

FORMATION OF CHLORO-COMPLEXES OF NICKEL IN OCTANOL-2

By

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Bachelor of Science

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Rock Island, Illinois

1950

Submitted to the Faculty of the Graduate School of

the Oklahoma Agricultural and Mechanical College

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

1952

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ACKNOWLEDGMENTS

This study was made possible by the Oklahoma A. and M. Research Foundation under contract to the Atomic Energy Commission. The work was carried out under the direction of Dr. Tom E. Moore, who was assisted by Dr. Paul C. Yates. The author is deeply grateful to these men for the generosity of their patience and advice.

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INTRODUCTION

A major problem in the field of inorganic chemistry is the separation of mixtures of ions of metals having similar chemical properties. One technique for such separation uses the partition of inorganic materials between organic and aqueous phases, so that a particular constituent may be removed almost exclusively and quantitatively. This method of separation is termed liquid-liquid extraction or extraction for removal.¹

Solvent extraction in the organic field is a familiar technique which has long been in practice; however, its counterpart in the inorganic field has not received considerable attention until recently. As a result, not a great deal of progress has been made in formulating a theory correlating the factors influencing and promoting this type of separation.

The vast importance of such a separation technique is not to be denied in the light of the recent advances in the chemistry of the heavier and transuranic elements made possible by solvent extraction. Such a means of separation should also be of great value in the manufacture of pure chemicals.

The present investigation was part of a larger project set up for the purpose of extending fundamental knowledge in the field of solvent extraction, and for bringing the field

closer to widespread application in the separation of metal ions.

Studies of the liquid-liquid extraction of nickel and cobalt chlorides from aqueous solution into an immiscible organic phase were reported by Garwin and Hixon.² The cobalt salt was found to concentrate in the organic phase, while the nickel tended to remain in the aqueous phase. The extent of extraction and separation was appreciable only in the presence of certain strong electrolytes such as calcium chloride and hydrogen chloride. Octanol-2 was reported to be one of the most efficient organic solvents for the separation of cobalt from nickel.

This particular extraction process is recognized as one of a general type which occurs in the presence of a high concentration of an ion of charge opposite to that of the extracted component.

Following the work of Garwin and Hixon, it was decided that an initial intensive study would be carried out by the project on the system NiCl_2 , CoCl_2 , octanol-2, and MCl_n , where MCl_n is a chloride classed as a strong electrolyte.

Irving¹ suggested that the dissolving of metal halides in an organic phase in the presence of high concentrations of halide ion was caused by the formation of complexes which reduced the compatibility of the metallic compound with water, and conferred on it something of an organic character.

Accordingly, some of the things to be investigated by the project were the nature and stability of any complexes of cobalt and nickel which might be formed in the octanol phase. It was thought that a comparison of the stabilities and configurations of any complexes formed by cobalt with the same properties of any complexes formed by nickel would point out some of the reasons for the difference in behavior of the cobaltous and nickel chlorides under the conditions of the extraction.

W. B. Estill³ studied the chloro-complexes formed by cobalt in octanol-2 using Job's method of continuous variations⁴ as modified by Vosburgh and Cooper⁵.

The purpose of the present investigation was to determine the stoichiometry, the configurations, and the order of magnitude of the instability constants of any complexes which might be formed by nickel chloride in the presence of a high concentration of added chloride ion in octanol-2.

REVIEW OF LITERATURE

A search was made for reports of the formation of metal halide complexes in aqueous solution, organic phases, and in mixed solvents.

S. S. Schaffer and N. W. Taylor⁶ reported the effect of complex ion formation on magnetic susceptibilities of NiCl_2 and NiBr_2 . Susceptibilities were measured for the pure aqueous solutions before and after addition of excess chloride ion. A definite reduction of paramagnetism was observed suggestive of complex ion formation.

M. Pavlik⁷ suggested from polarographic studies that the reversible deposition of nickel ions in aqueous solutions heavily concentrated in chloride occurred from the complex $\text{NiCl}_n^{(n-2)-}$. The complex ion was assumed to be formed by dehydration of the hydrated nickel ions, and penetration of the chloride ions into the inner coordination sphere. Using layers varying in thickness from 2 to 100 mm., Pavlik⁸ also measured the absorption spectra of aqueous NiCl_2 solutions containing calcium or lithium chlorides, HCl , glycerol, ethyl alcohol or methyl alcohol. Large additions of inorganic chlorides greatly increased the absorption in the blue part of the spectrum. The complex $\text{NiCl}_n^{(n-2)-}$ was suggested as being responsible for the optical phenomena.

In 1931 R. Samuel⁹ recorded the changes in absorption spectra that occurred in aqueous solutions of complex ammonia compounds of nickel upon addition of large amount of inorganic chlorides. The NH_3 groups were said to be progressively replaced by chloride ions.

Kiss, Beor, and Gerendas¹⁰ made determinations of the molecular extinction coefficients of NiCl_2 in aqueous salt solutions and in HCl. It was maintained that changes in the spectrum of NiCl_2 were caused by formation of complexes and dehydration, but the constitution of the color-forming entity was unexplained. Later, however, Kiss and Csokan¹¹ identified the complex ion in aqueous mixtures of NiCl_2 and HCl as NiCl_4^{2-} .

Paul Job¹² added increasing amounts of HBr to aqueous NiSO_4 and found the change in color to be due to varying proportions of NiBr_2 and NiBr_4^{2-} . He also calculated the values of the

$$\text{constants } K = \frac{[\text{NiBr}_2]}{[\text{Ni}^{++}](\gamma m)^2} \quad \text{and} \quad K' = \frac{[\text{NiBr}_4^{2-}]}{[\text{NiBr}_2](\gamma m)^2}$$

as 6.03×10^{-4} and 1.32×10^{-5} respectively.

Eleonora Major¹³ determined extinction curves of NiCl_2 , and NiBr_2 in aqueous salt and acid solutions of various concentrations at room temperature and compared them to a curve of $\text{Ni}(\text{ClO}_4)_2$ as a standard. In the presence of complex-forming anions, the complexes $[\text{NiX}_4]^{2-}$ seemed to exist, and in saturated solutions of NiCl_2 , NiI_2 , and NiBr_2 a neutral molecule of NiX_2 was found to be present.

PRELIMINARY INVESTIGATIONS

A review was made of the various means used for the study of complex ions, and the first plan was to use the method of continuous variations ^{4,5} in a manner similar to that of Estill's study of CoCl_2 . The method was to be applied by adding a solution of lithium chloride in octanol-2 in varying amounts to a solution of anhydrous nickel perchlorate in octanol-2, both at the same molal concentration, so that the total weight after mixing remained constant in each case. Use of the perchlorate salt was desirable because the perchlorate ion has such a low complexing tendency.

One problem was to obtain anhydrous nickel perchlorate. Sidgwick¹⁴ stated that the salt occurs in anhydrous form, while Chaney and Mann¹⁵ reported that attempts to prepare the anhydrous salt resulted at best in the dihydrate.

Nickel perchlorate was prepared by boiling C. P. grade nickel shot (low in cobalt content) in dilute reagent grade perchloric acid. Evaporation of the supernatant liquid gave long green needles of some hydrate of nickel perchlorate as described in the literature.¹⁶ This hydrate was recrystallized twice, and dried in a vacuum pistol at several fixed temperatures using a range of boiling liquids. Samples were removed at the various temperature intervals, and tested with an

aqueous solution of silver nitrate for any presence of chloride ion which might indicate decomposition of the salt. Analyses for nickel content were also performed on these samples. Although temperatures well above 200° were finally employed, the lowest hydrate obtained was the dihydrate.

Since the anhydrous salt as such could not be prepared by this method, an attempt was then made to form an anhydrous solution of nickel perchlorate by metathesis directly in the octanol phase. Stoichiometric proportions of dried NiCl_2 and AgClO_4 were introduced into a weighed quantity of octanol-2. This mixture was made up in a brown glass cell which was fitted with a mercury-sealed stirrer. The mixture was stirred for several hours at room temperature, and the resulting AgCl filtered off and weighed as a check. Several such attempts showed that the reaction was within 98% of being quantitative, and this method appeared satisfactory.

One of the nickel perchlorate solutions prepared by metathesis was mixed in varying amounts with a solution of LiCl in octanol-2 of the same molal concentration after the manner prescribed by the method of continuous variations. However, within a few minutes after mixing, yellow NiCl_2 was observed to precipitate in the solutions. It was thereby concluded that the method of continuous variations would not be applicable to this study owing to the low solubility of NiCl_2 in octanol-2.

Several qualitative experiments were tried on a saturated solution. A blue color developed when large quantities of HCl

gas were passed into the solutions, or when an excess of dry lithium chloride was introduced into the solution with agitation, indicating some change in the nature of the NiCl_2 entity in solution. This seemed to parallel the observations of Pavlik.⁸

METHODS

A solubility method^{17,18} for studying complex ions appeared feasible in view of the apparently low solubility of NiCl_2 and the development of a color in the solution on the addition of excess chloride ions.

This method is based upon the fact that the addition of a certain molecular or ionic species sometimes causes a large increase in the solubility of a sparingly soluble substance.¹⁷ The increase in solubility is due to the formation of complex ions from the simple ions. According to the mass action principle more of the slightly soluble substance must dissolve in order to preserve the solubility product constant. Although the complex must possess some appreciable stability under the conditions if it is to influence the solubility appreciably, it is probable that there is always an equilibrium between it and the simple ions from which it is formed.



Upon application of the equilibrium law,

$$K_2 = \frac{[\alpha \text{Ni}^{++}][\alpha \text{Cl}]^n}{[\text{NiCl}_n^{(n-2)-}]} \quad (2)$$

where a is the activity of the designated entity. The constant K_2 is a measure of the tendency of the complex to dissociate into simple ions, and is called the instability constant of the complex. Generally, concentrations rather than activities are employed for lack of knowledge of the activities, i. e.,

$$k_2 = \frac{[Ni^{+2}][Cl^-]^n}{[NiCl_n^{(n-2)}]} \quad (3)$$

where k_2 is the approximate instability constant. If a solution is in equilibrium with solid anhydrous nickel chloride, then by the approximate solubility product principle,

$$K_{s.p.} = \frac{[Ni^{+2}][Cl^-]^2}{[NiCl_2]} \quad (4)$$

Under the above conditions it can be assumed that

$$[NiCl_2] = K \quad (5)$$

Then,

$$K K_{s.p.} = [Ni^{+2}][Cl^-]^2 \quad (6)$$

or,

$$k_{s.p.} = [Ni^{+2}][Cl^-]^2 \quad (7)$$

It is seen that,

$$[Ni^{++}] = \frac{k_{s.p.}}{[Cl^-]^2} \quad (8)$$

and substituting this value for the nickel concentration into equation (3),

$$k_i = \frac{k_{s.p.} [Cl^-]^n}{[Cl^-]^2 [NiCl_n^{(n-2)}]} \quad (9)$$

or,

$$\frac{k_i}{k_{s.p.}} = \frac{[Cl^-]^{n-2}}{[NiCl_n^{(n-2)}]} \quad (10)$$

and taking logarithms,

$$\text{LOG} [NiCl_n^{(n-2)}] = (n-2) \text{LOG} [Cl^-] + \text{LOG} \frac{k_{s.p.}}{k_i} \quad (11)$$

The nickel concentration found by analysis was assumed to be equal to the concentration of free nickel ion plus the concentration of the nickel complex,

$$[Ni^{++}]_A = [Ni^{++}]_F + [NiCl_n^{(n-2)}] \quad (12)$$

where again

$$[Ni^{++}]_F = \frac{k_{s.p.}}{[Cl^-]^2} \quad (13)$$

Thus the concentration of a single nickel complex could be experimentally determined by,

$$[NiCl_n^{(n-2)}] = [Ni^{+2}]_A - \frac{k_{s.p.}}{[Cl^-]} \quad (14)$$

From equation (11) it is seen that if the logarithm of the concentration of the complex is plotted as ordinate versus the logarithm of the free chloride ion concentration as abscissa, the slope of the resulting curve will have the value (n-2), and the intercept will be $\text{LOG} \frac{k_{s.p.}}{k_i}$.

An alternative method for measuring the concentration of the complex may be possible for colored complexes. From the Beer-Lambert law, optical density is proportional to the length of the light path through the absorbing medium, and the concentration of the light-absorbing entity. Thus,

$$\text{O.D.} = \epsilon \ell C \quad (15)$$

or

$$\frac{\text{O.D.}}{\epsilon \ell} = C \quad (16)$$

and for a one-centimeter light path,

$$\frac{\text{O.D.}}{\epsilon} = C \quad (17)$$

In a region of absorption due to two entities,

$$O.D._{TOTAL} = O.D._1 + O.D._2 \quad (18)$$

if no interaction occurs between them. Letting $O.D._1$ equal the absorption due to nickel chloride, and $O.D._2$ equal that due to the complex,

$$O.D._{COMPLEX} = O.D._{TOTAL} - O.D._{NiCl_2} = \Delta O.D. \quad (19)$$

Substituting this into the Beer-Lambert expression, we can obtain the concentration of the complex as,

$$[NiCl]_{n^{(n-2)-}} = \frac{O.D._{COMPLEX}}{c} = \frac{\Delta O.D.}{c} \quad (20)$$

Then substituting this value for the concentration of the complex into equation (11) gives,

$$\text{Log } \frac{\Delta O.D.}{c} = (n-2) \text{Log}[Cl^-] + \text{Log } \frac{k_{s.p.}}{k_i} \quad (21)$$

or

$$\text{Log } \Delta O.D. = (n-2) \text{Log}[Cl^-] + \text{Log } \frac{(c)(k_{s.p.})}{k_i} \quad (22)$$

If $\text{log } \Delta O.D.$ is plotted as ordinate against the logarithm of the free chloride ion as abscissa, the slope will equal $(n-2)$,

and the intercept will be $\text{LOG} \frac{(\mathcal{C})(k_{sp})}{k_i}$

Thus the instability constant may be evaluated from the intercept on the ordinate axis as,

$$\text{LOG } k_i = \text{LOG } k_{s.p.} + \text{LOG } \mathcal{C} - \text{VALUE OF INTERCEPT (23)}$$

Equation (23), however, requires a knowledge of \mathcal{C} which may be impossible to obtain without making assumptions concerning the concentration of the complex in solution.

EXPERIMENTAL PROCEDURE

A. Materials

In the first two attempts to apply the methods described, C. P. nickel chloride hexahydrate from the Eimer and Amend Company was pulverized in a mortar and dried at 120°. The anhydrous form is supposed to be obtainable by heating the hydrate on a water bath.¹⁹ In the third series of solutions, C. P. nickel chloride was recrystallized once from a solution of water and C. P. acetone, and twice from an entirely aqueous solution. The recrystallized hydrate was then dried at least three days at 120°.

C. P. anhydrous lithium chloride was pulverized and dried at 120° for at least twenty-four hours before using.

In the first two series, the best grade of "anhydrous" octanol-2 available from the Matheson Company was used. In the third series, the octanol-2 was dried by refluxing with sodium alkoxide prepared by allowing C. P. metallic sodium to react with an excess of octanol-2. After refluxing, the octanol-2 was redistilled for use.

B. Analytical Methods

The chloride content of the solutions was determined directly in the organic phase using an excess of alcoholic

silver nitrate and back-titration with an aqueous solution of potassium thiocyanate in a modified Volhard method.

Nickel analyses were performed using a colorimetric method described by Snell.²⁰ In the first series, the solvent was evaporated from each solution, the residue taken up in water, and the nickel precipitated with alcoholic dimethylglyoxime. The precipitate was collected on a fritted glass filter, then dissolved by washing with reagent grade pyridine. The pyridine washings were diluted to twenty-five milliliters, and removed to a Beckman model DU spectrophotometer where the optical density were measured at a wave length of 360 millimicrons. The nickel content was then determined by comparing the measured optical density with a calibration curve.

In the second series of solutions the dimethylglyoxime reagent was added directly to the octanol-2 solution, which was then diluted to twenty-five milliliters with reagent grade pyridine. Thus the processes of evaporation and filtration were eliminated. Another colorimetric method using sodium diethyldithiocarbamate^{21,22} was investigated, and it was found to be very sensitive, but the scatter of the data intended for use in the preparation of a Beer-Lambert law calibration curve for this method showed that it would probably not be as accurate as the pyridine method. Accordingly, the procedure for nickel analysis used in series 2 was repeated for series 3.

The calibration curve for nickel analysis was prepared by weighing out three samples of dried nickel chloride into

volumetric flasks where each was mixed with alcoholic dimethylglyoxime, octanol-2, and pyridine. The resulting mixtures were warmed to dissolve all of the solid nickel chloride, and after cooling, diluted to volume with pyridine. Approximately the same proportions of reagents were used in the preparation of these solutions as might be expected to occur in the analyses proper. Standards of various lower concentrations were made from these three stock solutions by dilution with additional pyridine. The optical densities of these solutions were plotted against the respective nickel concentrations as shown in Figure 1. The slope and the intercept for these data were found by applying the method of averages. According to the Beer-Lambert law,

$$\text{O.D.} = K \ell C \quad (24)$$

The cells used had a length of 1 centimeter, therefore,

$$\text{O.D.} = KC \quad (25)$$

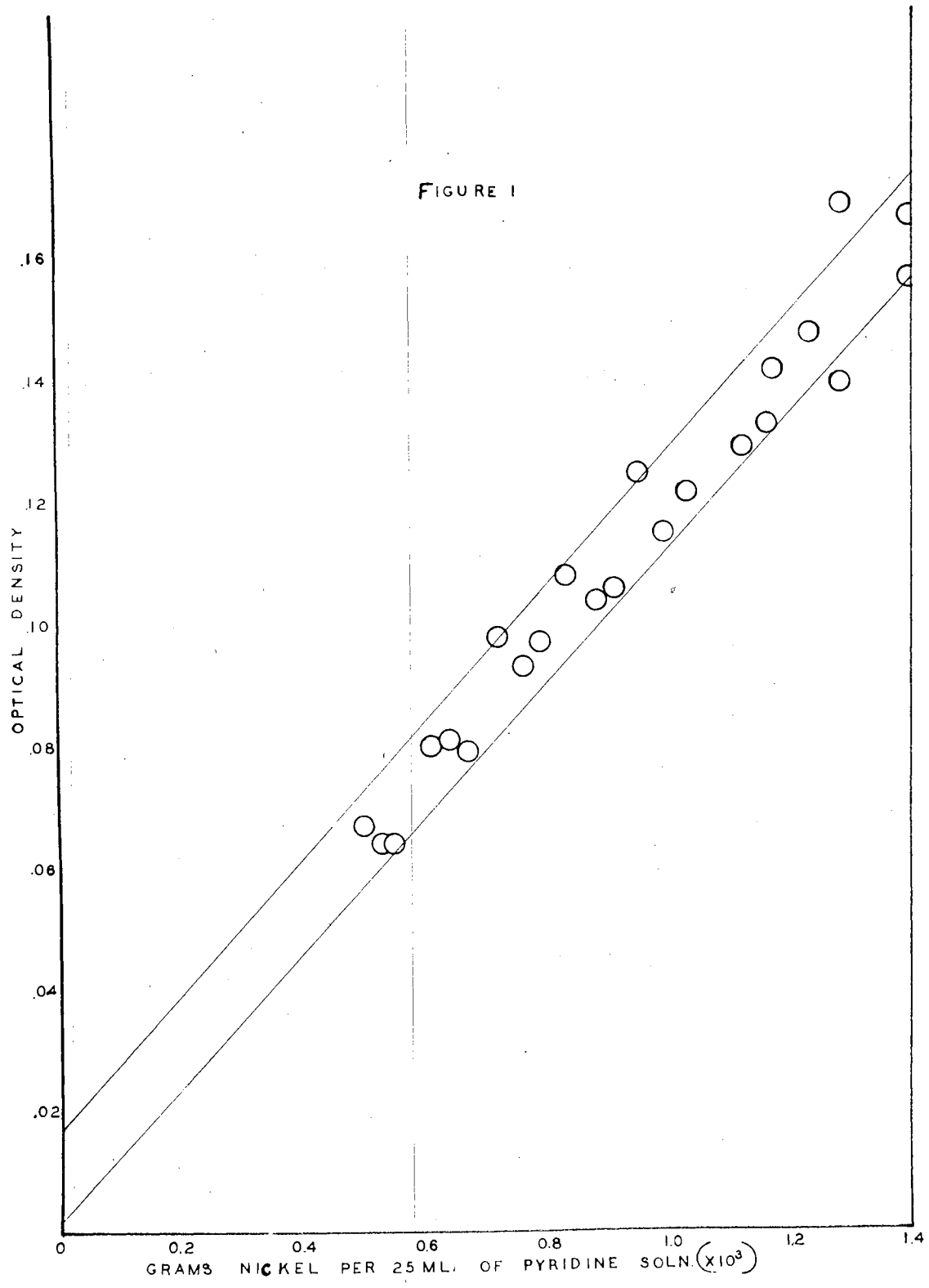
Thus when optical density is plotted as ordinate versus concentration as abscissa, the slope will be the constant K . This constant was evaluated as 120.96, and the grams of nickel present in twenty-five milliliters of pyridine solution were determined in the actual analysis by dividing the optical density of the particular pyridine solution by 120.96. This constant was used for evaluating nickel contents in both series 2 and series 3, and later series 1 was re-calculated

TABLE I

OPTICAL DENSITIES OF NICKEL STANDARDS

(Measured by Beckman model DU Spectrophotometer at
wave lengths of 360 millimicrons)

grams of nickel x 10 ³ /25 ml pyridine solution	optical density
1.52	0.166
1.47	0.177
1.39	0.172
1.39	0.157
1.28	0.140
1.28	0.169
1.23	0.148
1.17	0.142
1.16	0.133
1.12	0.129
1.03	0.122
0.99	0.120
0.95	0.125
0.91	0.106
0.88	0.104
0.83	0.108
0.79	0.097
0.76	0.093
0.72	0.098
0.67	0.079
0.64	0.081
0.61	0.080
0.55	0.064
0.53	0.064
0.50	0.067



using this value. Theoretically, the intercept of such a curve should be zero, but in practice it is usually not, owing probably to imperfect matching of the spectrophotometric cells.

From the data obtained in the preparation of this calibration curve for nickel analysis, it was estimated that an error of $\pm 3\%$ was to be expected from the average of three determinations made on the same sample.

B. Procedure

In a first application of the methods, dried lithium chloride was allowed to remain in contact with octanol-2 for a period of at least two weeks. The excess lithium chloride was filtered off, and ten solutions of lower concentration were made by dilution of this stock solution with pure octanol-2. A small excess amount of the dried nickel chloride was introduced into each of the solutions which were placed in a thermostat regulated for $30 \pm 0.2^\circ$, and shaken at frequent intervals. A blue color developed which was deepest in those solutions having the greatest chloride content. Samples were removed from one of the solutions for measurements of optical density, and it was assumed that equilibrium had been reached when the optical density approached a constant value. After two weeks in the thermostat, the solutions were removed, filtered, and analyzed for chloride and nickel.

The second trial was carried out in much the same manner except that the lithium chloride stock solution was prepared

by agitation on a mechanical shaker. In the third trial, the lithium chloride stock solution was prepared by continuous agitation for twenty-four hours at room temperature. The resulting solution was decanted from the excess solid lithium chloride and thirty solutions of lower concentration were prepared by dilution with dried octanol-2. A small amount of dried, powdered nickel chloride was then introduced into each of the solutions, and they were agitated at approximately 50° for several hours. This was done in an attempt to promote a more rapid attainment of equilibrium. The solutions were then placed in a thermostat regulated for 30°. After a period of more than two weeks they were removed, filtered, and analyzed for nickel and chloride content by the methods described.

ANALYSIS OF DATA

A. Spectra of solutions

The absorption spectra of the equilibrated solutions were recorded in the visible region. Figure 2 shows a graph of percent transmission as ordinate versus wave length as abscissa. Two main absorption maxima are observed at wave lengths of approximately 650 and 700 millimicrons. These data were taken from the solutions of the first series in which the octanol-2 was assumed to be anhydrous, and was not dried before use. However, it was shown later that the presence of small amounts of water in the octanol solutions appeared to cause no change in the location of the absorption maxima of the blue solutions.

B. Test of solubility methods

Figures 3 and 4 show the change of total nickel molality with total chloride molality for series 1 and 2 respectively. The curves exhibit roughly the expected shape in that there is a minimum somewhere in the regions of lower chloride concentration due to common ion effect, and a steady increase in the regions of higher chloride concentration due to complex ion formation. Logarithmic plots for the first two series using the direct spectrophotometric determination of the concentration of a colored complex are presented in Figures 5 and 6. No correction was made in either case for the amount of

TABLE II

VALUES OF PERCENT TRANSMISSION FOR NICKEL CHLORIDE
SOLUTIONS IN OCTANOL-2 CONTAINING VARIOUS
AMOUNTS OF LITHIUM CHLORIDE

Wave Length	Total Chloride Molality								NiCl ₂ Only
	1.12	1.03	.890	.646	.550	.448	.335	.304	
520	90.6	91.3	95.3	91.7	92.1	94.2	94.6	94.8	99.2
530	89.1	90.2	94.8	90.5	91.2	93.2	93.9	94.2	99.2
540	85.8	87.4	92.9	87.9	88.7	91.4	92.9	93.4	99.1
550	81.0	83.6	89.9	84.6	85.5	89.2	91.5	92.6	99.0
560	74.0	78.0	86.3	79.8	81.4	86.0	89.3	90.7	98.5
570	65.8	71.5	82.1	74.9	77.2	83.0	87.3	89.3	98.2
580	58.6	65.9	78.8	69.7	73.2	80.1	85.4	87.8	97.8
590	56.2	58.2	73.7	64.9	69.0	77.3	83.6	86.4	97.5
600	46.5	55.2	70.5	61.4	66.0	74.8	81.4	84.8	97.2
610	43.2	52.1	67.3	58.6	63.4	72.3	79.0	82.7	96.6
620	40.8	50.0	65.5	56.8	61.8	71.0	77.8	81.6	96.4
630	38.2	47.6	63.7	54.8	60.1	69.8	76.5	80.5	95.8
640	34.8	44.7	61.4	52.8	58.8	68.8	76.0	80.2	95.8
650	32.5	42.5	58.7	50.8	57.0	67.5	75.2	79.8	95.1
660	34.0	43.9	60.3	51.8	57.8	67.8	74.5	78.9	94.8
670	38.3	47.7	63.0	55.4	60.9	69.7	75.3	79.2	94.8
680	38.0	47.3	62.9	55.0	60.4	69.5	75.3	79.2	94.9
690	33.7	43.3	59.2	51.9	57.8	67.5	74.0	78.0	95.3
700	32.0	41.8	58.5	50.7	57.1	67.1	73.9	78.3	96.2
710	35.2	45.2	61.9	53.6	60.2	69.9	76.8	81.2	96.7
720	43.2	52.8	68.2	60.2	66.1	75.2	81.3	85.0	96.6
730	52.7	61.2	75.0	67.8	72.9	79.8	84.8	87.6	96.9
740	61.7	69.1	80.8	73.7	77.8	83.9	87.6	89.7	96.8
750	68.2	74.7	84.3	79.1	82.6	87.0	89.8	91.1	97.1
760	74.8	79.8	87.5	83.2	85.7	89.2	91.2	92.0	97.0
770	79.5	83.6	90.0	86.1	88.1	90.9	92.2	92.6	97.2
780	83.1	86.4	91.8	88.4	90.0	92.3	93.1	93.2	97.0
790	85.7	88.2	92.9	90.2	91.5	93.5	94.0	94.0	97.2
800	87.7	89.9	93.9	91.5	92.7	94.0	94.2	94.1	97.2

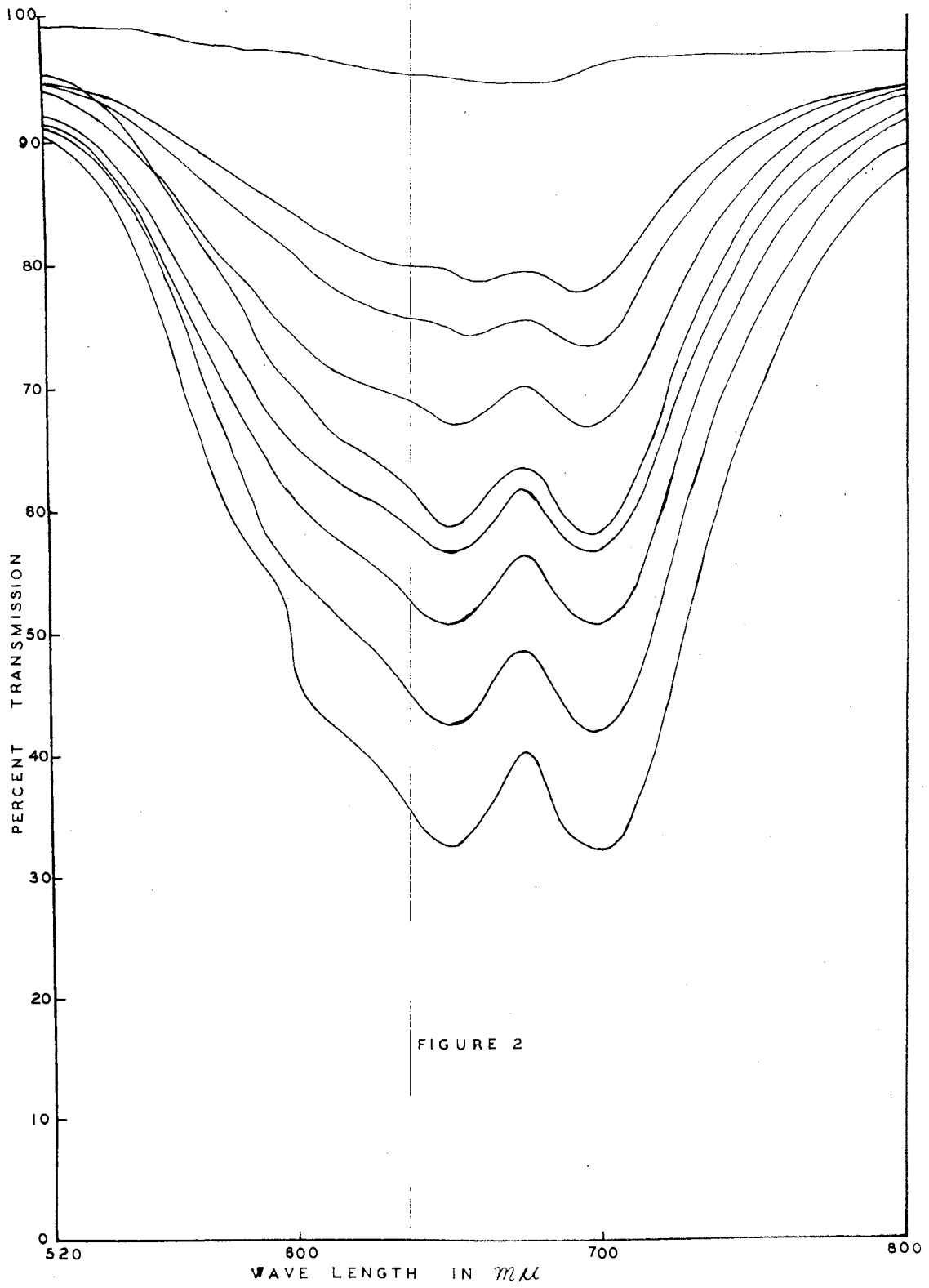


TABLE III

TOTAL NICKEL AND CHLORIDE MOLALITIES

Series 1

Nickel	Chloride
0.0118	1.119
0.00951	1.030
0.00525	0.8899
0.00786	0.7533
0.00819	0.6463
0.00920	0.5505
0.00781	0.4485
0.00907	0.3346
0.0109	0.3041
0.00854	0.1344

Series 2

Nickel	Chloride
0.00328	1.251
0.00223	1.112
0.00196	1.005
0.00237	0.8844
0.00096	0.7385
0.00127	0.6432
0.00150	0.4869
0.00060	0.3003
0.00135	0.2400
0.00126	0.1905

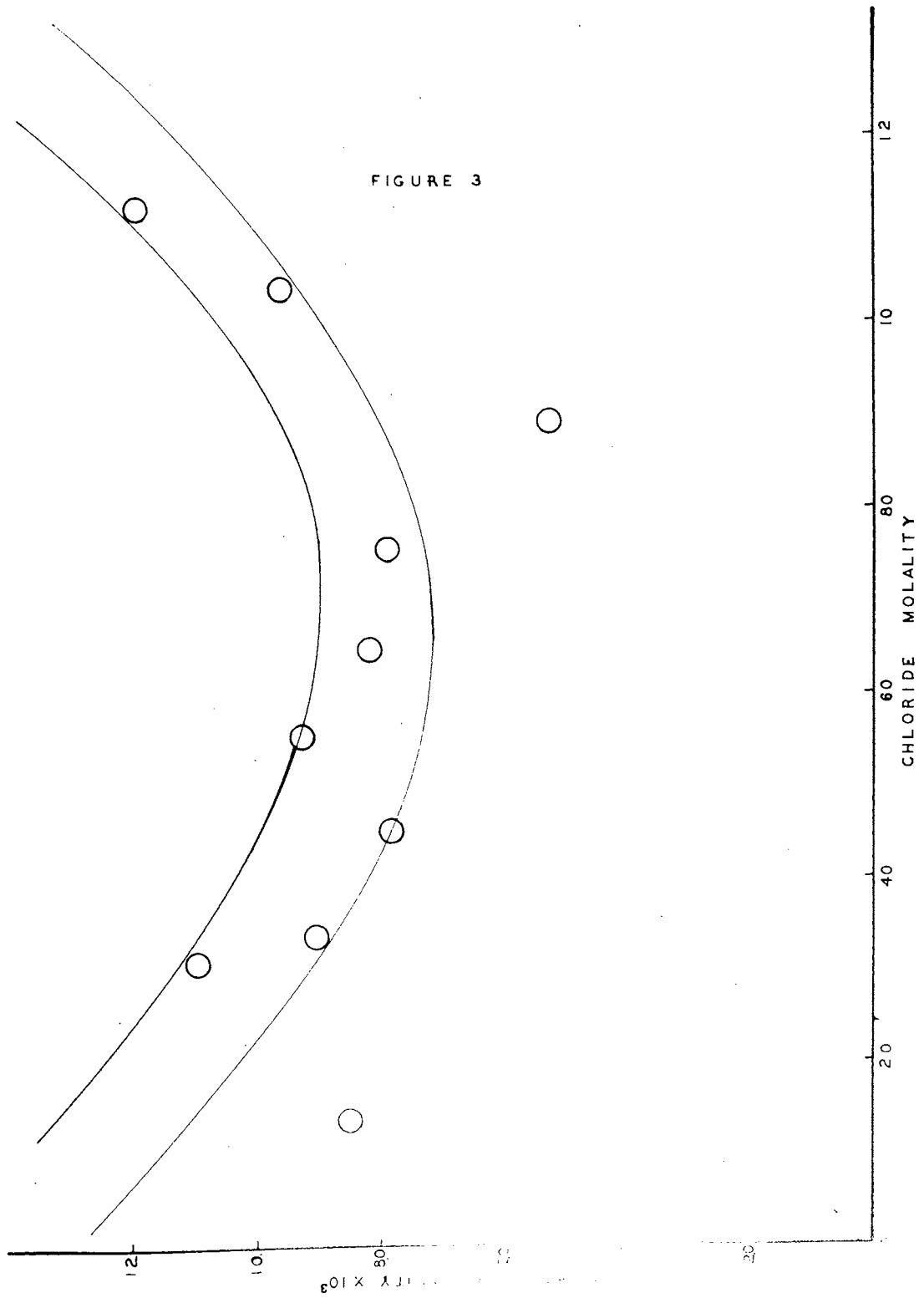


FIGURE 3

FIGURE 4

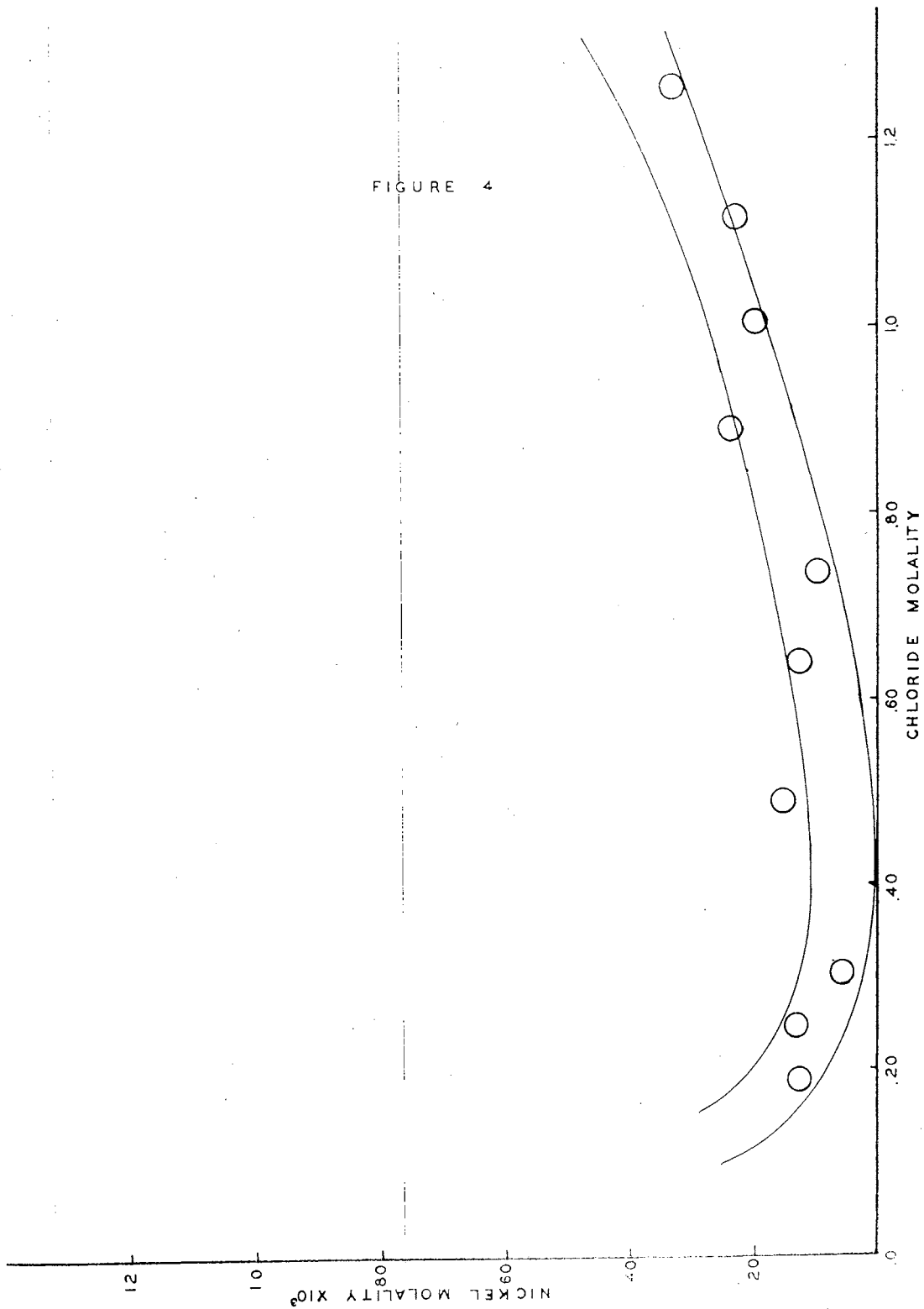


TABLE IV

Series 1

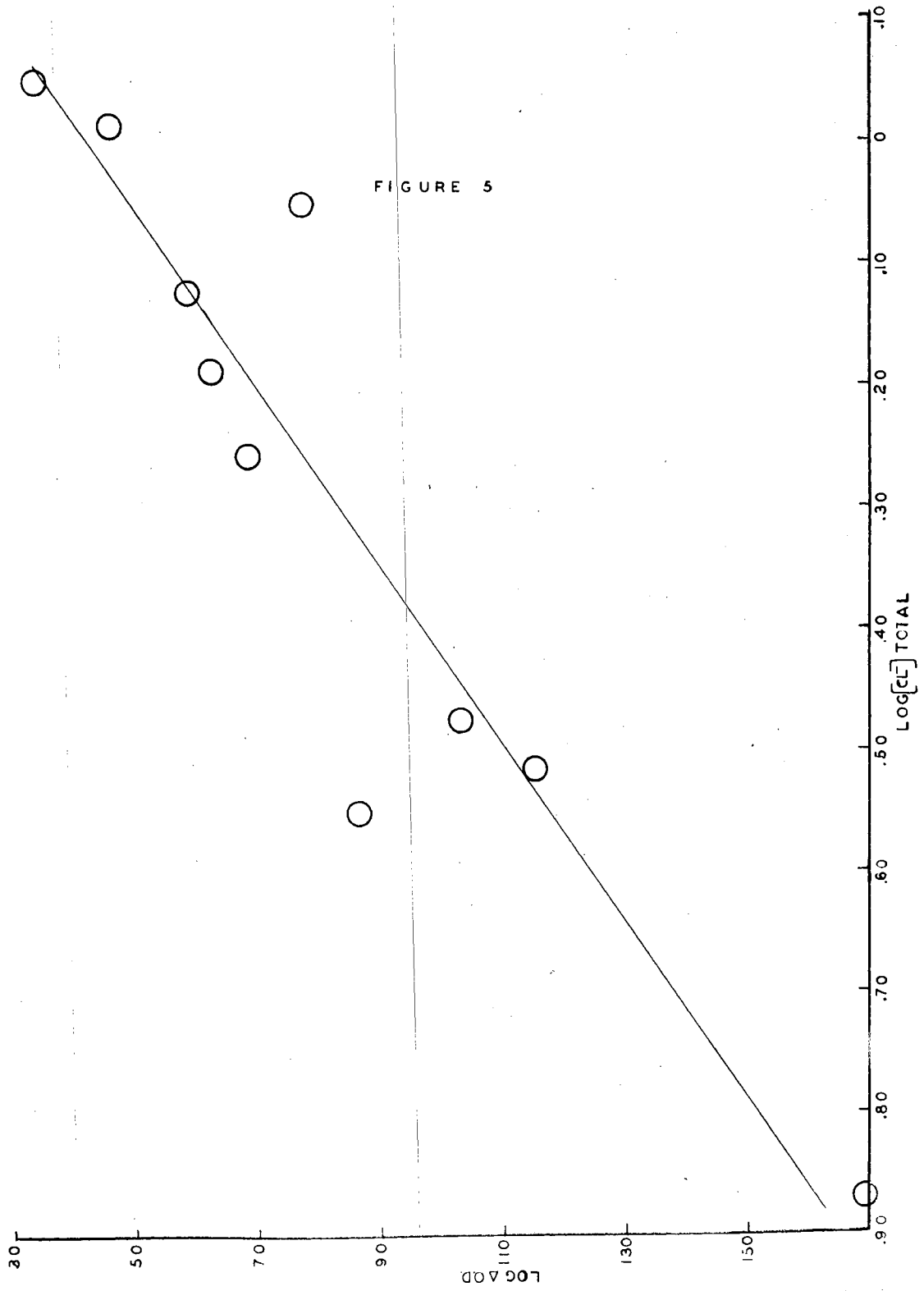
$$k_{s.p} = 15.5 \times 10^{-5}$$

$\text{Log}[\text{Cl}^-]_A$	$\text{Log} \Delta \text{O.D.}$
0.4875	-0.3401
0.1275	-0.4673
-0.0507	-0.7077
-0.1230	-0.5850
-0.1896	-0.6289
-0.2592	-0.6861
-0.5515	-0.8665
-0.4755	-1.0315
-0.5170	-1.1549

Series 2

$$k_{s.p} = 7.78 \times 10^{-5}$$

$\text{Log}[\text{Cl}^-]$	$\text{Log} \Delta \text{O.D.}$
0.0976	-0.1979
0.0461	-0.4976
0.00217	-0.7144
-0.0534	-0.8601
-0.1317	-1.0809
-0.1917	-0.9066
-0.3126	-1.0044
-0.5224	-1.7272
-0.6198	-1.7447
-0.7201	-2.3979



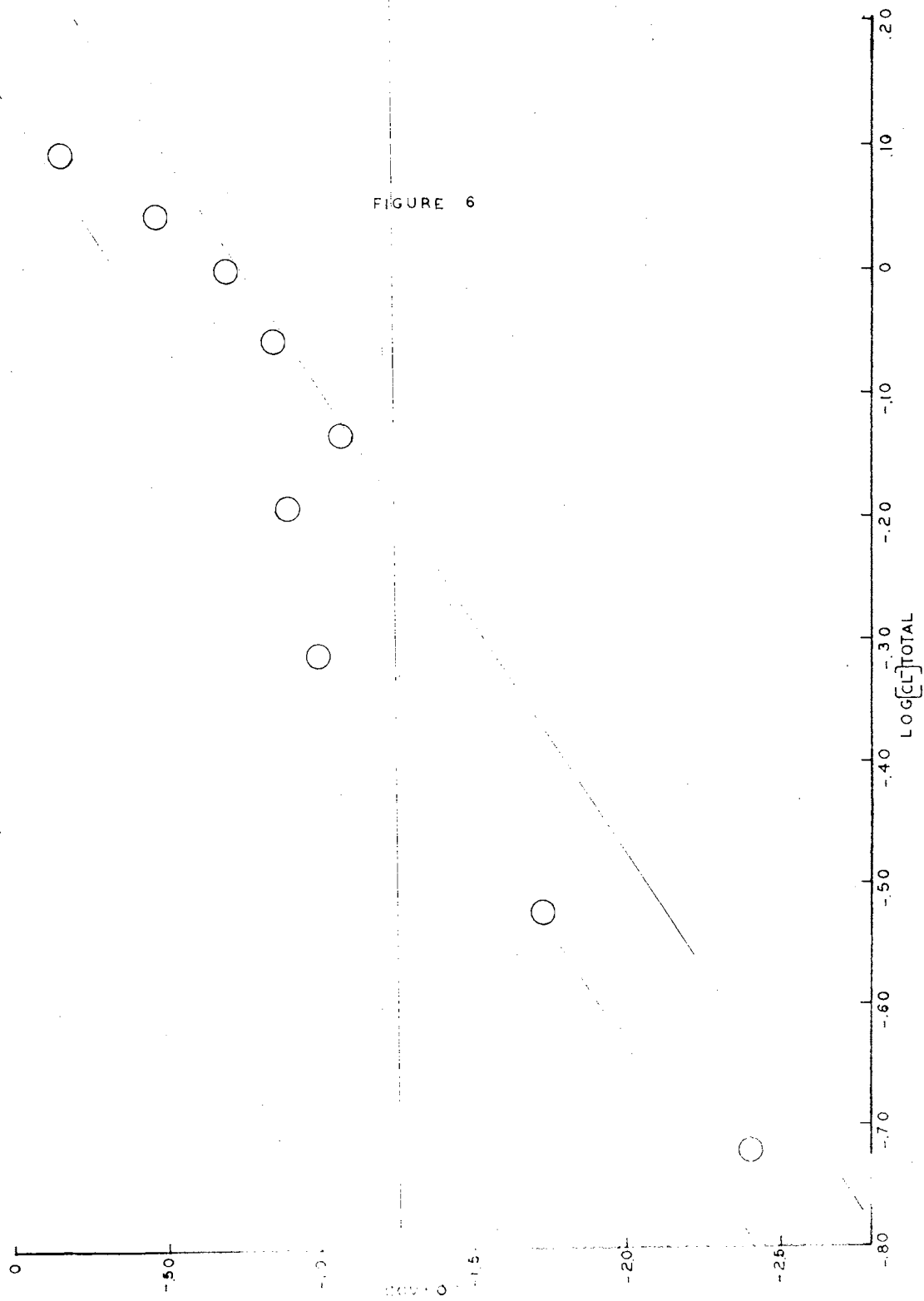


FIGURE 6

chloride tied up in any coordination compound. The optical densities were measured at a wave length of 700 millimicrons where the difference between the absorption of the chloride solutions and that of pure nickel chloride appeared to be almost a maximum. A Beckman model DU spectrophotometer was used for these measurements.

Thirty solutions of various added chloride concentration were used in the third series in an effort to collect an amount of data which would better allow interpretation in view of the scattered patterns shown by the results of the first two series. Figure 7 depicts for series 3 the change in the solubility of nickel chloride as increasing amounts of lithium chloride are added. Figure 8 shows the logarithmic plot (Eq. 11) of the series 3 data where the concentration of the complex is based on the solubility method. No attempt was made to correct for the amount of chloride present in the complex, as it was thought to be a minor correction relative to the very appreciable amount of scattering.

In treating the data from the spectrophotometric determination of the concentration of the colored entity, the logarithm of the change in optical density was plotted as ordinate versus the logarithm of the total chloride molality as a first approximation. The data appeared to fall within a definite band which had a slope of approximately 3.15. According to Eq. (11) this would suggest a nickel coordination number of five.

TABLE V

TOTAL NICKEL AND CHLORIDE MOLALITIES

Nickel	Chloride
0.0873	1.453
0.0498	1.386
0.0447	1.318
0.0483	1.334
0.0171	1.329
0.0568	1.244
0.0641	1.177
0.0596	1.146
0.0460	1.177
0.0456	1.030
0.0466	0.990
0.0501	0.918
0.0438	0.904
0.0196	0.840
0.0377	0.822
0.0247	0.889
0.0139	0.684
0.0108	0.652
0.0138	0.606
0.0095	0.547
0.0112	0.517
0.0183	0.479
0.0180	0.438
0.0138	0.345
0.0141	0.287
0.0143	0.596
0.0192	0.173
0.0255	0.140
0.0207	0.0952
0.0221	0.0428

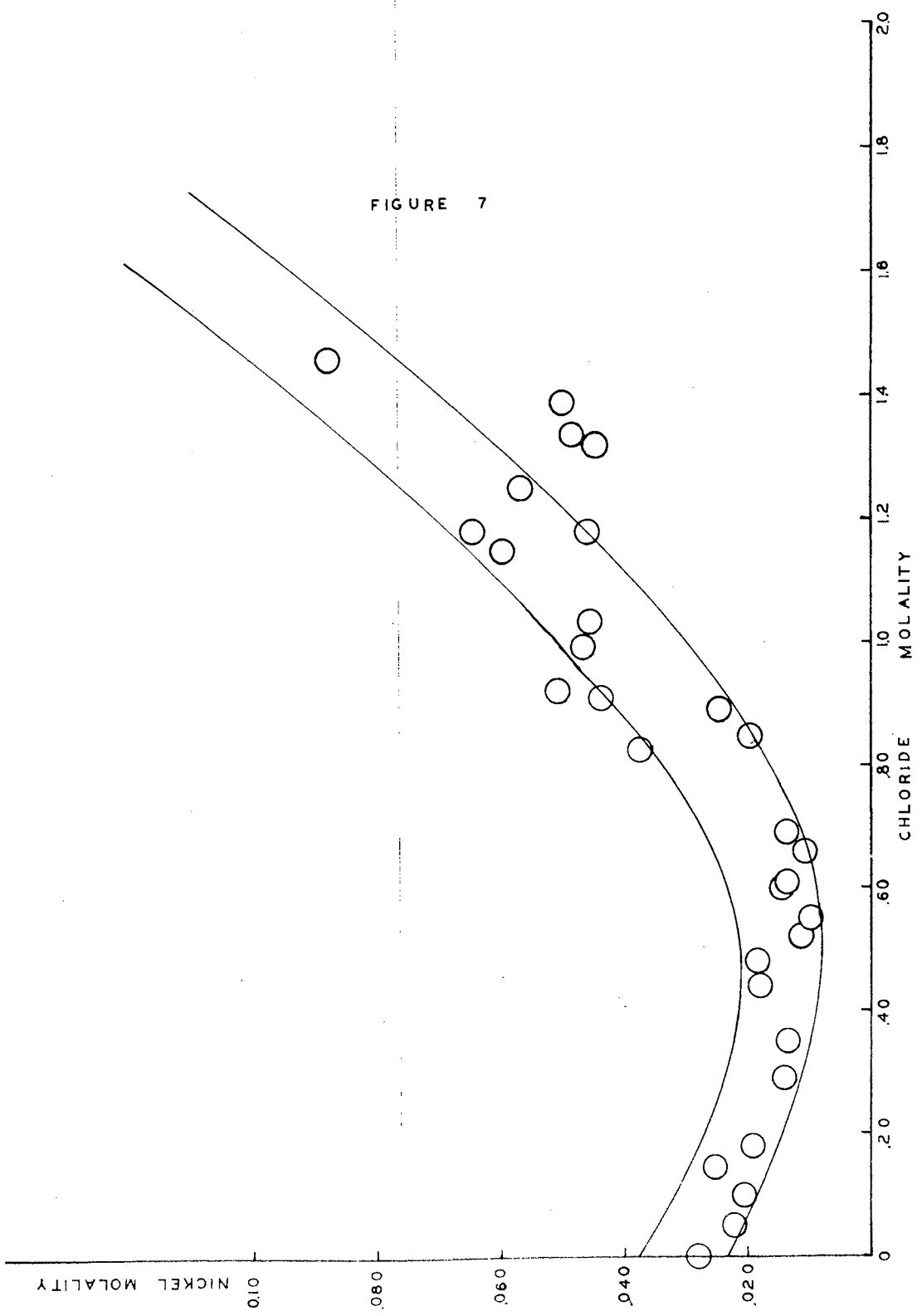


TABLE VI

Series 3

$$k_{s.p.} = 4.05 \times 10^{-5}$$

$\text{LOG} \left([\text{Ni}^{++}]_A - \frac{k_{s.p.}}{[\text{Cl}^-]^2} \right)$	$\text{LOG} [\text{Cl}^-]_A$
-1.059	0.1623
-1.303	0.1418
-1.350	0.1199
-1.316	0.1252
-1.767	0.1235
-1.246	0.0948
-1.193	0.0778
-1.225	0.0592
-1.337	0.0778
-1.341	0.0128
-1.332	-0.0044
-1.300	-0.0369
-1.358	-0.0440
-1.304	-0.0756
-1.424	-0.0852
-1.607	-0.0509
-1.860	-0.1648
-1.971	-0.1855
-1.863	-0.2177
-2.027	-0.2622
-1.955	-0.2864
-1.742	-0.3193
-1.750	-0.3588
-1.870	-0.4617
-1.866	-0.5420
-1.880	-0.2251

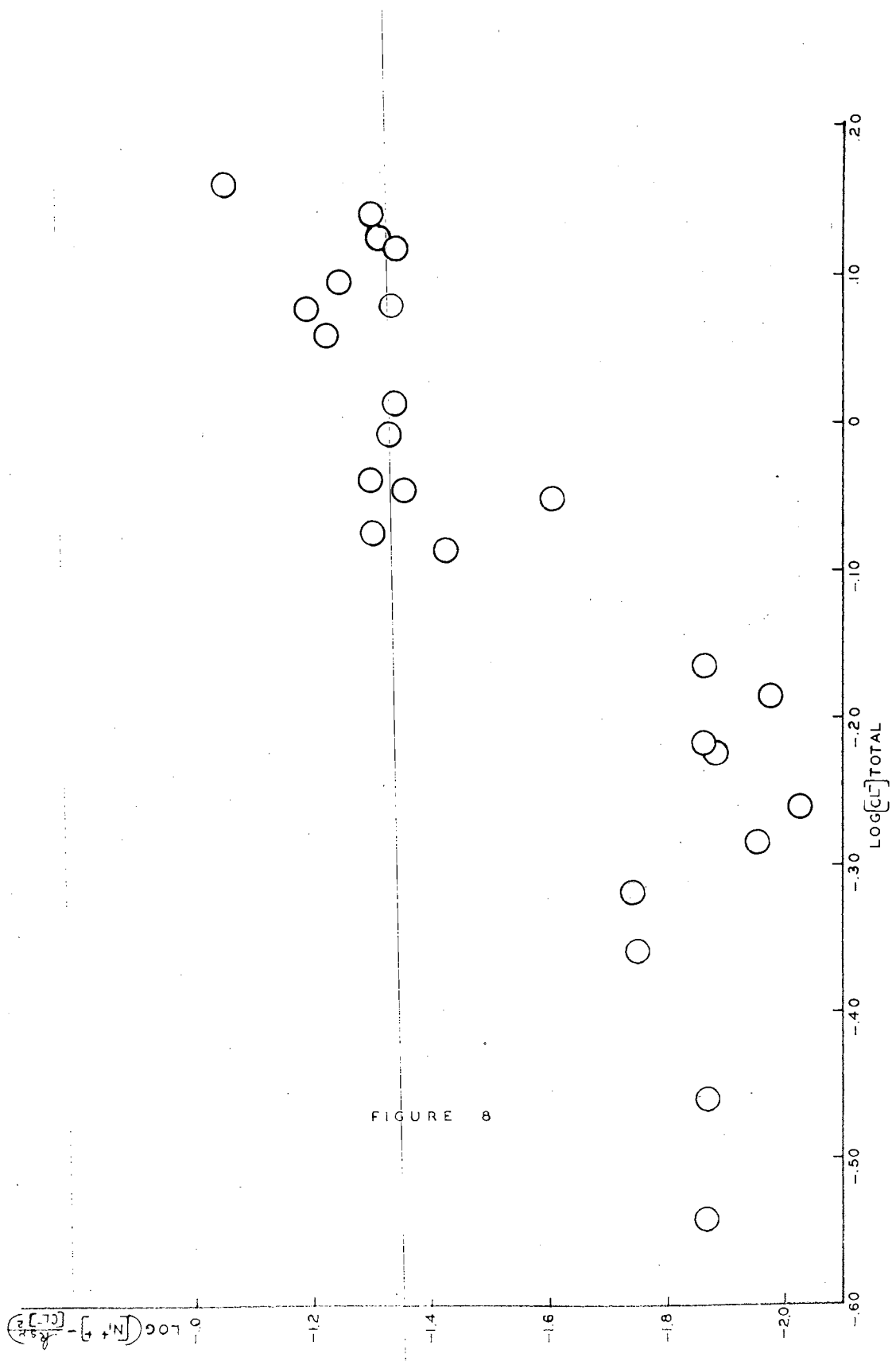


FIGURE 8

Corrections for the amount of chloride present in the nickel complex were then made from the following considerations: By the Beer-Lambert relation, the concentration of the complex is proportional to the excess optical density,

$$\text{CONCENTRATION OF COMPLEX} \propto \Delta \text{O.D.} \quad (26)$$

and also,

$$\text{CONCENTRATION OF COMPLEX} \propto \Delta \text{SOLUBILITY} \quad (27)$$

where solubility, as shown by "Eq. 15), is the difference between the total nickel found by analysis and the free nickel to be expected from the solubility product constant.

Then

$$\frac{\Delta \text{O.D.}}{\Delta \text{SOLUBILITY}} = \mathcal{E} \quad (28)$$

where \mathcal{E} is the apparent extinction coefficient. Values for \mathcal{E} were computed, but the constant exhibited a drift with change in chloride concentration. An average value for \mathcal{E} was chosen from the region where the added chloride concentration was greatest, for in this region the ratio of complexed nickel to free nickel ion is a maximum, and the value for \mathcal{E} could be expected to approach the true extinction coefficient most closely. It was also in the more concentrated region that the

change of ϵ with chloride concentration was slightest. The value chosen was 6.67, and accordingly,

$$[\text{concentration of complex}] = \frac{\Delta \text{O.D.}}{6.67} \quad (29)$$

The concentration of free chloride ion was assumed to be equal to the difference between the total chloride found by analysis and the concentration of the complex multiplied by the nickel coordination number. Thus,

$$[\text{Cl}^-]_F = [\text{Cl}^-]_A - n[\text{NiCl}_n^{(n-2)}] \quad (30)$$

or,

$$[\text{Cl}^-]_F = [\text{Cl}^-]_A - n \frac{\Delta \text{O.D.}}{6.67} \quad (31)$$

Taking n equal to five as suggested by the first approximation, a second graph was plotted with $\log \Delta \text{O.D.}$ as ordinate, and $\log \left([\text{Cl}^-]_A - 5 \frac{\Delta \text{O.D.}}{6.67} \right)$ as abscissa.

This second approximation gave a graph with a slope of about 3.93. This would suggest a coordination number of six, and a third approximation was made in which $\log \Delta \text{O.D.}$ was plotted versus $\log \left([\text{Cl}^-]_A - 6 \frac{\Delta \text{O.D.}}{6.67} \right)$. The resulting curve

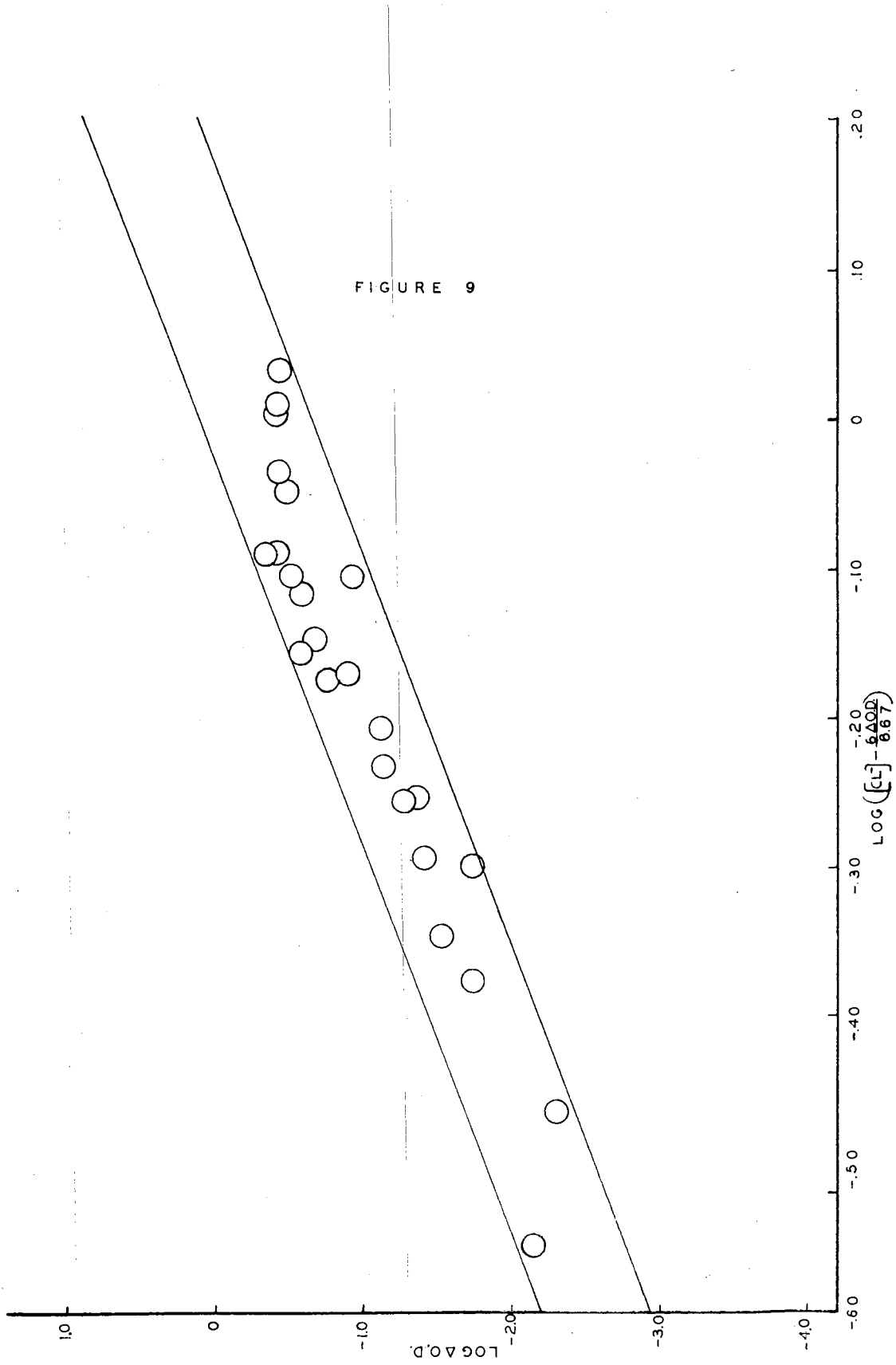
(Figure 9) had a slope of about 3.96. It was seen that the successive approximations could be carried no further, and it

TABLE VII

Series 3

(Optical densities measured by Beckman
model B spectrophotometer)

LOG Δ O.D.	LOG $([Cl^-]_A - 6 \frac{\Delta O.D.}{6.67})$	LOG γ_{\pm}	LOG $[Cl^-]_A$
-0.4962	0.0342		
-0.4685	0.0103		
-0.4461	0.0064		
-0.4584	-0.0302		
-0.3925	-0.0887	-0.5977	
-0.4341	-0.0877	-0.7158	
-0.5157	-0.0444		
-0.5703	-0.1027	-0.6419	
-0.6056	-0.1143	-0.7162	
-0.6180	-0.1530	-0.7455	
-0.6840	-0.1433	-0.7392	
-0.9244	-0.1675	-0.4450	
-0.7773	-0.1723	-0.7189	
-0.9547	-0.1018	-0.7353	
-1.1487	-0.2071	-0.4984	
-1.1487	-0.2300	-0.0778	
-1.2840	-0.2522	-0.5724	
-1.4202	-0.2903	-0.6685	
-1.7696	-0.2992	-0.6106	
-1.5229	-0.3445	-0.6138	
-1.7696	-0.3740	-0.6110	
-2.3010	-0.4670	-0.5247	
-2.1549	-0.5511	-0.2603	
-1.3979	-0.2517	-0.6039	
		-1.1518	-.7620
		-1.0912	-.8539
		-0.6957	-1.0214
		-0.0000	-1.3686



was concluded that the data are probably best represented by a slope of four.

Estimation of the value for the instability constant of the colored complex was also made from the use of equation (24). The band shown in Figure 9 intercepted a region on the ordinate axis having the limits of about +0.20 and -0.68 . These limits corresponded to 1.7×10^{-4} and 13×10^{-4} respectively.

DISCUSSION OF RESULTS

From a consideration of Figure 2, there appears to be no shift in the location of the absorption maxima characteristic of the blue complex as the amount of added chloride ion is varied. If the solutions were saturated and in equilibrium with anhydrous NiCl_2 at a constant temperature, the only independent variable was the concentration of added chloride ion. The conclusion drawn from these facts was that there appeared to be only one light-absorbing complex present under the conditions of the experiment. If colorless complexes were present under the given conditions, their presence might be indicated by definite inflection points in the curve in Figure 8. If such indications are present in the data, their detection is rendered impossible by the scattered positions of the points. The blue entity may be the only complex ion present, but Burkin²³ says it is to be expected that the addition of a coordinating group to a metal ion always proceeds in a step-wise fashion, and that a series of complexes is obtained. If other coordination compounds were present during the experiments, the properties observed were probably those of the most stable one, and the estimated instability constant would be an overall constant, equal to the product of the successive constants. In view of the large value of the instability constant

obtained in this work, no intermediate complexes of large stability would appear to be present.

Analyses for both nickel and chloride ion were carried out in triplicate in series 2 and 3, and since fairly good precision was obtained, some other means were sought for explaining the discord in the data evident from Figure 8. All of the solutions were kept in the same water bath for a period of at least two weeks, so that it was improbable that the variations were caused by a temperature effect. It is quite probable, however, that equilibrium was incompletely attained in a number of the solutions. The original lithium chloride stock solution had a very high viscosity as did a number of the solutions even after dilution with pure octanol-2. The solutions were agitated for a number of hours on a mechanical shaker after the introduction of dried nickel chloride. However, it is possible that, due to the viscosity of the solution, the solid nickel chloride was not washed sufficiently by the solvent in the shaking process to insure the attainment of equilibrium. The distance of a particular solution from equilibrium conditions might have been dependent upon its viscosity, as well as its actual position on the mechanical shaker, since some solutions received a more violent agitation than others. Also, the state of subdivision of the dried nickel chloride might have varied from one solution to another. Since the medium is one of low dielectric constant, one might expect relatively slow attainment of equilibrium because

ionization in such a medium would probably be slight and hence the reaction themselves might not be simple ionic addition or displacements.

A brief but significant study was made of the effect of water on the blue color. Pure octanol-2 was equilibrated with water at 30°, and a series of solutions of varying water content was made by adding various amounts of the water-saturated octanol to samples of one of the blue solutions. The effect observed was the settling out of a fine, yellow precipitate accompanied by a decrease in optical density. Some of the erratic results in the early series might be explained by failure to completely exclude water from the system, although a good deal of care was exercised in series 3 to protect the solutions from moisture.

The above conditions would have affected the results of both means of determining the concentration of the complex. The scatter is much worse in the results from the solubility method than the optical method, and it was thought that perhaps any errors resulting from incomplete attainment of equilibrium might have been magnified in the solubility method by a rapidly changing activity coefficient. Such a possibility was then briefly explored.

For the true solubility product constant,

$$K_{s.p.} = [\gamma_{\pm}]^3 [Ni^{+2}] [Cl^-]^2 \quad (32)$$

where γ_{\pm} is the mean activity coefficient of NiCl_2 and $[\text{Ni}^{++}]$ and $[\text{Cl}^-]$ are the assumed ionic concentrations. was arbitrarily assumed equal to unity in the most dilute solutions, and therefore the solubility product constant 4.05×10^{-5} obtained from a solution in this dilute region is a thermodynamic constant. For solutions in which the spectra indicated no appreciable complex formation,

$$3 \text{Log } \gamma_{\pm} = \text{Log } K_{\text{SP}} - \text{Log} [\text{Ni}^{++}]_{\text{A}} - 2 \text{Log} [\text{Cl}^-]_{\text{A}} \quad (33)$$

For solutions in which the colored complex is assumed to be the only one binding up chloride ions, Eq. (33) may be written as

$$3 \text{Log } \gamma_{\pm} = \text{Log } K_{\text{SP}} - \text{Log} \left([\text{Ni}^{++}]_{\text{A}} - \frac{\Delta \text{O.D.}}{\epsilon} \right) - 2 \text{Log} \left([\text{Cl}^-] - \frac{6 \Delta \text{O.D.}}{\epsilon} \right) \quad (34)$$

thus correcting for the amounts of nickel and chloride tied up in the colored complex. Values of $\log \gamma_{\pm}$ were evaluated for the various solutions, and were plotted against the logarithm of the concentration of the free chloride ion as in Figure 10 merely for the purpose of depicting the rate of change of such a coefficient with the change of chloride concentration. The fact that the values of γ_{\pm} obtained by Eq. (34) do not correlate well with those found by Eq. (33) in the more dilute region is indicative that both Eq. (33) and (34) should contain corrections for colorless or nearly colorless complexes. This

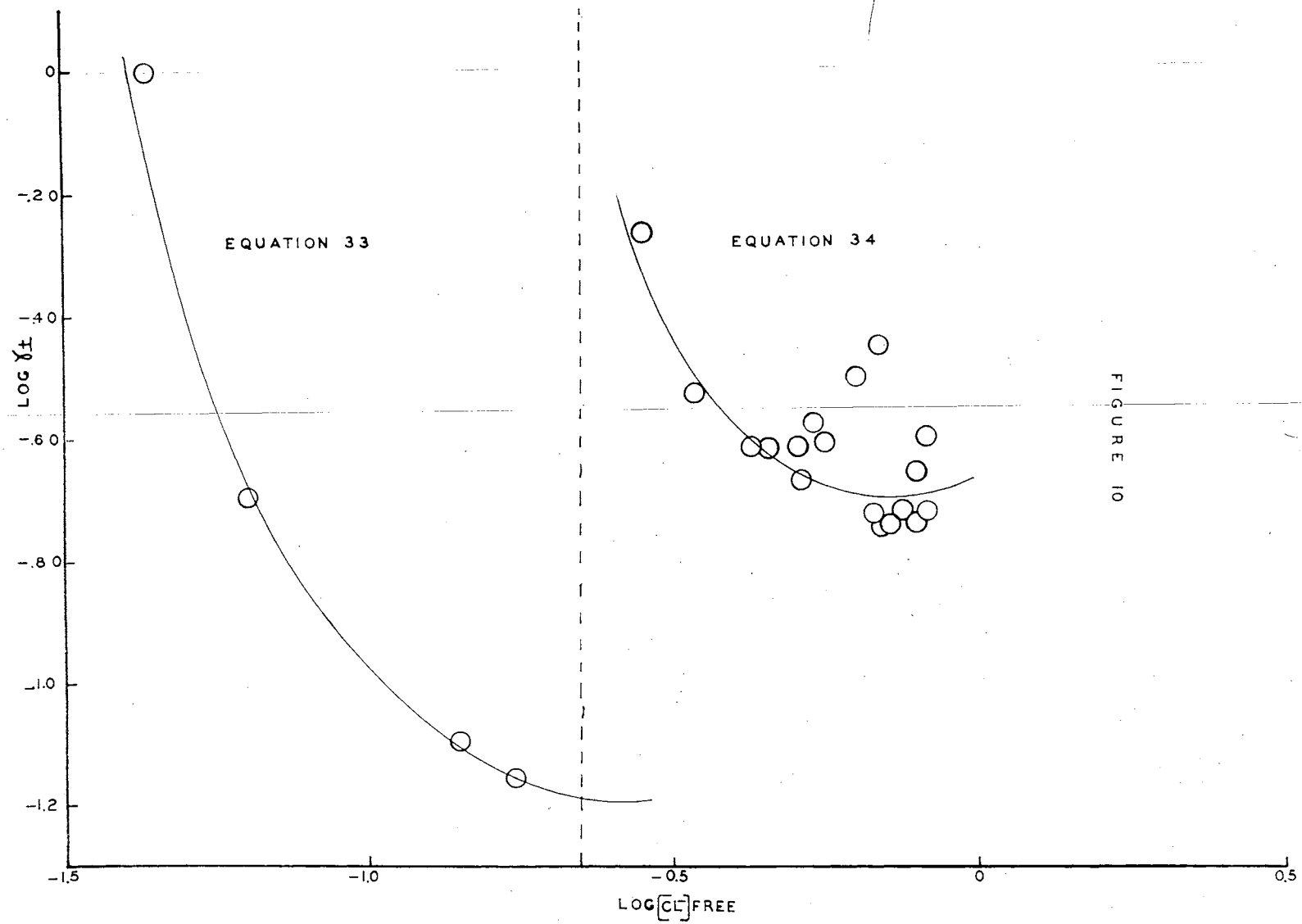


FIGURE 10

would not be unexpected as stepwise formation of complexes is usually found. The substitution of stoichiometric values of the ionic concentrations is probably not justified even in the most dilute regions. The error due to activity considerations, however, might be expected to cause a smooth deviation from linear shape of the graph in Figure 2. The graph from the results of the spectrophotometric determination of the concentration of complex shows that the data definitely fall within a reasonably narrow band about a straight line. A slope of about four was evaluated by a series of successive approximations, and the coordination number for nickel which is best represented by the available data is six. This is not an unreasonable coordination number for nickel. In a discussion of the relation between color and coordination number, Pauling²⁵ observes that a number of nickel complexes which exhibit a blue color are characterized by octahedral coordination. The value of the instability constant probably lies somewhere between 1.7×10^{-4} and 13×10^{-4} .

SUMMARY

Both the solubility method and optical measurements were used in an attempt to estimate the configurations and instability constants of the complexes formed in a solution of nickel chloride in octanol-2 upon the addition of large amounts of lithium chloride. A blue color developed in the solutions under the above conditions, and the absorption spectra of the solutions indicated that the blue color was due to only one colored complex. It was not possible to draw any conclusions as to the existence of other, colorless complexes in the system. A chloro-coordination number of six for nickel in the blue complex best represented the data. The instability constant of the complex was estimated to be somewhere between 1.7×10^{-4} and 13×10^{-4} .

BIBLIOGRAPHY

- (1) Irving, Quarterly Reviews, 5, 200 (1951)
- (2) Garwin and Hixon, Ind. Eng. Chem., 41, 2298 (1949),
Ibid. 41, 2303 (1949)
- (3) Estill, Master's Thesis, Oklahoma A. and M. College,
1951
- (4) Job, Compt. rend. 196, 181 (1933)
- (5) Vosburgh and Cooper, J. Am. Chem. Soc. 63, 437 (1941)
- (6) Schaffer and Taylor, J. Am. Chem. Soc. 48, 843 (1921)
- (7) Pavlik, Collection Czechoslav. Chem. Comm. 3, 223-37
(1931)
- (8) Ibid., 3, 302-13 (1931)
- (9) Samuel, Z. Physik. 70, 43-73 (1931), via C. A. 25:5096
- (10) Kiss Boer and Gerendas, Acta Lit. Sci. Regiae Univ.
Hung. Fransico-Josephine, Sect. Chem., Mineral. Phys.
4, 259-71 (1935) via C. A. 30:7036⁴
- (11) Kiss and Csokan, Z. Anorg. allgem. Chem., 245, 355-64
(1941) via C. A. 35:7829³
- (12) Job, Compt. rend., 200, 831 (1935)
- (13) Major, Acta. Univ. Szegediensis, Acta Chem. et Phys.
N. S. 1, 17-34 (1942) via C. A. 41:7257a
- (14) Sidgwick, "The Chemical Elements and Their Compounds,"
Oxford University Press, London, 1950, p. 1438.
- (15) Chaney and Mann, J. Phys. Chem. 35, 2289 (1938)
- (16) Goldblum and Terlikowski, Bull. soc. chim., 11, 103
(1890); via C. A. 6:1108⁸
- (17) Glasstone, "Textbook of Physical Chemistry", second ed.,
D. Van Nostrand Company, Inc., New York, 1946, p. 972.

- (18) Garrett, Noble, and Miller, J. Chem. Ed., 19, 485 (1942)
- (19) Ephraim, "Inorganic Chemistry", 4th ed., Nordeman Publishing Company, Inc., New York, N. Y., 1943, p. 269.
- (20) Snell and Snell, "Colorimetric Methods of Analysis", 3rd ed., D. Van Nostrand Company, Inc., New York, 1949, Vol. II, p. 345.
- (21) Ibid., p. 347.
- (22) Alexander, Godar, and Linde, Ind. Eng. Chem., Anal. Ed. 18, 206-8 (1946)
- (23) Burkin, Quarterly Reviews, 5, 6 (1951)
- (24) Bjerrum, Z. Physikal Chem., 106, 238 (1923) via Burkin, Quarterly Reviews, 5, 9 (1951)
- (25) Pauling, "The Nature of the Chemical Bond", 2nd ed., Cornell University Press, Ithaca, New York, 1940, pp. 122-3.

BIOGRAPHY

LaVerne Everett Trevorrow, son of Winona Trevorrow and the late Barney Trevorrow, was born in Moline, Illinois on November 1, 1928. He attended Moline public schools, and was graduated from Moline High School in 1947. His college studies were pursued at Augustana College in Rock Island, Illinois, from whence he was graduated in June, 1950.

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THESIS TITLE: FORMATION OF CHLORO-COMPLEXES OF NICKEL
 IN OCTANOL-2

NAME OF AUTHOR: LaVerne E. Trevorrow

THESIS ADVISER: Dr. Tom Moore

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