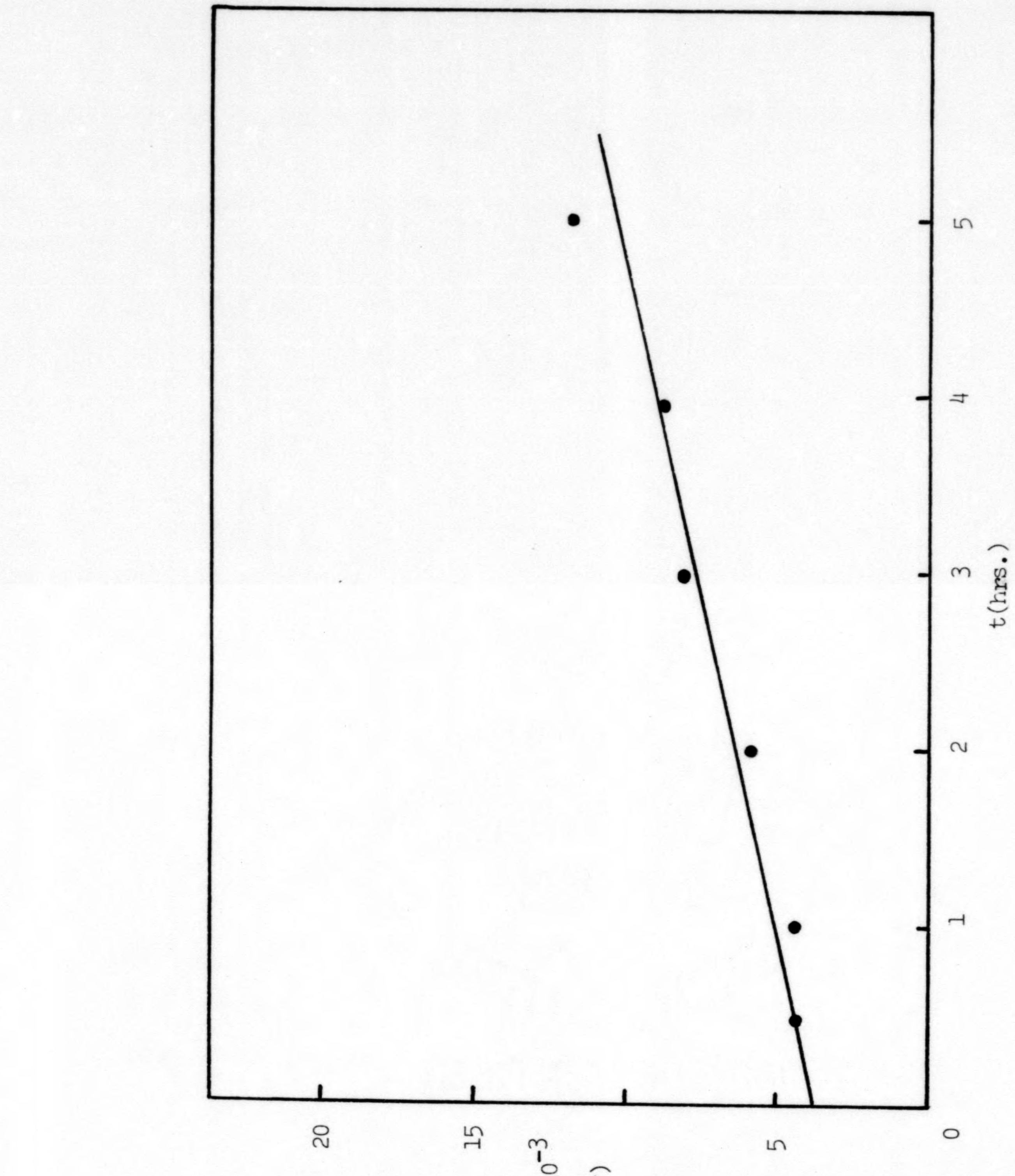

1/c x 10^{-3}
($1.M^{-1}$)
0
5
15
20
t(hrs.)
1
2
3
4
5

Fig. 5. Reciprocal concentration versus time graph for Run 3

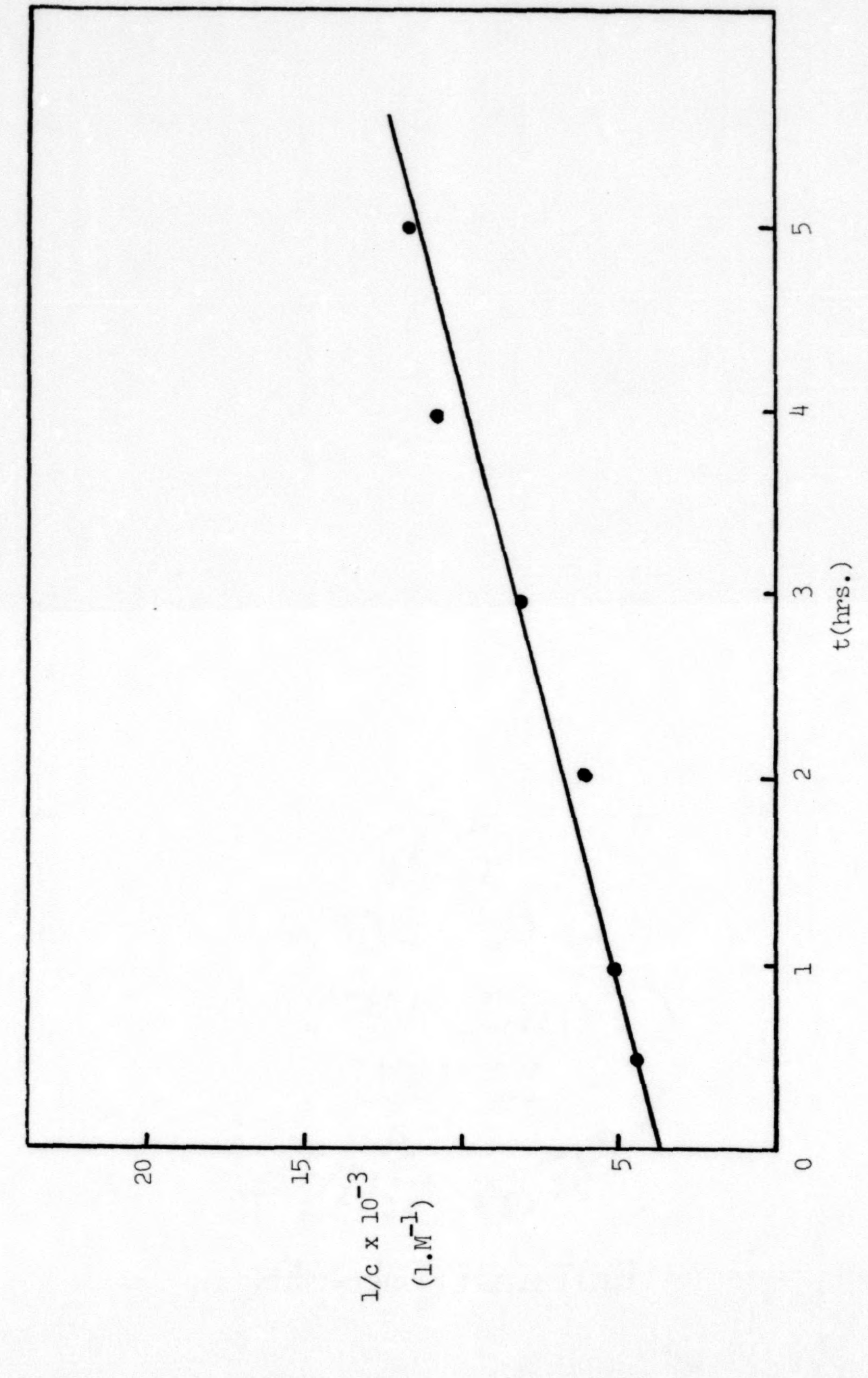
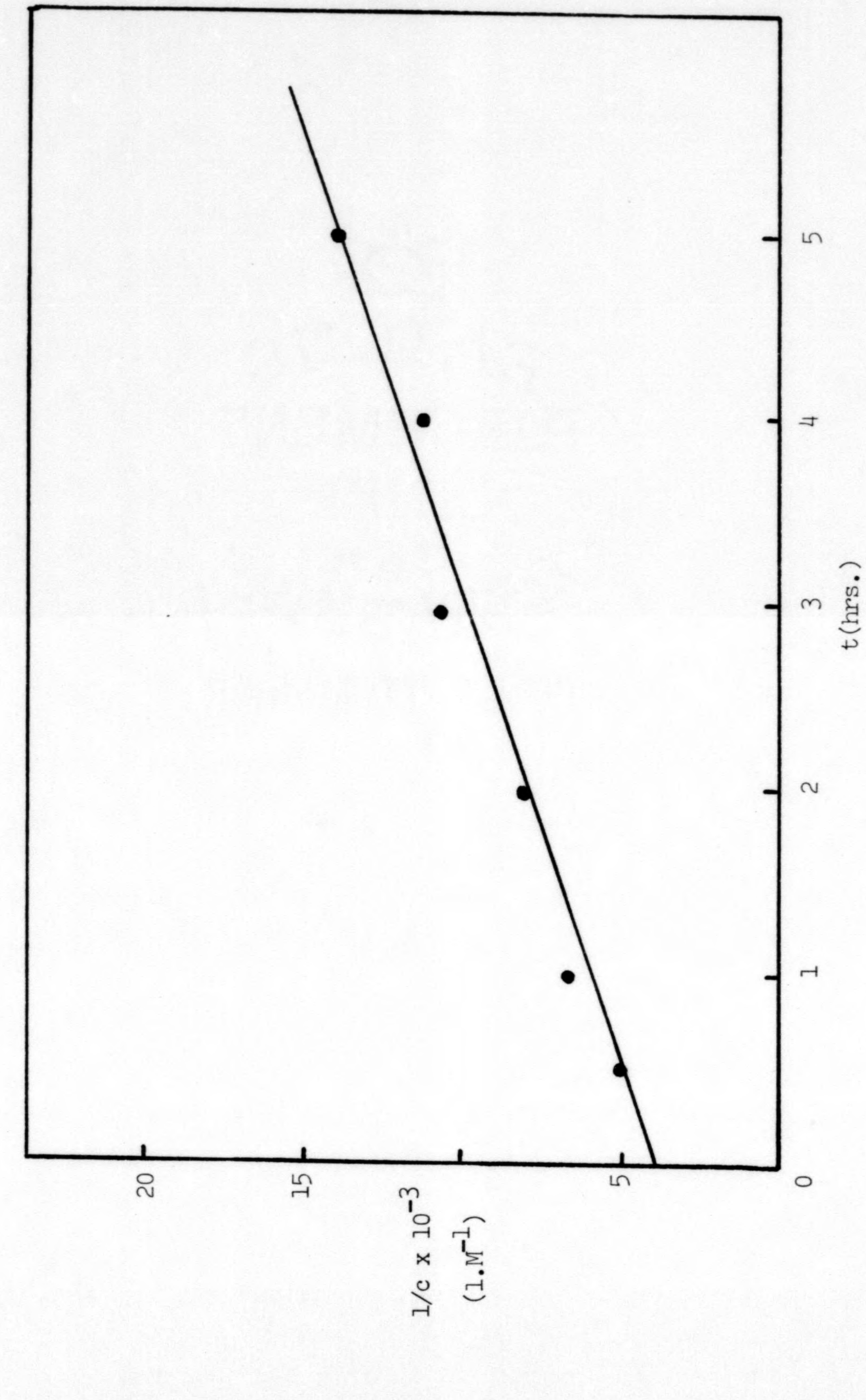

1/c x 10^{-3}
(1.M^{-1})
20
15
5
0
1
2
3
4
5
t(hrs.)

Fig. 6. Reciprocal concentration versus time graph for Run 4


0
1
2
3
4
5
t(hrs.)
5
15
20
$1/c \times 10^{-3}$
$(1.M^{-1})$

In the preliminary experiments, it was apparent that the extraction rate varied strongly with the initial hydrogen ion concentration in the aqueous phase. Stary (1) reported that the extraction equilibrium of nickel with oxine in chloroform was reached at a low pH value and a low oxine concentration after several hours. It was also indicated that at higher pH value, the equilibrium was reached more rapidly. Since it was proposed by the author to maintain constant hydrogen ion concentration during the extraction time, it was necessary to employ a buffer solution. Potassium dihydrogen phosphate with sodium hydroxide were used to prepare buffer solutions as recommended by Clark and Lubs (35) for the pH range of 5.80-8.00 values. The extraction rate data at different initial hydrogen ion concentrations were collected and contained in table 5. Plots of the reciprocal of concentration versus time yielded a straight line (see Fig. 7, 8 and 9) and extraction rate constants contained in Table 6 were determined in the same manner as formerly mentioned.

The variation of extraction rate constants with H^+ concentration can be expressed in mathematics form as:

$$k_{ext.} \propto (H^+)^n$$

$$\text{or} \quad k_{ext.} = A(H^+)^n$$

where A is a constant of variation. A plot of log $k_{ext.}$ versus pH was used to determine the reaction order with respect to hydrogen ion concentration. (see Fig.10). The straight line plot had a slope of 0.92.

TABLE 5

EXTRACTION RATE DATA FOR NICKEL WITH OXINE IN CHLOROFORM AT DIFFERENT pH AND TEMP. 25°C.

Time (min.)	pH 6.4	
	Aqueous	Organic
0	15.0 ppm.	0.00 ppm.
30	9.64	5.36
60	6.80	8.20
90	5.15	9.85
120	4.48	10.5

Time (min.)	pH 6.8	
	Aqueous	Organic
0	13.0 ppm.	0.00 ppm.
30	6.93	6.07
60	4.50	8.50
90	3.51	9.49
120	2.88	10.1

Table 5 (continued)

Time (min.)	pH 7.2	
	Aqueous	Organic
0	15.0 ppm.	0.00 ppm.
10	6.93	8.07
20	4.70	10.3
40	3.33	11.7

TABLE 6

CALCULATED EXTRACTION RATE CONSTANT OF NICKEL WITH OXINE IN CHLOROFORM AT 25°C. AND VARYING pH

pH	Slope ($l.M.^{-1}min.^{-1}$)	$k_{ext.}$ ($l.M.^{-1}min.^{-1}$)
6.0	30.8	15.4
6.4	78.9	39.5
6.8	133	66.7
7.2	423	211

Fig. 7. Reciprocal concentration versus time graph for pH 6.4 value

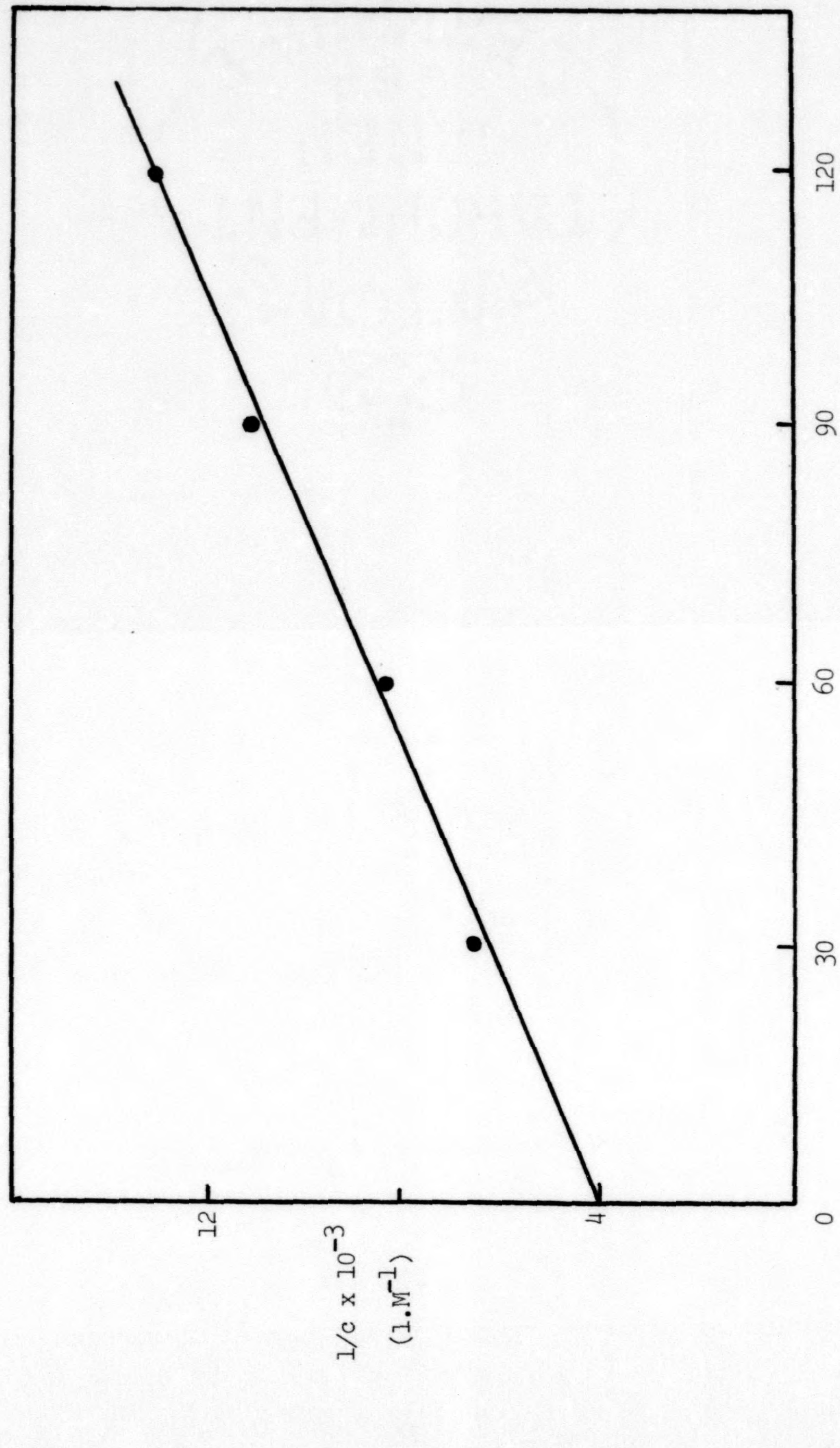

1/c x 10^{-3}
($1.M^{-1}$)
12
4
0
30
60
90
120
t(min.)

Fig. 8. Reciprocal concentration versus time graph for pH 6.8 value

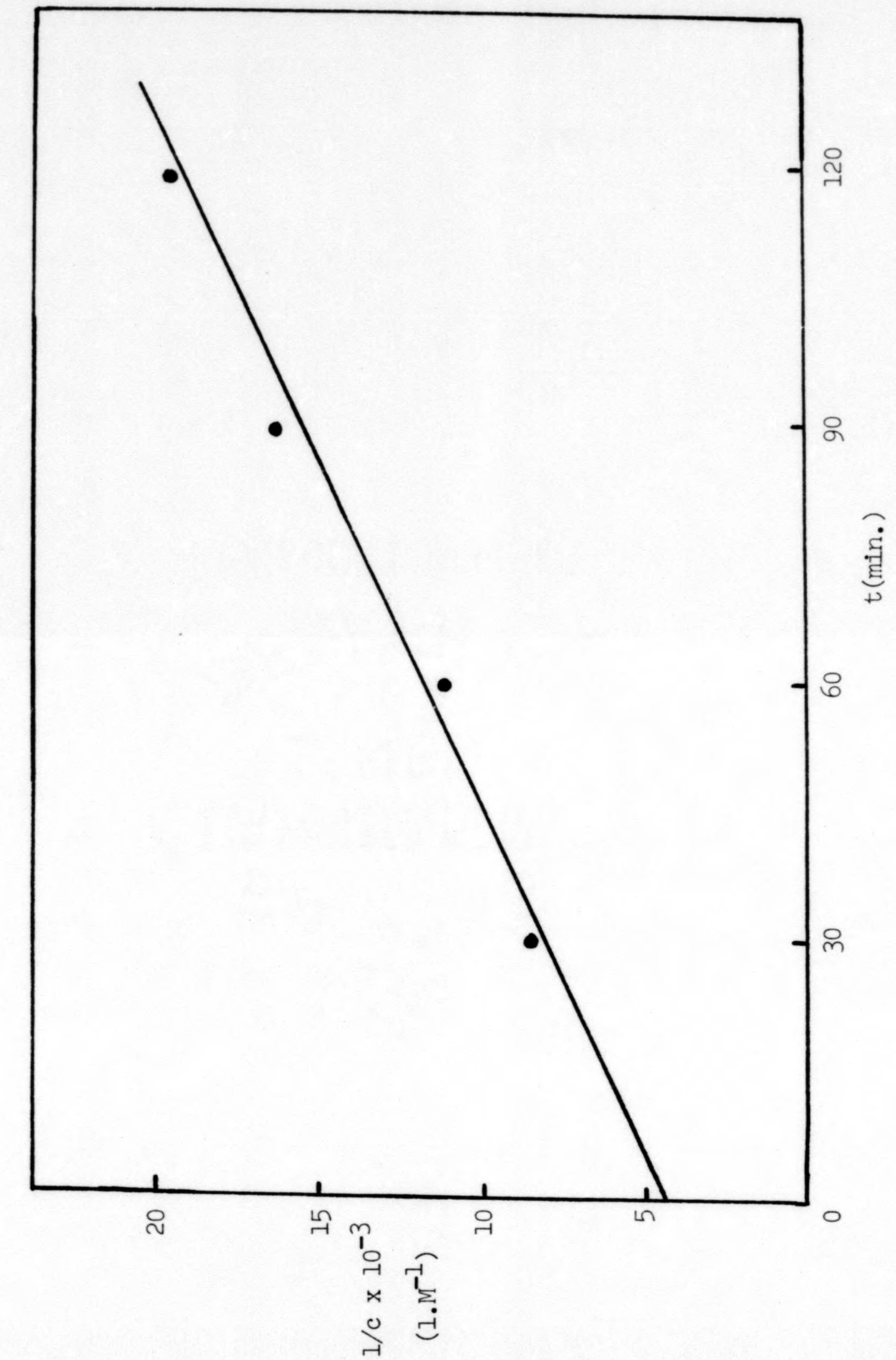

1/c x 10^{-3}
(1.M^{-1})
20
15
10
5
0
30
60
90
120
t(min.)

Fig. 9. Reciprocal concentration versus time graph for pH 7.2 value

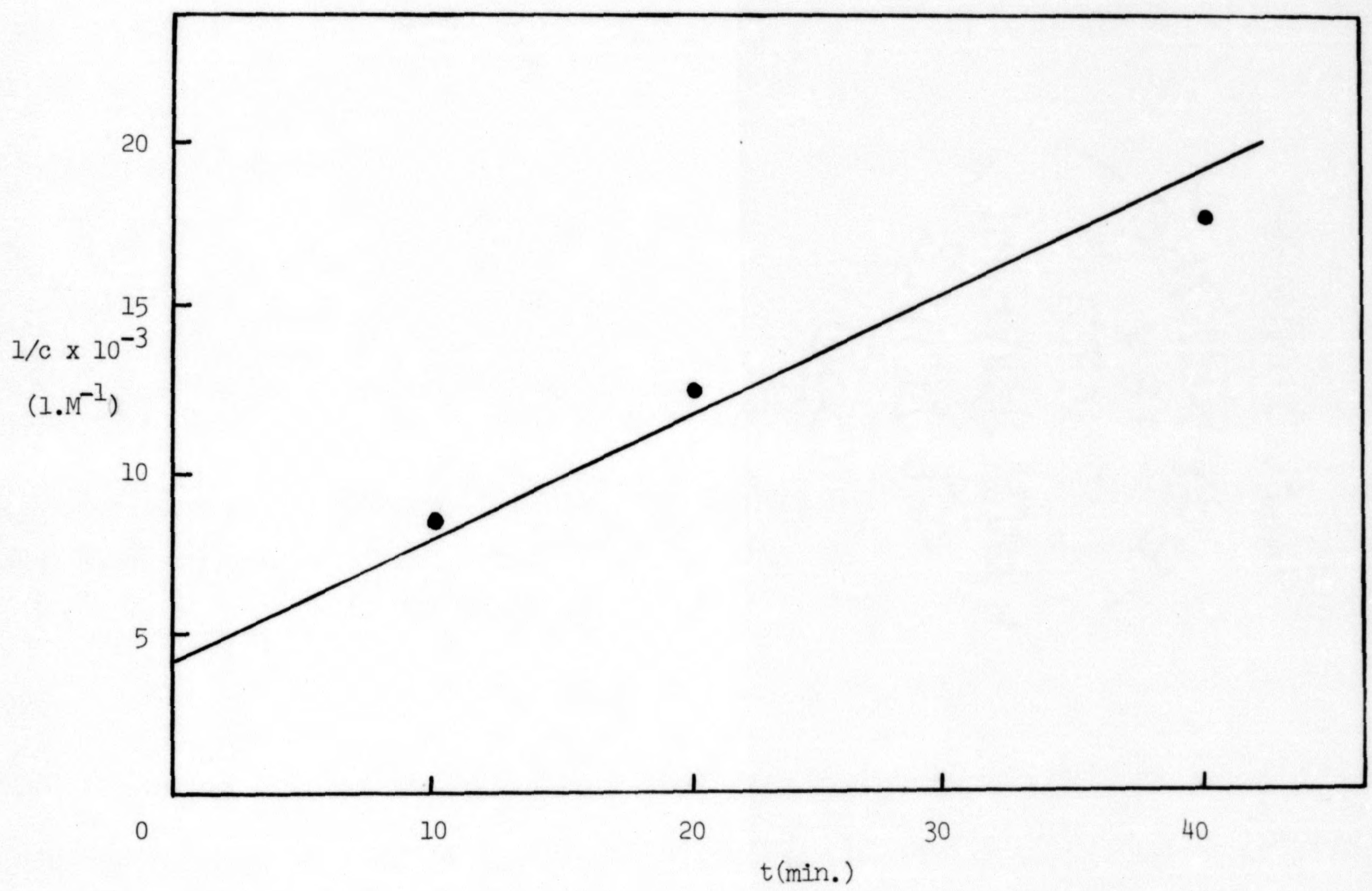
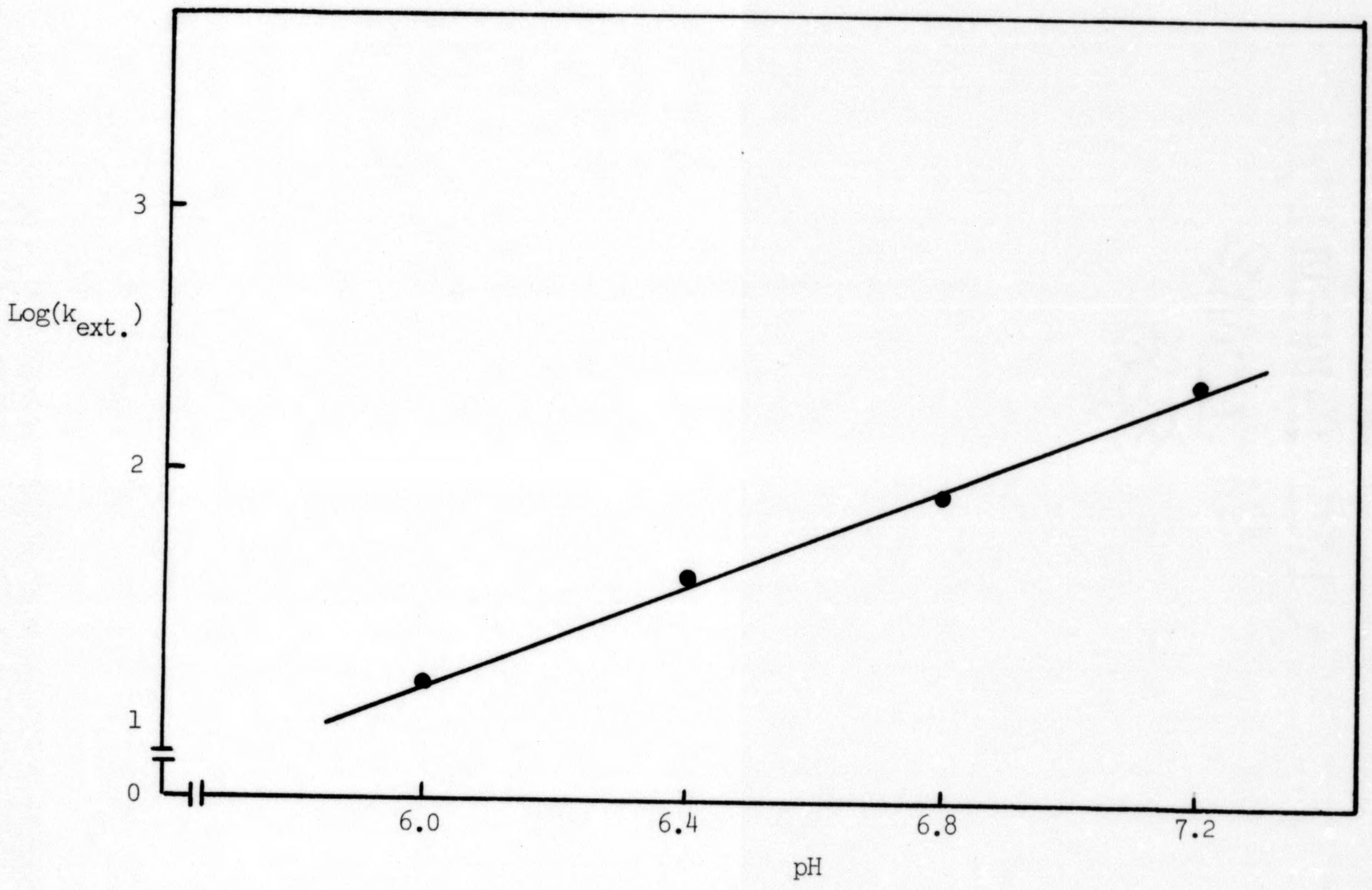

1/c x 10^{-3}
($1.M^{-1}$)
20
15
10
5
0
10
20
30
40
t(min.)

Fig. 10. Determination of extraction order with respect to hydrogen ion concentration at temperature 25°C.


Log(k_ext.)
3
2
1
0
6.0
6.4
6.8
7.2
pH

In a study of the ionic strength effect, sodium perchlorate solution was added quantitatively into aqueous buffer solution. To see a significant change in extraction rate, a large change in ionic strength was considered to be necessary. However, this was not experimentally obtained. A problem in preparing high ionic strength solutions at these pH values arose from the precipitating tendency of sodium perchlorate. An ionic strength of about 0.3 was the highest value that allowed the salt solution to be soluble in the aqueous layer in the pH value range of 6-7. The change of extraction rates due to the addition of salt, reflecting ionic strength effect, are within the limits of experimental error of the analytical method.

The nature of the organic solvent also affects the rate of extraction since it influences the distribution of both the organic ligand and the extracted metal chelate. If the chelation occurs in the aqueous layer, as proposed by Freiser and co-workers (2, 32), an organic solvent with a low distribution coefficient (higher chelating agent concentration in aqueous layer) would show a faster rate of extraction. If the mechanism is interfacial, a solvent with a large distribution coefficient (higher chelating agent concentration in the organic phase) would show a faster rate. Mottola and Freiser (23) have conducted experiments to determine distribution constants of oxine in various organic solvents. (see table 7). The significantly higher value of distribution constant of oxine in chloroform compared to carbon tetrachloride was explained by the possible hydrogen bonding ability of the oxine-chloroform system.

The effect of different distribution constants of oxine, in chloroform and carbon tetrachloride, on the extraction rate was determined. Extraction data using carbon tetrachloride as a solvent is contained in Table 8. The reciprocal nickel concentration versus time graph as shown

TABLE 7

THE DISTRIBUTION OF OXINE BETWEEN A SERIES OF HALOGENATED HYDROCARBONS AND THE AQUEOUS PHASE (pH = 6.5-7.0; I = 0.10) AT 25.0°C.

Organic solvent	Distribution constant
Dichloromethane	377
Chloroform	433
Carbon tetrachloride	116
Dibromomethane	449
n-Hexane	21.2

TABLE 8

EXTRACTION DATA FOR NICKEL WITH OXINE IN CARBON TETRACHLORIDE AT pH 6.0 AND TEMP. 25°C.

Time	(Ni^{+2}) in aqueous phase
0 min.	15 ppm.
10	9.24
20	6.30
30	4.90
40	4.20

$k_{ext.} = 111\ l.M.^{-1}min^{-1}$.

in Fig. 11, indicative of second order extraction rate of carbon tetrachloride as a solvent, shows a 7.2 time faster extraction rate for the carbon tetrachloride solvent than for the chloroform solvent. The results of such rate studies lead to the conclusion that the formation of metal chelate occurs in aqueous phase.

The influence of temperature on the extraction rate was also investigated. Extraction runs of three different temperatures (25, 31 and 37°C.) were performed. Concentrations of nickel ion of 15 ppm. at pH value 6.0 and oxine of $5x10^{-4}$M. were used. Experimental data are shown in Table 9. The rate of extraction increased as temperature increased as expected by the author. It is believed that temperature may affect the solubility of the extracted nickel oxinate and of oxine itself. Since the values of K_a/K_d (dissociation constant/distribution coefficient of oxine) at 31° and 37°C. were not found from the literature, a true energy of activation of nickel-oxine complex formation in this study could not be obtained.

TABLE 9

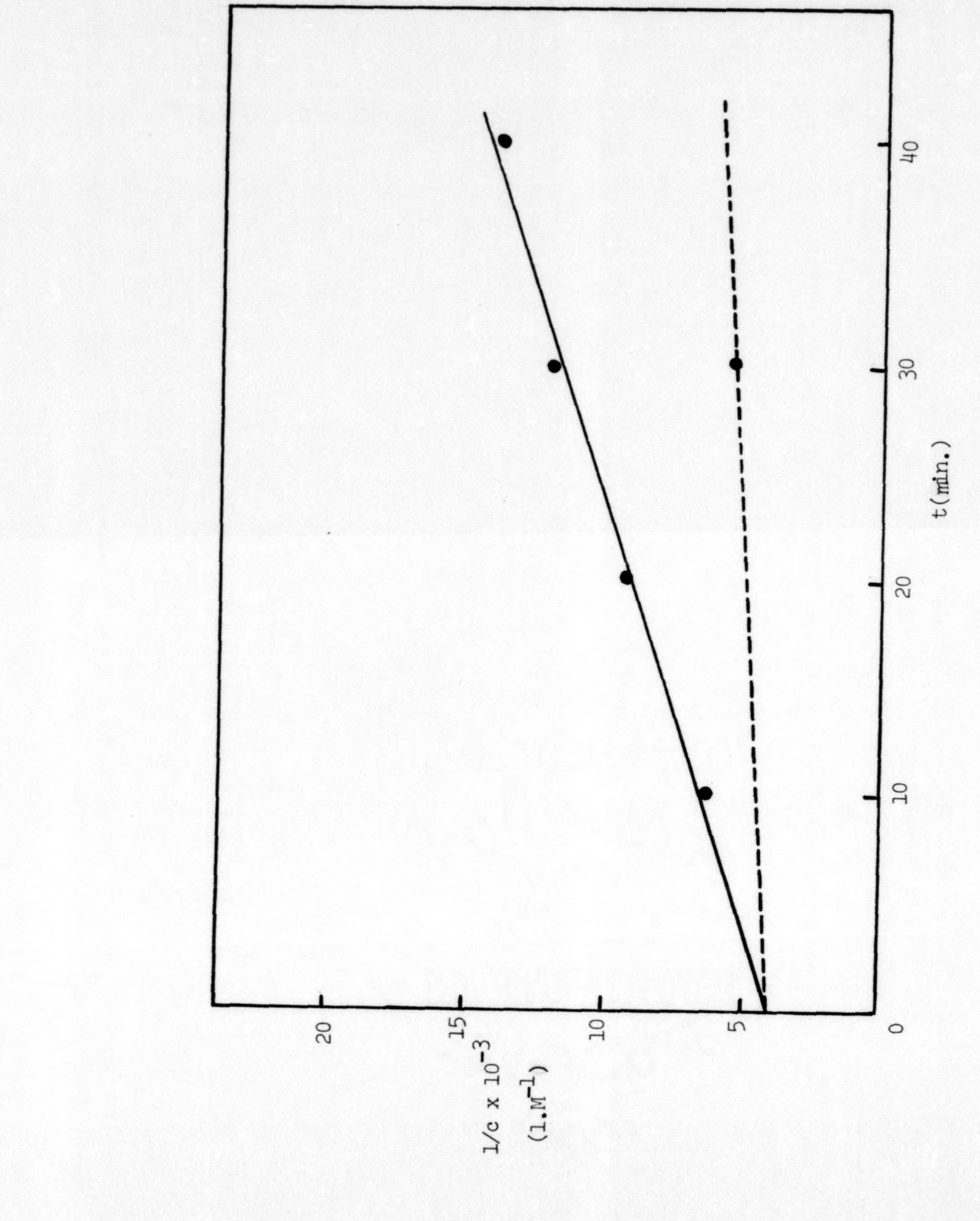
EXTRACTION DATA FOR NICKEL WITH OXINE IN CHLOROFORM AT THREE DIFFERENT TEMPERATURES

Temperature	Initial (Ni^{+2})	average (Ni^{+2}) ext. in 2 hrs.
25°C.	15 ppm.	7.80 ppm.
31°C.	15 ppm.	8.13 ppm.
37°C.	15 ppm.	9.80 ppm.

Fig. 11. Reciprocal concentration versus time graph for extraction of Ni(II) with oxine in carbon tetrachloride. (for comparison, a part of Fig. 3. is presented)

———————— Carbon tetrachloride

— — — — — — — — — Chloroform


1/c x 10^{-3}
($1.M^{-1}$)
20
15
10
5
0
10
20
30
40
t(min.)

Taking into consideration the composition of the compound extracted and the experimental extraction rate data, a possible process of extraction may be represented in the form of:

$$\mathrm{HOx}_{(org)} = \mathrm{HOx}_{(aq)} \quad (1)$$

$$\mathrm{HOx}_{(aq)} = \mathrm{H}^{+} + \mathrm{Ox}^{-} \quad (2)$$

$$\mathrm{Ni}^{+2} + \mathrm{Ox}^{-} = \mathrm{Ni(Ox)}^{+} \quad (3)$$

$$\mathrm{Ni(Ox)}^{+} + \mathrm{Ox}^{-} = \mathrm{Ni(Ox)}_{2(aq)} \quad (4)$$

$$\mathrm{Ni(Ox)}_{2(aq)} = \mathrm{Ni(Ox)}_{2(org)} \quad (5)$$

The rate of the entire process is determined by the rate of the slowest step. The first and last steps can be disregarded as rate controlling since neither would give rise to a pH dependence. Step 2 can not be the slowest step; the system was found to be first order with respect to nickel ion concentration. Furthermore, the extraction rate of copper with oxine in chloroform proceeded much more rapidly than that of nickel with oxine in chloroform. If step 4 were the rate-controlling step, a second order rate dependence upon the concentration of oxine should have been found. These considerations suggest step 3 as the rate-controlling step.

The expression representing the reaction rate can be derived from step 3 as:

$$\begin{aligned} -d(\mathrm{Ni}^{+2})/dt &= k(\mathrm{Ni}^{+2})(\mathrm{Ox}^{-}) \\ &= \frac{k\,K_a(\mathrm{Ni}^{+2})(\mathrm{HOx})_{aq}}{(\mathrm{H}+)} \\ &= \frac{k\,K_a(\mathrm{Ni}^{+2})(\mathrm{HOx})_{org}}{K_d \quad (\mathrm{H}^{+})} \end{aligned} \quad (6)$$

Where K_a and K_d are the ionization constant and distribution coefficient of oxine respectively. When (H^{+}) is maintained constant during the extraction process the rate equation 6 reduces to:

$$-d(\mathrm{Ni}^{+}2)/dt = k_{ext.}(\mathrm{Ni}^{+2})(\mathrm{HOx})_{org.}$$

which is in agreement with our experimental results.

It should be noted that the above mentioned extraction process is similar to a solvent extraction mechanism proposed earlier by Freiser (2). His kinetic studies of zinc, nickel, cobalt and cadmium with dithizone were found to be first order with respect to both metal and chelating agent.

It is of interest to compare the results of our study with a similar extraction rate study of nickel oxinate in chloroform performed by Bodnya and Alimarin (36). Their study employed working solutions of nickel nitrate and 0.1 M sodium nitrate but without any buffer components to regulate the pH of the working solutions. Nickel extractions were performed at a pH range of 3.3 - 5.0 and the analysis was conducted photometrically in the form of a complex of Ni(III) with dimethylglyoxime (a solution of iodine was used as the oxidizing agent). They found the extraction reaction to be first order in the metal ion and second order in the molecular form of the reagent (HOx). They stated that a change in the initial pH of the aqueous phase was found to have little effect upon the rate of extraction in the pH range they were using. However, their suggested reaction mechanism leads to a rate dependence upon H^+ concentration.

Further work on the role of the buffer component and the nature of the extraction process as it relates to various pH ranges needs to be done.

An attempt was made to observe the extraction rate of copper with oxine in chloroform. In this system, even though the copper concentration was reduced to an extremely low value, the extraction occurred too rapidly to be studied by the solvent extraction method. Equilibration was found to be attained in less than five minutes in every run. Consequently, no rate data on this system will be presented in this report.

C. SEPARATION OF Cu(II) AND Ni(II) WITH OXINE BASED ON DIFFERENCE IN RATE OF EXTRACTION

Although studies of the kinetics of extraction of various systems have been carried out for the last two decades, the use of these studies for practical analytical applications has been minimal. In the selection of a system for the study of the separation based on the differential extraction rates, it was desired to find a system in which it was not possible to separate both metals by simply controlling the equilibrium conditions. In this respect, the copper-nickel-oxine system was found to be well suited. These two metals formed stable complexes with oxine which remained stable upon extraction with many different solvents. Their extraction curves (pH versus percent extraction) were found to lie very close together thereby preventing simple control of equilibrium conditions to selectively separate one in the presence of the other (1). Masking agents possibly could have been employed to effect selective separation but the method developed here was based on a non-equilibrium approach to extraction. It was hoped that fundamental rate data could be obtained in this study and that this could lead to a selective separation of the two metals.

Basolo and Pearson (87) have noted the effect of the three variables of the charge of the metal ion, the size of the metal ion and the crystal field stabilization on the rate of exchange of water molecules from the first coordination sphere of metal ions. McClellan and Freiser (12) have found that the rate constants of extraction for Zn(II), Ni(II), Co(II) and Cd(II) parallel the rates of water exchange with three substituted diphenylthiocarbazones. A general mechanism of solvent extraction of metal ion from aqueous solutions under kinetic conditions was developed by V.V. Formin (38). Employing this mechanism, the rate of extraction can be shown to depend on the distribution coefficient and stability constant of the extracted compound formed. In our study the rate of extraction of the two metal oxinates was found to parallel the rate of exchange of water suggesting that the removal of the water molecule from the first coordination sphere might be involved in the rate determining step.

These aforementioned observations allow for a simple, although not strict, rule by which relative rates of extraction of metals may sometimes be predicted qualitatively. In addition to the consideration of the extraction rate in the actual separation method, the $pH_{\frac{1}{2}}$ (the pH at which 50% of the metal is extracted) must be considered, since it is desired to effect complete extraction.

At the outset of this separation study, it was necessary to gain some knowledge of the relative rates of extraction of Cu(II) and Ni(II) experimentally. The experiments to separate Cu(II) from Ni(II) by the variation of the appropriate kinetic parameters are shown in table 10. All experiments were done at a constant temperature of 25°C and an ionic strength of 0.05. The initial ion concentrations of Cu(II) and Ni(II) were 3.1×10^{-5}M. It was noted by McClellan and Sabel (16) in a similar study that the initial metal ions concentrations showed no effect on the separation efficiency.

An examination of the separation data is contained in Table 10. Table 11 shows the conditions of pH, oxine concentration and extraction time which give efficient selective separation of Cu(II) and Ni(II). The use of a different solvent was studied in one experiment using the same favorable pH, oxine concentration and extraction time found for chloroform except substituting carbon tetrachloride as the solvent (see table 11).

TABLE 10

SEPARATION DATA OF Cu(II) FROM Ni(II) WITH OXINE IN CHLOROFORM AT TEMP. 25°C. AND I = 0.05

(HOx)	pH	Time (min.)	% Ext. (Ni^{+2})	%Ext. (Cu^{+2})
Shaking time				
10^{-3}M.	4.4	2.5	7.50	>99
10^{-3}M.	4.4	5	19.0	>99
10^{-3}M.	4.4	20	37.0	>99
pH				
10^{-3}M.	4.0	5	11.0	>99
10^{-3}M.	4.4	5	19.0	>99
10^{-3}M.	5.8	5	52.0	>99
Oxine Concentration				
10^{-3}M.	5.8	5	52.0	>99
5.0×10^{-4}M.	5.8	5	20.1	>99
2.5×10^{-4}M.	5.8	5	7.0	>99

TABLE 11

SEPARATION DATA OF Cu(II) FROM Ni(II) WITH OXINE IN TWO SOLVENTS (25°C. AND I = 0.05)

Organic solvent	pH	(HOx)	Time (min.)	% Ext. (Ni^{+2})	% Ext. (Cu^{+2})
$CHCl_3$	4.2	2.5×10^{-4}M.	5	3.20	99
CCl_4	4.2	2.5×10^{-4}M.	5	48.0	95.8

An attempt was made to observe the separation efficiency of the ions of Zn(II) and Ni(II) with oxine in chloroform. (see Table 12).

TABLE 12

SEPARATION DATA OF Zn(II) AND Ni(II) WITH OXINE IN CHLOROFORM AT TEMP. 25°C. AND I = 0.05

(Ni^{+2}) (ppm.)	(Zn^{+2}) (ppm.)	pH	(HOx)	Time (min.)	% Ext. (Ni^{+2})	% Ext. (Zn^{+2})
1.8	2.0	6.0	1×10^{-2}M.	5	95.0	98.1
1.8	2.0	6.0	1×10^{-3}M.	5	66.2	88.7
1.8	2.0	6.0	5×10^{-4}M.	5	27.5	43.7

The separation was incomplete. This less effective separation could be explained by noting that the extraction curve, which must be considered if quantitative extraction is desired, of Ni(II) lies on the acid side of Zn(II) (1). In a solution containing both zinc and nickel, the pH must be raised in order to obtain quantitative extraction of zinc. Raising the pH increases the extraction rate of Ni(II) correspondingly and causes the separation difficulty.

IV. SUMMARY

The extraction rate study of the nickel-oxine chloroform system at 25°C indicates first order dependence on both the metal ion concentration in the aqueous phase and the oxine concentration in chloroform layer. Negative first order with respect to hydrogen ion concentration was found in the pH range of 6.0 - 7.2. Extraction rates in carbon tetrachloride are higher than those in chloroform. This is explained by the higher distribution constant of oxine in carbon tetrachloride compared to that in chloroform. A mechanism is given which accounts for the observed reaction orders.

The separation of copper and nickel ion by a simple, efficient method utilizing a non-equilibrium extraction has been demonstrated. The method is reliant on the much faster extraction rate for Cu(II), than for Ni(II), with oxine in chloroform at 25°C. A system of 2.5×10^{-4}M. oxine, pH 4.2 and 5 minutes extraction time appears to optimize the efficiency of the separation. Using these conditions, the method of differential rates separates the metals virtually quantitatively. Of the copper originally in the aqueous layer, more than 99% is extracted into the organic layer. Only 3.2% of the nickel originally in the aqueous layer is extracted into the organic layer. This separation efficiency compares well with that of other separations in other systems based on differential extraction rates.

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