

A STUDY OF THE FORMATION OF AQUO- AND CHLORO-COMPLEXES
OF COBALT(II) IN 2-OCTANOL AND ETHANOL

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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
May, 1953

JUL 6 1953

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ACKNOWLEDGMENTS

To Dr. Tom E. Moore and Dr. Paul C. Yates I extend my sincere thanks for the help so generously given during the study of this problem. My thanks also goes to the Atomic Energy Commission under whose sponsorship this investigation was made.

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INTRODUCTION

Garwin and Hixson¹ have studied the relative distribution of cobalt and nickel chlorides between aqueous solutions and various organic solvents. This study indicated that in most organic solvents, including 2-octanol, cobalt chloride had a greater solubility than nickel chloride. Although the solubilities were sufficiently different, the quantity of salt extracted was insufficient for practical purposes. The extraction, however, could be satisfactorily promoted by the addition of considerable amounts of certain strong electrolytes such as HCl and CaCl₂.

Following the initial study by Garwin and Hixson, considerable work has been done at Oklahoma A. and M. College in an effort to determine factors which affect the distributions of cobalt and nickel chlorides between water and 2-octanol.

A difference in the extent of association in the organic phase appears to offer a reasonable explanation of the difference in the extractabilities of nickel and cobalt. This difference may be explained on the basis that cobalt forms both the undissociated molecule and higher complex ions more easily in 2-octanol than does nickel.

However, in practice, the system is complicated by the fact that extraction conditions usually involve excesses both of promoting salts and water, since considerable amounts of

each are extracted along with the cobalt. The presence of such salt excesses and water in the organic phase have been found to greatly affect the type of complex formed and its stability. Trevor² found this to be the case in a study of the chloro-complexes of nickel in 2-octanol.

A preliminary study of the chloro-complexes of cobalt in 2-octanol has been made by Estill³. His work, however, was confined to anhydrous systems and to those which contained only a small and constant amount of water. Furthermore, the effect of large excesses of other metal chlorides such as are frequently encountered in extraction was not studied. On this basis it was considered desirable to extend the study of Estill to systems more closely approximating those involved in extraction with the purpose of determining the composition and relative stabilities of the aquo- and chloro-complexes which exist under varying conditions of salt and water concentrations.

LITERATURE SURVEY

The literature records a considerable number of studies on the color change of from red to blue associated with solutions of cobaltous chloride in various solvents. Since there is little agreement among the authors as to the probable cause, merely a review of their conclusions would appear confusing unless accompanied by some indication of the nature of the experiments. It was considered best, therefore, to list the studies in tabular form. They are listed in Table I together with the salts and solvents studied, methods applied, and important conclusions. The work most closely associated with the present investigation will be discussed in more detail.

The conclusions of these workers may in general be divided into two groups. One group explains the color changes on the basis of dehydration effects or a change in the coordination number for cobalt, and the other interprets the changes on the basis of complex formation between the cobalt and chloride ions.

Among the adherents of the complex ion theory, there is considerable disagreement as to the composition of the complex or complexes responsible for the blue color. Barbinok⁴, from investigations in acetone, claims to have found a tetrachloro-complex on the basis of spectrophotometric studies, while Wormser⁵, from studies in the same solvent, believes,

on the basis of his conductivity work, that the complex is trichloro. However, Katzin and Gebert⁶ have pointed out errors in the studies of Barbinok and have concurred with Wormser that the principal complex is the trichloro complex. There seems to be little doubt that such a complex exists in organic solvents and probably in water as well.

Bobtelsky and Spiegler⁷ from spectrophotometric data in ethanol have found evidence for the tetrachloro-complex in the presence of large excesses of chloride ions and for the CoCl_2 entity formed at lower chloride concentrations. It would therefore appear that chloro-complexes having Cl/Co ratios of from 1:1 to 4:1 exist under suitable conditions in solutions in alcohols and in acetone.

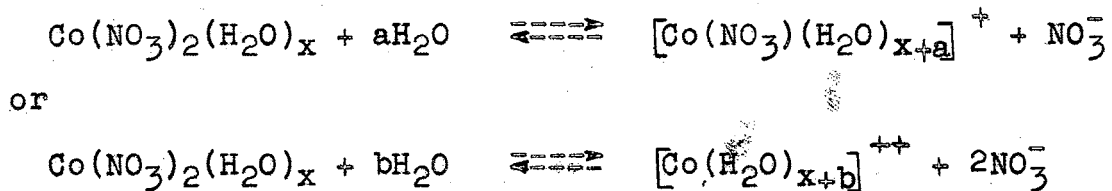
Although the majority of investigations have pointed to chloro-complex formation as an important cause of the color changes noted in solutions containing cobalt and chloride ions, evidence showing the occurrence of a change of hydration or coordination number of the cobalt cannot be ignored. Bobtelsky and Spiegler⁷, for example, point out from their measurements of the extinction coefficient in alcohol-water mixtures that whereas in water a high concentration of chloride is necessary to replace the water in the coordination sphere of the hydrated cobalt ion, the introduction of chloride is facilitated in the alcohol-water mixtures. This, they claim, is due to the smaller concentration of water and the association between alcohol and water molecules. In absolute alcohol the chloride enters the coordination sphere readily,

and therefore the reaction between chloride and cobalt ions is nearly quantitative. Thus they have proposed that the deep color is characteristic of the covalent bond formed between cobalt and chloride causing deformation of the electronic orbits. In the absence of water and at high chloride concentrations, these bonds could form easily and the distance between the cobalt and chloride ions would be relatively small. This would correspond to a coordination number of four. However, in the presence of water and lower chloride concentrations, the distance between cobalt and chloride ions would be increased due to the shielding action of the molecular dipoles of the water. This would allow an increased coordination number for cobalt, probably six, as has been suggested by several workers. Katzin and Gebert⁸, in studies on CoCl_2 solutions by the spectrophotometric methods, noted the appearance of a peak at 530 millimicrons in methanol, believed due to a CoCl_2 entity, and a stronger peak at 570 millimicrons in acetone which also seemed to be due to a CoCl_2 entity. They thus postulated that the difference in the two absorptions was the result of a difference in the coordination number of the cobalt in the two cases. In methanol the coordination number would be six, and in acetone, four.

Katzin and Gebert⁸ also noted that the addition of small amounts water to the solutions in acetone, tertiary butyl alcohol, and dioxane reduced all parts of the absorption curve above about 550 millimicrons, and at concentrations of water about 15% or higher, the absorption approaches that of the

hydrated cobalt ion.

Through their studies on $\text{Co}(\text{NO}_3)_2$ in various solvents, Katzin and Gebert⁹ have extended the idea of a competitive reaction between the nitrate ions, water molecules, and molecules of solvent for positions in the coordination sphere of cobalt. The presence of water tends to raise the dielectric constant and to provide the solution with a strong electron donor which is able to replace the nitrate ion in the following manner:



Reference has already been made to studies on solutions of cobaltous chloride in octanol in the presence of lithium chloride by Estill³ in which he indicated the important complex to be the CoCl_3^- entity. Estill employed the method of continuous variations as developed by Job¹⁰ and modified by Vosburgh and Cooper¹¹ and Katzin and Gebert⁶. While his results were interpreted as indicating the existence of a CoCl_3^- complex, some evidence was also found for the entity CoCl_2 . However, certain difficulties in interpretation of results are inherent in the application of the continuous variation method to regions involving the existence of more than one complex. In addition, disproportionation of the CoCl_2 is a possibility and this would interfere with a clear interpretation. These difficulties prohibited Estill from positively

identifying both complexes by the variations method. Later experiments in which small excesses of lithium chloride were added to cobalt chloride failed to demonstrate the formation of any higher complex beyond CoCl_2^{12} .

A preliminary study has been made in these laboratories on the effect of water in such systems. Gootman¹³, using the method of continuous variations, found that the addition of small amounts of water to solutions of CoCl_2 in 2-octanol produced no change in the extinction coefficient. In another series of studies by the same method, he added small amounts of water to an octanol solution containing CoCl_2 and LiCl in the ratio of $\text{CoCl}_2/\text{LiCl} = 1/5$. In this case a minimum in excess optical density was found as the water concentration varied, indicating some reaction between water and cobalt leading to a stoichiometric ratio of $\text{Co}/\text{H}_2\text{O} = 1/1$. Since the addition of water in these studies was made by adding it directly to the octanol solution, there may be some question as to how well the water dissolves in the octanol under such conditions. Gootman also made a variation study to test the formation of complexes higher than CoCl_2 , (e.g. CoCl_4^{--}), in octanol-water mixtures. His results indicated no complexes of ratio Cl/Co greater than 2/1.

In connection with a study made in these laboratories¹⁴ of the promoting effect of CaCl_2 , LiCl , and HCl on the extraction of CoCl_2 from an aqueous into a 2-octanol phase, the extinction coefficient of CoCl_2 in the octanol phase was determined under widely varying conditions of excess chloride

ion concentration and water content. Fig. 1 shows the apparent extinction coefficient at 690 millimicrons as a function of excess chloride for the promoted extractions with CaCl_2 , LiCl , and HCl . The dotted line is the extinction coefficient of CoCl_2 taken from the continuous variations studies by Estill³. This figure suggests that more than one complex exists under extraction conditions since values of the extinction coefficient fall below and above that for the CoCl_2 entity in anhydrous octanol. This leads one to believe that Estill's experimental conditions did not correspond closely to those occurring in the systems under extraction as previously noted. That the complex formation may not be due entirely to a variation in chloride ion concentration is shown by the different curves obtained for the LiCl - and HCl -promoted extractions in Fig. 1.

It would seem from this survey that the complexity of relationships encountered in these systems makes a comparison of results difficult and leads to apparent disagreement even though results from many of the individual systems, as applied to the particular concentration region and solvent studied, are probably valid.

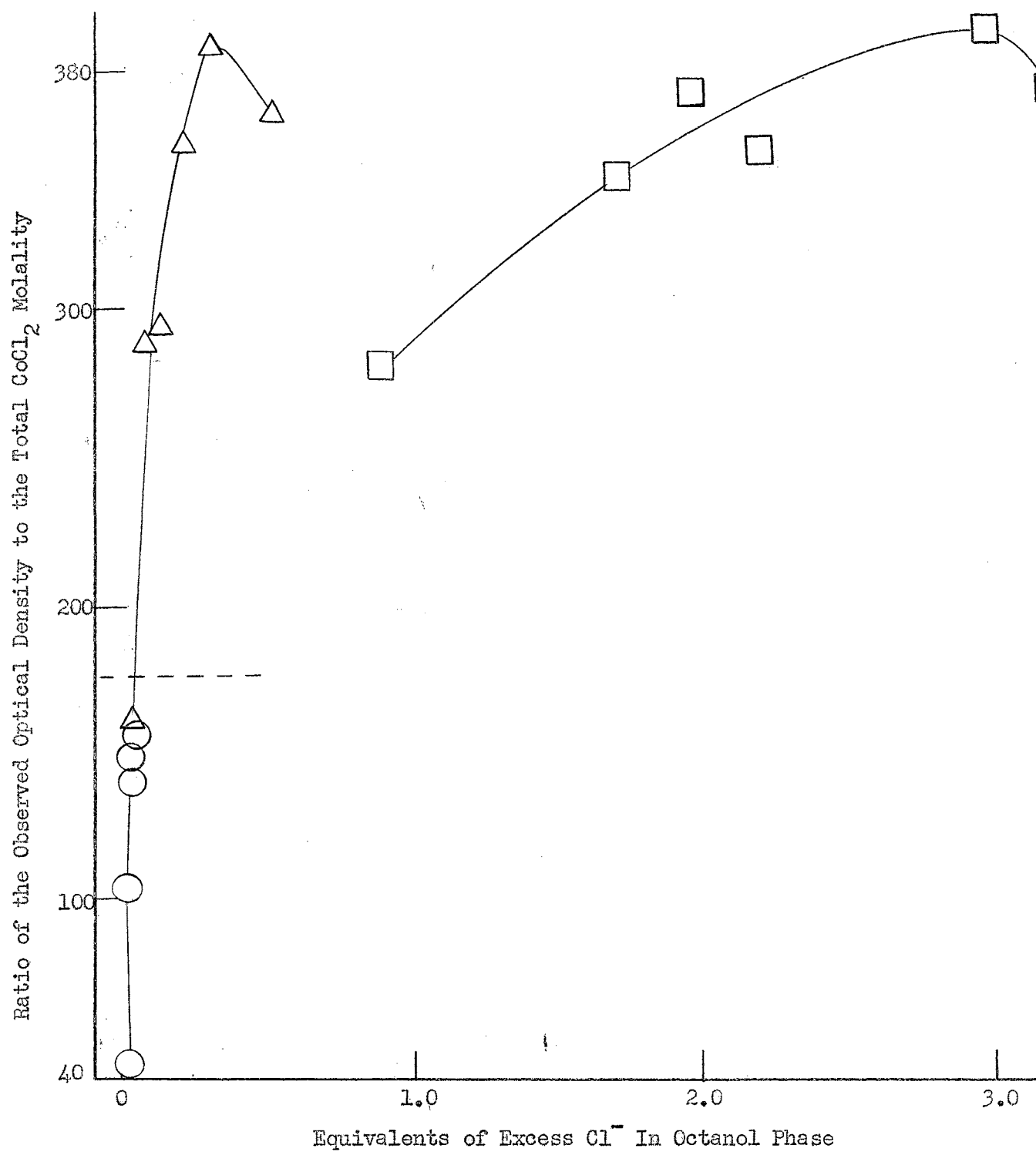


Fig. 1: Apparent Extinction Coefficients for the System CoCl_2 -salt- H_2O -octanol-2. \square -- HCl ; \triangle -- LiCl ; \circ -- CaCl_2 .

TABLE I

Investigations on the Color Change of Cobalt(II) Salts in Solution

Ref.	Author	Solute	Solvent	Method*	Conclusions
15	Bassett, Donnan	CoCl ₂	H ₂ O	(a)	Blue color migrated to anode indicating some anionic complex.
16	Cooper	Co(II)& Cu(II) salts	H ₂ O	(b)	Absorption depends on the solvent and probable solvates.
17	Jones	Co(II) salts	H ₂ O	(b)	Phenomena due to change in hydration.
18	Brown	CoCl ₂	H ₂ O EtOH	(b)	Proposes three distinct phases of CoCl ₂ : anhydrous, hexahydrate and polyhydrate?
19	Houston	CoCl ₂ CoBr ₂	Various	(b)	Color change depends on change in hydration.
20	Kochubei	CoCl ₂	EtOH	(c)	Groups responsible for blue color are such as CoCl ₂ (EtOH) ₂ and CoCl ₄ ²⁻ .
21	Groh	CoCl ₂ LiCl	H ₂ O MeOH EtOH PrOH	(b)	CoCl ₄ ²⁻ is responsible for the blue color.
22	Hill, Howell	Co(II) salts	H ₂ O	(b)	The red color corresponds to a coordination number of 6, blue to a coordination number of 4.

TABLE I (Continued)

Ref.	Author	Solute	Solvent	Method*	Conclusions
23	Mazzetti	CoCl ₂ +	H ₂ O, MeOH	(d), (e)	Both hydration and complex formation responsible for the change. Red form due to hydrated CoCl ₄ ⁻ .
24	"	added	EtOH, PrOH	(b), (f)	
25	"	salts	BuOH		
26	Hantzsch	Co(II) halides	Various	(b)	Color change due to change in coordination number of cobalt.
27	Groh, Schmid	CoCl ₂ LiCl	Acetone	(b), (d) (g), (a)	CoCl ₄ ⁻ responsible for the blue color.
28	Brdicka	CoCl ₂	H ₂ O	(b)	CoCl ₄ ⁻ and possibly others of the type CoCl _n ⁿ⁻² are present.
29	Torpescu	CoCl ₂	MeOH, EtOH PrOH, BuOH AmOH	(b)	Color change accounted for by relation between dielectric constant and degree of polymerization.
30	Dirking	CoCl ₂ CoBr ₂	MeOH EtOH	(b), (c) (h)	Formation of complex ions of the type CoCl ₄ ⁻ evident.
31	Howell, Jackson	CoCl ₂	H ₂ O	(b)	Proposed the mechanism: Co(H ₂ O) ₆ ⁺⁺ → Co(H ₂ O) ₄ Cl ₂ → Co(H ₂ O)Cl ₃
32	Kiss, Arpad, Gerendas	CoCl ₂	H ₂ O	(b)	Indicated the presence of complexes but could not identify them.
33	Kiss, Csokan Richter	CoCl ₂	MeOH, EtOH PrOH Pyridine Quinoline	(b)	Color change due to change in the coordination number which for the red form is 6 and for the blue form is 4. (e.g. CoCl ₄ ⁻ , Co(MeOH) ₂ Cl ₂ , Co(MeOH) ₄ Cl ₂).

TABLE I (Continued)

Ref.	Author	Solute	Solvent	Method*	Conclusions
34	Richter	CoCl ₂ LiCl	MeOH, EtOH PrOH	(b)	Red absorber is Co(H ₂ O) ₆ ⁺⁺ , blue is CoCl ₄ ⁻⁻ . In the absence of H ₂ O and excess Cl ⁻ , blue is of the type: CoCl ₂ (X) ₂ or 4. X=Solvent.
4	Barbinok	CoCl ₂	Acetone	(b)	Absorption due to CoCl ₄ ⁻⁻ with other complexes (CoCl ₃ ⁻ and CoCl ₄ ⁺) indicated present.
35	"	CoBr ₂	MeOH	(b)	
36	"	Co(ClO ₄) ₂	EtOH	(b)	
37	"	LiCl	PrOH	(b)	
38	Robinson, Brown	CoCl ₂ Co(NO ₃) ₂	H ₂ O	(b)	Mechanism for color change is: Co(H ₂ O) ₆ ⁺⁺ + 2Cl ⁻ → CoCl ₂ (H ₂ O) ₄ + 2H ₂ O
7	Bobstelsky	Co(NO ₃) ₂ + salts	EtOH	(b) (d)	Indicated the presence of undissociated CoCl ₂ and CoCl ₄ .
39	Varadi	CoCl ₂ HCl	H ₂ O	(b)	Color change due to coordination number change from 6(red) to 4(blue). (i.e. Co(H ₂ O) ₆ ⁺⁺ → CoCl ₄ ⁻⁻ .)
6, 8, 9	Katzin, Gebert	CoCl ₂ Co(NO ₃) ₂ + salts	Acetone t-BuOH MeOH Dioxane	(b)	Evidence for undissociated CoCl ₂ , CoCl ⁺ , CoCl ₃ ⁻ , and possibly CoCl ₄ ⁻⁻ . Strong effects due to water addition.
40	Lehne	Co(SCN) ₂	H ₂ O	(b)	Complexes of the type Co(SCN) _n ²⁻ⁿ form stepwise with n=1, 2, 3, or 4, accompanied by change in coordination number.
5	Wormser	CoCl ₂ LiCl	Acetone PrOH	(d)	Blue color due to the CoCl ₃ ⁻ complex.

TABLE I (Continued)

Ref.	Author	Solute	Solvent	Method*	Conclusions
41	Katzin	Co(II), Ni(II) halides	t-BuOH	(b)	Indicated the presence of mono-, di-, and tri-halide complexes.

*Methods:

- (a) Electrolysis
- (b) Spectrophotometric analysis
- (c) Transport number determinations
- (d) Conductance measurements
- (e) Viscosity measurements
- (f) Diffusion studies
- (g) Solubility determinations
- (h) Molecular weight determinations

EXPERIMENTAL

A. Reagents

Anhydrous nickel chloride and cobalt chloride were prepared from the corresponding recrystallized C.P.-grade hydrated salts by first pulverizing and then drying them in air at 120°.

Anhydrous silver perchlorate, for use in preparing cobalt and nickel perchlorates, was also obtained by pulverizing the C.P.-grade salt and drying in air at 120°.

A saturated solution of lithium chloride in dry 2-octanol prepared by Trevor² from anhydrous C.P.-grade lithium chloride was diluted as needed with additional dry octanol.

Anhydrous methanol and ethanol were prepared from the best commercial grade reagent by refluxing with a small amount of magnesium turnings and iodine, followed by distillation according to the method of Lund, Hakon, and Bjerrum⁴².

The 2-octanol used was the best grade of anhydrous reagent from the Matheson company. A water analysis showed the water content to be approximately 0.002%.

Conductance water was prepared by redistilling water from a slightly basic potassium permanganate solution as described by Kendall⁴³.

B. Preparation of Stock Solutions

Solutions of NiCl_2 and CoCl_2 in methanol, ethanol and 2-octanol were prepared by adding anhydrous salt to the anhydrous

solvent and shaking the mixture for several hours to facilitate solution. The excess salt was then filtered off in an atmosphere of dried air. The solutions were stored in glass-stoppered flasks.

Anhydrous solutions of $\text{Ni}(\text{ClO}_4)_2$ and $\text{Co}(\text{ClO}_4)_2$ in methanol, ethanol, and octanol were prepared by the metathesis of anhydrous AgClO_4 solutions with stoichiometric quantities of NiCl_2 or CoCl_2 solutions in the corresponding solvents. The solutions were shaken to allow complete reaction and the precipitated AgCl filtered off. Trevor² found by determining the quantity of AgCl precipitated in such a preparation that the reaction may be considered as quantitative.

A stock solution of water in octanol was prepared by shaking an excess of water with octanol for several hours. The two phases were separated by means of a separatory funnel and the water in the octanol phase determined as described below.

All equipment used in the preparation of these solutions was oven-dried, and other necessary precautions were taken to insure the exclusion of water from the system.

C. Analytical Procedures

The determination of water in 2-octanol and in the octanol solutions was made using the Karl Fischer method⁴⁴.

The concentrations of the prepared stock solutions and methods of analysis are listed in Table II.

D. Apparatus

For the conductance measurements, a bridge, oscillator, and amplifier similar to those described by Luder⁴⁵ were used. A sensitivity of 1-2 parts in 100,000 and a maximum resistance measurement of 200,000 ohms are possible with this bridge. The cell was of Washburn design. A value of 0.6843 ± 0.0001 was determined for the cell constant by measuring the resistance of a KCl solution of known concentration at 0, 18, and 25°. The specific conductance values used were determined by Jones and Bradshaw⁴⁶. The cell was thermostatted by being placed in a kerosene-filled metal container which had been placed in a larger constant-temperature water bath. Both baths were stirred constantly. By such a procedure, the temperature could be controlled easily within better than $\pm 0.01^\circ$.

Spectrophotometric studies were carried out using a Beckman model DU quartz spectrophotometer using both Corex and silica cells, all of 1 cm. light path. The cells were maintained at 30° during the measurements.

E. Procedure

All solutions used in conductance measurements were prepared by weight from the appropriate alcohol stock solutions and conductance water keeping the salt concentration constant. The conductance cell was rinsed with the anhydrous solution of each series until a constant resistance reading was obtained. Then the remaining solutions were measured in order of increasing water concentration without additional rinsing.

The amount of error that would be involved in such a procedure was estimated and found to be insignificant. Sufficient time was allowed for each solution to reach a constant temperature of 25°.

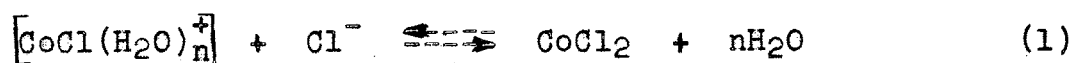
The solutions that were studied spectrophotometrically were prepared by weighing out the desired amounts of both the stock salt solutions and the octanol solution of water into a 10-ml. volumetric flask and adding anhydrous octanol to volume. After thorough mixing, these solutions were transferred to the Corex or silica cells for measurement in the spectrophotometer. The cells were paraffined around the top to exclude the possible entrance of water during measurement.

TABLE II
Stock Solutions

Solute	Solvent	Concentration (moles/1000 g. soln.)	Method of Analysis
CoCl_2	MeOH	0.4321	Electrolytic ⁴⁷
CoCl_2	EtOH	0.2462	Electrolytic ⁴⁷
CoCl_2	2-octanol	0.4551	Electrolytic ⁴⁷
NiCl_2	MeOH	0.4012	Electrolytic ⁴⁸
NiCl_2	EtOH	0.02270	Amperometric ⁴⁹
NiCl_2	2-octanol	0.00405	Amperometric ⁴⁹
AgClO_4	MeOH	0.4151	Gravimetric ⁵⁰
AgClO_4	EtOH	0.6140	Gravimetric ⁵⁰
AgClO_4	2-octanol	0.8140	Gravimetric ⁵⁰
$\text{Co}(\text{ClO}_4)_2$	MeOH	0.1460	Calculated
$\text{Co}(\text{ClO}_4)_2$	EtOH	0.1422	Calculated
$\text{Co}(\text{ClO}_4)_2$	2-octanol	0.2420	Calculated
$\text{Ni}(\text{ClO}_4)_2$	MeOH	0.1424	Calculated
$\text{Ni}(\text{ClO}_4)_2$	EtOH	0.0213	Calculated
$\text{Ni}(\text{ClO}_4)_2$	2-octanol	0.0040	Calculated

TREATMENT OF DATA

A method for determining the extent of salt hydration in a CoCl_2 -2-octanol system containing a varying amount of water may be developed as follows. In such a system, if the reaction of water may be assumed to be represented by the equilibrium:



and if the concentration of CoCl_2 at equilibrium is C_2 and the concentration of $[\text{CoCl}(\text{H}_2\text{O})_n^-]$ is C_1 , an approximate mass action expression may be written as:

$$K_2 = \frac{C_2 [\text{H}_2\text{O}]^n}{C_1 [\text{Cl}^-]} \quad (2)$$

where K_2 is a measure of the instability of $[\text{CoCl}(\text{H}_2\text{O})_n^-]$. Concentrations are used rather than activities since the activities are generally not known. Rearranging Eq. (2) gives:

$$\frac{C_2}{C_1} \times [\text{H}_2\text{O}]^n = K_2 \times [\text{Cl}^-] \quad (3)$$

and taking the logarithm of both sides results in:

$$\log C_2 - \log C_1 - \log [\text{Cl}^-] = -n \log [\text{H}_2\text{O}] + \log K_2 \quad (4)$$

Values for C_1 and C_2 may be calculated through a series of approximations. This requires either a knowledge of the extinction coefficients of CoCl_2 and $[\text{CoCl}(\text{H}_2\text{O})_n^-]$ at some wave length in a region of absorption or an experimental value of

the one of higher optical density and the assumption of a reasonable value for the other. The first step, therefore, assuming that the complex CoCl_2 is the one having the higher optical density at the wave length selected, is to ascribe all of the observed optical density to this complex and calculate a value of C_2 and C_1 based upon this assumption as a first approximation. The optical density of the solution may be expressed as:

$$\text{O.D.}_{\text{observed}} = l \epsilon C \quad (5)$$

where l is the distance light must travel through the absorbing medium, C is the molar concentration of the absorber, and ϵ is the extinction coefficient of the absorber. When l is 1 cm., the expression reduces to:

$$\text{O.D.}_{\text{obs.}} = \epsilon C \quad (6)$$

Thus,

$$C_2 = \frac{\text{O.D.}_{\text{obs.}}}{\epsilon_2} \quad (7)$$

and

$$C_1 = [\text{Co}]_t - C_2 \quad (8)$$

where $[\text{Co}]_t$ equals the total cobalt concentration. The optical density due to C_1 is then obtained from the product of $C_1 \epsilon_1$ where ϵ_1 has been independently evaluated. From this consideration, the optical density of CoCl_2 becomes:

$$\text{O.D.}_{\text{CoCl}_2} = \text{O.D.}_{\text{obs.}} - C_1 \epsilon_1 \quad (9)$$

An improved value for C_2 is then obtained:

$$C_2' = \frac{\text{O.D.}_{\text{obs.}} - C_1 \epsilon_1}{\epsilon_2} \quad (10)$$

and from it, an improved value for C_1 :

$$C_1^0 = [Co]_t - C_2^0 \quad (11)$$

This series of approximations is continued until further change in C_1 and C_2 is insignificant. The free chloride ion concentration may then be determined by subtracting $2C_2$ and C_1 from the total chloride concentration. The total water concentration may be substituted for free water concentration as an approximation since only a very small part of the total water will be tied up as water of hydration. If Eq. (1) correctly represents the reaction involved, a plot of the left-hand side of Eq. (4) against $\log H_2O$ should yield a straight line with slope \underline{n} and intercept $\log K_2$.

In regions of high water concentration, it seems likely that an additional equilibrium between aquo-complexes would be of importance. This might be represented as:



A value for \underline{m} may be determined in a manner similar to that for \underline{n} in Eq. (1). Thus the extent to which the nonchloro-complexed cobalt ion is hydrated may be found by adding the values of \underline{m} and \underline{n} .

A test of the correctness of C_1 and C_2 , if desirable, may be made by examining absorption at a new wave length. Using the predetermined values of C_1 and C_2 from calculations made at the original wave length and a known value of ϵ_2 at the new wave length, the value of ϵ_1 may be determined, and

then should remain reasonable constant over the range of co-existence of the two complexes.

This type of procedure may be applied to anhydrous systems as well, where two complexes may coexist within a particular concentration range (e.g. CoCl_2 and CoCl_3^-). It can be seen, therefore, that composition of the complexes, their concentrations, and instabilities may be determined by this method in favorable cases.

RESULTS AND DISCUSSION

A. Conductance Studies

It was decided to make some preliminary investigations of the effect of water on the conductivity of solutions of CoCl_2 , $\text{Co}(\text{ClO}_4)_2$, NiCl_2 , and $\text{Ni}(\text{ClO}_4)_2$ in methanol and ethanol as well as in 2-octanol. It was hoped that a significant change in the conductance of the solutions would occur at definite water-to-salt ratios.

The first studies were made on 8 solutions containing 0.1 mole CoCl_2 per 1000 grams of a mixture of methanol plus the very small amount of water required in the variations. The ratio of moles of water to moles of CoCl_2 was varied from 0 to 13:1. An increase in conductance was noted, especially between ratios of $\text{H}_2\text{O}/\text{Co}$ of 2:1 and 5:1, but the resistances of the solutions were too small to give desirable differences in bridge resistance readings. A second and third series of solutions were prepared in the same manner as the first, except for a change in the concentration of CoCl_2 to 0.01 mole CoCl_2 per 1000 grams of aqueous methanol. The mole fraction of water in such solutions never exceeded a value of 9×10^{-3} . In a plot of conductance vs. the ratio $\text{H}_2\text{O}/\text{Co}$, the points were scattered too widely to give a clear picture of any occurring reaction, except to show the tendency toward an increase in conductance between ratios of $\text{H}_2\text{O}/\text{Co}$ from 0 to 6:1. An examination of the solutions a few hours after preparation

showed the appearance of a solid phase indicative of solvolysis which might account for the erratic results.

The studies were then shifted to $\text{CoCl}_2\text{-C}_2\text{H}_5\text{OH}$ systems. Twenty solutions containing 0.01 moles CoCl_2 per 1000 grams of ethanol plus water were prepared in an analogous manner to those in methanol, the water-to-cobalt ratio being varied from 0 to 18:1. The results of measurements on two such series again show some scattering of points in a plot of conductance vs. the ratio $\text{H}_2\text{O/Co}$ but the consistency of the results is much better than in the case of methanol. A plot showing the results on these two series taken from Table III is given in Fig. 2. A rapid increase in conductance between ratios of $\text{H}_2\text{O/Co}$ of 0 and 2:1, followed by a leveling-off between 2:1 and 10:1 and a renewed increase in conductance above 10:1, suggests the existence of two aquo-complexes.

The third phase of the study was to have been an extension of the same type of measurements to the 2-octanol system. However, it was found that the resistance of octanol solutions was entirely too high to make accurate measurements with the available conductivity apparatus. These resistances were estimated as being of the order of 10^7 ohms.

Some qualitative measure of the effect of water on the conductance of various salts in 2-octanol was obtained by conductance measurements using a known fixed resistance in parallel with the cell. These results are presented in Table IV. It is apparent that in every case, the conductance of the solution of the salt was increased by the addition of

water. It may also be noted that $\text{Ni}(\text{ClO}_4)_2$ and $\text{Co}(\text{ClO}_4)_2$ form better conducting solutions than the corresponding chlorides and that the effect of water was greater in the case of CoCl_2 than with NiCl_2 .

Since the principal objective of the investigation was to study the 2-octanol phase, it was considered inadvisable to continue studies in methanol and ethanol.

B. Spectrophotometric Studies

These studies will be discussed first from a qualitative viewpoint. A description of a partial quantitative analysis of the data which has been carried through in certain concentration ranges will then be presented.

1. Qualitative Observations

Seventeen solutions were prepared in the system $\text{Co}(\text{ClO}_4)_2$ - LiCl -2-octanol with the cobalt concentration constant and equal to 8×10^{-4} molar and LiCl concentration varying from 0 to 1000 times the cobalt concentration. The optical densities of these solutions were determined at 5- and 10-millimicron intervals over the wave length range from 420 to 700 millimicrons and are listed in Table V. The spectral curves of a number of these solutions are plotted in Fig. 3.

Several important observations may be made from a study of these curves. At a wave length of 575 millimicrons, the absorption increases with an increase in chloride ion concentration reaching a maximum at a chloride-to-cobalt ratio of 2:1 as shown in Fig. 4. This indicates the increasing

concentration of an absorbing entity, and the fact that the maximum absorption occurs at the chloride-to-cobalt ratio of 2:1 indicates that its composition might be CoCl_2 . This conclusion is supported by the evidence obtained by Estill³ using the method of continuous variation.

The decrease in absorption at 575 millimicrons beyond a chloride-to-cobalt ratio of 2:1 may be explained by a decrease in concentration of the CoCl_2 . The fact, however, that the absorption never reaches zero as the chloride concentration continues to increase indicates either that a complex or complexes are formed having a small value for their extinction coefficients at this wave length, or that the conversion from CoCl_2 to higher complexes is not complete even at a 1000:1 ratio. At 660 millimicrons a continued increase in absorption beyond a ratio of 2:1 was found. The decrease in absorption at 575 millimicrons beyond a ratio of 2:1 coupled with the continued increase in absorption at 660 millimicrons beyond this same ratio again points to the formation of a higher complex. Since Estill's³ continuous variation studies indicated a maximum interaction between cobalt and chloride ions at a 2:1 ratio in the presence of small excesses of LiCl in the wavelength region around 660 millimicrons, it would appear that a continued increase in absorption would be unlikely without higher complex formation.

The appearance of a second higher complex is indicated by the split of the main absorption peak into two peaks at 665 and 690 millimicrons accompanied by a continued increase

in absorption at high LiCl concentrations. Additional evidence for a second higher complex is found in the appearance of a new peak at approximately 630 and a trough at approximately 635 millimicrons. The fact that the concentration of the second higher complex is increasing while the concentration of the first higher complex is decreasing with increasing chloride ion concentration is indicated by an initial increase in absorption in the region 635 to 645 millimicrons followed by a decrease in absorption at higher chloride ion concentrations.

Observations of this type strongly suggest the possibility of at least two complexes of chloride-to-cobalt ratios greater than 2:1. If these complexes are formed stepwise, as proposed by some workers^{40,51}, their compositions would then be CoCl_3^- and CoCl_4^{--} .

It seemed of interest to investigate the effect of water on the formation of the complexes tentatively identified in the anhydrous system. Accordingly an investigation was made of the system consisting of $\text{Co}(\text{ClO}_4)_2$ -LiCl- H_2O -2-octanol. The first series of 15 solutions were prepared with the following concentrations: $\text{Co}(\text{ClO}_4)_2$, 1.6×10^{-3} molar; H_2O , 0.5 molar; and LiCl varying from 0 to 250 times the cobalt concentration. Four anhydrous solutions of the same cobalt concentration, but having concentrations of LiCl equal to 1.0, 2.0, 100.0 and 250.0 times the concentration of the cobalt, were prepared for comparison with corresponding solutions containing water. The optical densities of these solutions

were determined and are listed in Table VI. The spectral curves of several of these solutions containing water are plotted in Fig. 5.

A comparison of the spectra of two pairs of corresponding hydrous and anhydrous solutions is shown in Fig. 6. It may be noted that the effect of water is great for solutions #5 and 5-A but appears to be very small for solutions #14 and 14-A. This difference might be explained by the fact that the lithium ions tie up a number of water molecules and thus lower the concentration of free water in the system. Earlier work in these laboratories has indicated that one lithium ion combines with two water molecules at somewhat similar ratios of LiCl-to-H₂O in 2-octanol.

The general appearance of the spectral curves is not changed on addition of water to the system, but the absorption is decreased in every instance where free water is present. This probably means that water competes with chloride ions for coordinating positions about the cobalt ions and thus favors the formation of aquated lower chloro-complexes.

The study of the effect of water on the formation of complexes was extended to the system CoCl₂-H₂O-2-octanol. Fourteen solutions were prepared in the first series with a constant cobalt concentration of 1.6×10^{-3} molar. The water concentration was varied from a water-to-cobalt ratio of 0 to 600:1. The optical densities of these solutions were determined at 5- and 10-millimicron intervals between 420 and 700 millimicrons and are listed in Table VII. The optical

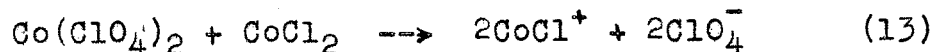
density vs. wave length for several of these solutions is plotted in Fig. 7.

It is seen from this figure that addition of water to CoCl_2 -2-octanol systems does produce a change in the spectral characteristics. The general shape of the curves seems to remain the same but the extinction coefficient decreases considerably and in the highest water concentrations becomes similar to that of cobalt perchlorate in hydrous 2-octanol. In solutions above a water-to-cobalt ratio of 400:1, the decrease in blue color of the solutions was quite noticeable.

The method of continuous variations developed by Job¹⁰, and extended by Vosburgh and Cooper¹¹, was used to confirm the presence of a chloro-complex with a chloride-to-cobalt ratio less than 2:1 in the system CoCl_2 - $\text{Co}(\text{ClO}_4)_2$ -2-octanol. Nine solutions with a constant total salt concentration of 1.6×10^{-3} molar were prepared. The variations covered a range of from 0 to 1.6×10^{-3} molar CoCl_2 . The optical densities of these solutions were measured at 5-millimicron intervals from 550 to 700 millimicrons and are listed in Table VIII. Fig. 8 is a plot of the excess optical density vs. relative concentrations of CoCl_2 and $\text{Co}(\text{ClO}_4)_2$ at wave lengths 585, 660, and 665 millimicrons.

A very pronounced change in the excess optical density, defined as the difference between the observed optical density and that calculated for the components on the assumption that no reaction had occurred, is found at all three wave lengths. Although the minimum at 585 and 665 millimicrons

is not sharply defined, at 660 millimicrons the minimum is clearly located at a position corresponding to a CoCl_2 -to- $\text{Co}(\text{ClO}_4)_2$ ratio of 1:1. This constitutes good evidence for the existence of a monochloro-complex formed by the reaction:



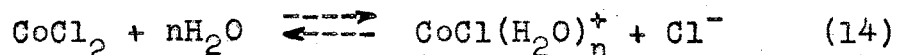
It must be assumed however, that the extinction coefficients for all entities having the same chloride-to-cobalt ratio are the same.

2. Analysis of Results

An attempt was made to calculate the concentration ratios in mass action-type expressions for the several equilibria in the three systems: CoCl_2 - H_2O -2-octanol, $\text{Co}(\text{ClO}_4)_2$ - LiCl - H_2O -2-octanol, and $\text{Co}(\text{ClO}_4)_2$ - LiCl -2-octanol. The results of these calculations will be discussed in that order.

a. System: CoCl_2 - H_2O -2-octanol

Since maximum interaction between cobaltous and chloride ions in systems containing only small excesses of chloride ion has been found to occur at a chloride-to-cobalt ratio of 2:1 and the addition of water decreases the absorption below the value corresponding to this ratio in the anhydrous system, it seems probably that a reaction occurs as follows:



Following the procedure outlined in TREATMENT OF DATA, a test of eq. (14) was made from data in Table VII at a wavelength of 660 millimicrons. The results of this test are found in Fig. 9. A value of 316.5 for the extinction

coefficient of CoCl_2 at this wave length was determined by dividing the optical density of the anhydrous solution by the total cobalt concentration. A value of 128 for the extinction coefficient of the monochloro-complex was determined from the solution corresponding to the minimum in the continuous variations study. In the evaluation and use of these extinction coefficients it was assumed that hydration of the respective chloro-complexes would not change the extinction coefficients and further that essentially all of the cobalt was in the form of each of these complexes at the stoichiometric chloride-to-cobalt ratio of the complex. The left-hand side of eq. (4) is represented along the ordinate. In this case the assumed chloride ion concentration will be equal to C_1 and the ordinate becomes $2\log C_1 - \log C_2$. The total water concentration represents the free water concentration without significant error and is plotted as the abscissa. The circled points are the experimental values. The best straight line through these points has a slope, or value of n , equal to 2 and an intercept of -2.50. From this K_2 is then determined to be 3.16×10^2 . Individual values of K_2 were computed from the data using eq. (2) and listed in Table IX.

A second series of 6 solutions in this system was prepared in a manner analogous to the first, having concentrations of water varying from a water-to-cobalt ratio of 450:1 to 650:1. A 750:1 ratio produced a cloudiness which corresponded to a separation of an aqueous phase. The optical densities were determined at 660 millimicrons and presented

in Table X.

The maximum interaction between CoCl_2 and $\text{Co}(\text{ClO}_4)_2$, as previously pointed out, occurs at a 1:1 ratio. Since in the region of highest water concentration the absorption is reduced below that of the monochloro-complex, dissociation of this complex may will occur. A reaction describing this further effect of water might be written as:



In order to determine whether or not the data given in Table X fits eq. (15), the following mass-action expression for this reaction was used:

$$K_1 = \frac{C_1 [\text{H}_2\text{O}]_f^m}{C_0 [\text{Cl}^-]_f} \quad (16)$$

where C_1 is the concentration of the monochloro-complex and C_0 is the concentration of the completely hydrated cobaltous ion. Rearranging eq. (16) gives:

$$K_1 C_0 [\text{Cl}^-]_f = C_1 [\text{H}_2\text{O}]_f^m \quad (17)$$

Taking the logarithm of both sides and rearranging gives:

$$\log C_0 - \log C_1 + \log [\text{Cl}^-]_f = m \log [\text{H}_2\text{O}]_f - \log K_1 \quad (18)$$

Values of C_0 and C_1 were obtained by successive approximations as described in an earlier section of the thesis using the values of 128 for the extinction coefficient of the monochloro-complex and 4.4 (determined from a solution of $\text{Co}(\text{ClO}_4)_2$ in 2-octanol) for the extinction coefficient of the hydrated cobaltous ion. The free chloride ion concentration, $[\text{Cl}^-]_f$, was taken as equal to the total chloride minus C_1 . To

determine the concentration of free water, an approximate value of \underline{m} was needed. A value of 10 for \underline{m} was found by solving simultaneous equations corresponding to eq. (18) for two solutions with increased water concentrations. The concentration of free-water was then calculated as equal to the total water less that assumed bound in the ionic complexes.

Thus:

$$[\text{H}_2\text{O}]_{\text{free}} = [\text{H}_2\text{O}]_{\text{total}} - 10 C_0 - 2 C_1 \quad (19)$$

Fig. 10 is a plot of the left-hand side of eq. (18) against $\log[\text{H}_2\text{O}]_f$. The best straight line has a slope of 11.1 and an intercept of -1.86 which corresponds to a value of 11 for \underline{m} and a value of 72 for K_1 . Individual values of K_1 were computed and are presented in Table XI.

b. System: $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$

A test of eq. (14) for this system was made at 660 millimicrons and at a constant concentration of 0.5 molar to see whether or not the equilibrium between the dichloro-complexes could be expressed by a mass-action type of expression shown to be valid in the system $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$. Free-water concentration was determined as total water minus $2 C_1$ and free chloride as total chloride minus $(2C_2 - C_1)$. Values of the extinction coefficients of CoCl_2 and the monochloro-complex were again assumed to be 316.5 and 128 respectively. Calculation of K_2 resulted in an average value of 57.2 over the LiCl concentration range of 4.0×10^{-3} to 6.4×10^{-3} molar. The individual K_2 values are found in Table IX.

In order to check the constancy of K_2 for this system at

other water concentrations, a second and third series of 4 solutions were prepared at 0.3 and 0.1 molar water concentrations respectively. They were prepared with LiCl concentrations in the range where K_2 had been found to be constant in the series containing 0.5 molar water. Optical densities were measured at several selected wave lengths and have been listed in Table XII. Average values found for K_2 are 3.76×10^2 at 0.3 molar and 4.10×10^2 at 0.1 molar water. The individual K_2 values for these series are also listed in Table IX. Points corresponding to solutions in these series have been plotted in Fig. 9 as triangular-shaped points.

It may be noted that the K_2 values at these two lower water concentrations compare favorably with K_2 values found for the $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$ system but disagree considerably with K_2 values at 0.5 molar water. This disagreement cannot be explained easily or completely satisfactorily. A 0.5 molar water concentration which corresponds to a water-to-chloride ratio of 312.5 in the $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$ system is intermediate between ranges of water concentrations found for the coexistence of CoCl_2 with $\text{CoCl}(\text{H}_2\text{O})_2^\dagger$ and ranges where only $\text{Co}(\text{H}_2\text{O})_{13}^{\dagger\dagger}$ and $\text{CoCl}(\text{H}_2\text{O})_2^\dagger$ exist. Thus the system at a water concentration of 0.5 molar likely contains all three complexes. Other possible influencing factors neglected in developing eq. (14) are changes in activity coefficients of the various species and changes in the dielectric constant of the solution.

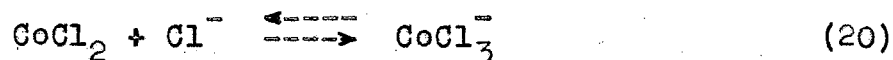
An effort was made to determine values of K_1 , the formation

constant of the monochloro-complex of eq. (15), by measuring the optical densities at 660 millimicrons of 5 solutions having a cobalt concentration of 1.6×10^{-3} molar, a water concentration of 0.5 molar, and LiCl concentrations varying from 4×10^{-4} to 20×10^{-4} molar.

Values of K_1 were calculated in a manner similar to that already described and are presented in Table XI. Free-water concentrations were taken to be equal to the total water minus the quantity $(11C_0 - 2C_1)$. A very decided trend towards increasing values of K_1 as the chloride ion concentration increases is noticeable. The value most nearly comparable to the K_1 value obtained for the $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$ system is still only 1.24 compared to 72. Differences in K_1 found for the two systems might again be the result of neglecting the activity coefficients.

c. System: $\text{Co}(\text{ClO}_4)_2\text{-LiCl-2-octanol}$

The reaction for the formation of a CoCl_3^- complex from CoCl_2 can be written as:



For this reaction the approximate mass action expression is:

$$K_3 = \frac{C_3}{C_2 [\text{Cl}^-]_f} \quad (21)$$

where

C_3 = concentration of CoCl_3^-

C_2 = concentration of CoCl_2

$[\text{Cl}^-]_f$ = total chloride - $(3C_3 + 2C_2)$

After rearranging and expressing in terms of logarithms, eq. (21) becomes:

$$\log \frac{C_3}{C_2} = \log [Cl^-]_f + \log K_3 \quad (22)$$

A wave length of 575 millimicrons was chosen as a suitable wave length at which to calculate C_2 and C_3 since $CoCl_3^-$ does not absorb greatly in this region and errors involved in an incorrect choice of an extinction coefficient for the trichloro-complex would not be so serious as in other regions. A value of 174 for the extinction coefficient of $CoCl_2$ at this wave length was calculated by assuming that all cobalt was in the form of $CoCl_2$ at a chloride-to-cobalt ratio of 2:1. A value of 40 was obtained for the extinction coefficient of the trichloro complex, by averaging the optical densities at the highest chloride concentrations and dividing by the total cobalt concentration. In so doing it was assumed that all of the cobalt existed in the form of $CoCl_3^-$ at these concentrations. The concentrations of the two complexes were then determined by successive approximations. Fig. 11 is a plot of $\log \frac{C_3}{C_2}$ vs. $\log [Cl^-]_f$. A straight line having a slope of 0.636 represents the data rather well.

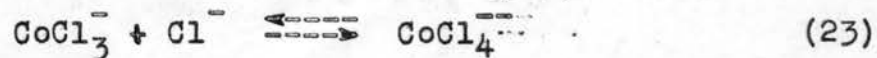
As a test of the validity of the assumptions involved in the calculation of C_2 and C_3 the values obtained were used to compute a value of the extinction coefficient of the trichloro-complex at 660 millimicrons. The values of this extinction coefficient are listed in Table XIII. These values remain reasonably constant over the chloride-to-cobalt concentration

ratio range of from 2.5:1 to 50:1. The continuous deviation beyond a ratio of 50:1 can probably be ascribed to the formation of the next higher complex, CoCl_4^{--} . This same test of the values of C_2 and C_3 was also applied at two other wave lengths, 630 and 675 millimicrons with comparable results, indicating that the values of C_2 and C_3 are close to being correct.

Values of K_3 were then determined using eq. (21) from the values of C_2 , C_3 , and the free chloride ion concentration. These results are listed in Table XIII. An average of the K_3 values is approximately 1.0×10^2 although there is a noticeable lack of constancy in K_3 .

The fact that the slope obtained in Fig. 11 is constant but is not unity as expected from eq. (22) is puzzling and is not easily explained except on the basis that concentrations rather than activities of the solution components have been used. This fact could also explain the variation in the values of K_3 in Table XIII.

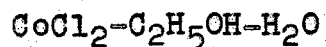
An attempt was made also to calculate a value of the reaction constant for the formation of CoCl_4^{--} :



However, it became evident that in any region where CoCl_4^{--} contributed to the optical density it was necessary to consider the existence of all three of the complexes CoCl_2 , CoCl_3^- , and CoCl_4^{--} . Efforts to calculate and then check the concentrations of these complexes were unsuccessful. However, perhaps they could be determined by further experimental investigation.

TABLE III

Conductance of Solutions of the System:

Concentration of $\text{CoCl}_2 = 0.01$ mole per 1000 g. of $(\text{C}_2\text{H}_5\text{OH}+\text{H}_2\text{O})$ Temperature = 25°

Series 1		Series 2	
Ratio $\text{H}_2\text{O}/\text{Co}$	Conductance (mhos $\times 10^5$)	Ratio $\text{H}_2\text{O}/\text{Co}$	Conductance (mhos $\times 10^5$)
0.0	9.2546	0.00	9.2220
0.5	9.5556	0.25	9.2618
1.0	9.6899	0.50	9.3291
2.0	10.2890	0.75	9.9072
3.0	10.3880	1.00	10.3939
4.0	10.2998	1.25	10.1553
5.0	10.4788	1.50	9.8794
6.0	10.4773	1.75	9.9571
7.0	10.7140	2.00	10.0584
8.0	10.5864	2.50	10.3651
9.0	10.5317	3.00	10.5503
10.0	10.6031	4.00	10.6633
11.0	10.7991	6.00	10.2783
12.0	10.9413	8.00	10.6328
13.0	11.1218	9.00	10.7731
14.0	11.2146	10.00	10.8068
15.0	11.6886	11.00	10.7383
16.0	11.6826	13.00	11.0011
17.0	11.7771	15.00	11.0953
18.0	11.8607	17.00	11.4156

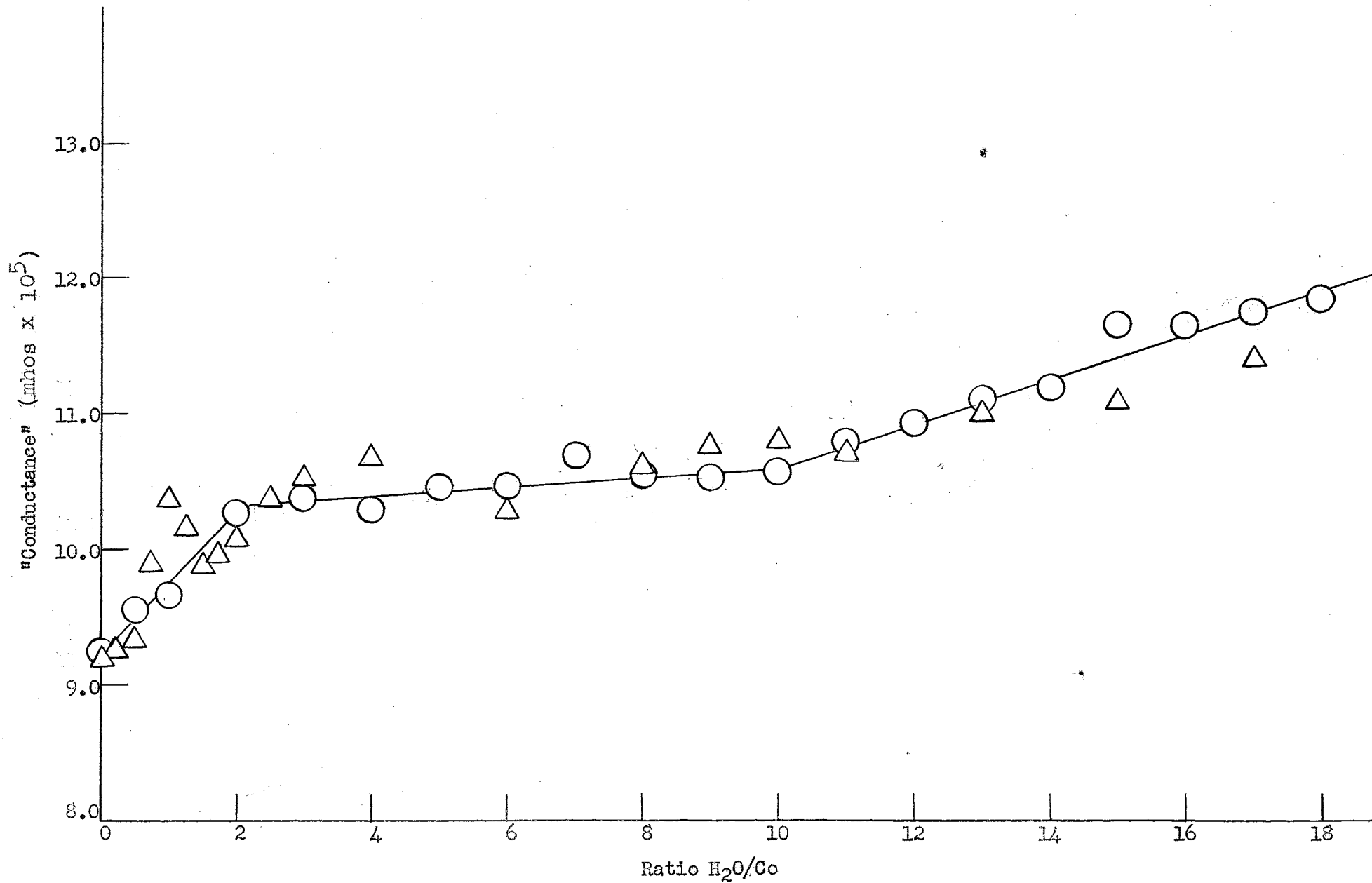


Fig. 2: Conductances of Two Series of Solutions for the System $CoCl_2-H_2O$ -ethanol.

TABLE IV

Conductance of Various Cobalt and Nickel
Solutions in Aqueous 2-octanol

Temperature = 25°

Salt	Salt Conc. (molal)	H ₂ O Conc. (molal)	Resistance (ohms)	Conductance (mhos)
CoCl ₂	0.01	0.00	4.17x10 ⁷	2.40x10 ⁻⁸
CoCl ₂	0.01	0.14	1.82x10 ⁷	5.50x10 ⁻⁸
Co(ClO ₄) ₂	0.01	0.00	1.94x10 ⁶	5.15x10 ⁻⁷
Co(ClO ₄) ₂	0.01	0.14	1.61x10 ⁶	6.21x10 ⁻⁷
NiCl ₂	0.00405	0.00	2.57x10 ⁷	3.89x10 ⁻⁸
NiCl ₂	0.00403	0.14	2.35x10 ⁷	4.25x10 ⁻⁸
Ni(ClO ₄) ₂	0.00401	0.00	1.81x10 ⁶	5.53x10 ⁻⁷
Ni(ClO ₄) ₂	0.00399	0.14	1.75x10 ⁶	5.72x10 ⁻⁷

TABLE V

Optical Densities for the System: $\text{Co}(\text{ClO}_4)_2$ -LiCl-2-octanol
 Temperature = 30° $\text{Co}(\text{ClO}_4)_2 = 8 \times 10^{-4}$ molar

Wave Length	Ratio Cl/Co						
	0.0	0.5	1.0	1.5	2.0	2.5	3.0
420	0.017	0.018	0.017	0.027	0.032	0.017	0.022
30	0.016	0.018	0.017	0.024	0.030	0.016	0.019
40	0.015	0.017	0.017	0.023	0.028	0.015	0.018
50	0.014	0.017	0.016	0.021	0.028	0.014	0.017
60	0.013	0.017	0.016	0.020	0.028	0.013	0.016
70	0.013	0.017	0.017	0.019	0.028	0.013	0.016
80	0.013	0.017	0.016	0.017	0.028	0.013	0.015
90	0.013	0.017	0.017	0.018	0.029	0.013	0.016
500	0.013	0.018	0.018	0.019	0.032	0.015	0.017
10	0.013	0.019	0.019	0.022	0.033	0.018	0.020
20	0.012	0.021	0.022	0.025	0.037	0.023	0.024
30	0.012	0.022	0.024	0.031	0.044	0.027	0.028
40	0.012	0.025	0.032	0.042	0.057	0.040	0.040
50	0.009	0.028	0.041	0.062	0.076	0.060	0.059
55	0.008	0.032	0.047	0.074	0.090	0.074	0.072
60	0.008	0.036	0.054	0.088	0.104	0.089	0.086
65	0.008	0.038	0.059	0.100	0.119	0.104	0.101
70	0.007	0.041	0.065	0.110	0.132	0.118	0.114
75	0.007	0.042	0.068	0.117	0.139	0.129	0.127
80	0.007	0.043	0.068	0.118	0.143	0.137	0.136
85	0.007	0.042	0.068	0.118	0.145	0.144	0.146
90	0.007	0.041	0.067	0.118	0.149	0.150	0.156
95	0.006	0.041	0.068	0.122	0.154	0.157	0.163
600	0.005	0.041	0.073	0.130	0.164	0.165	0.170
5	0.006	0.044	0.086	0.145	0.174	0.179	0.182
10	0.006	0.048	0.088	0.161	0.195	0.193	0.193
15	0.006	0.049	0.092	0.168	0.202	0.200	0.199
20	0.006	0.052	0.094	0.173	0.206	0.207	0.207
25	0.006	0.053	0.095	0.175	0.210	0.216	0.217
30	0.006	0.054	0.096	0.176	0.214	0.222	0.223
35	0.006	0.055	0.097	0.178	0.216	0.225	0.226
40	0.006	0.058	0.098	0.180	0.220	0.230	0.232
45	0.006	0.062	0.099	0.184	0.225	0.236	0.238
50	0.006	0.064	0.102	0.190	0.232	0.240	0.242
55	0.006	0.061	0.104	0.195	0.236	0.245	0.246
60	0.006	0.061	0.104	0.195	0.236	0.245	0.245
65	0.005	0.060	0.100	0.188	0.227	0.241	0.241
70	0.004	0.054	0.091	0.172	0.210	0.231	0.233
75	0.005	0.054	0.077	0.148	0.187	0.212	0.214
80	0.004	0.036	0.065	0.123	0.159	0.190	0.195
85	0.005	0.029	0.052	0.097	0.131	0.161	0.168
90	0.004	0.022	0.037	0.069	0.101	0.128	0.135
95	0.004	0.016	0.026	0.048	0.074	0.096	0.103
700	0.004	0.012	0.018	0.033	0.052	0.070	0.076

TABLE V (Continued)

Wave Length	Ratio Cl/Co						
	3.5	4.0	6.0	10.0	20.0	50.0	100.0
420	0.014	0.018	0.017	0.009	0.013	0.006	0.017
30	0.013	0.017	0.016	0.009	0.013	0.006	0.015
40	0.013	0.016	0.014	0.008	0.012	0.006	0.013
50	0.013	0.015	0.014	0.008	0.010	0.005	0.012
60	0.011	0.014	0.013	0.008	0.010	0.004	0.009
70	0.012	0.014	0.013	0.008	0.010	0.004	0.009
80	0.012	0.014	0.013	0.008	0.010	0.004	0.008
90	0.012	0.015	0.013	0.008	0.010	0.004	0.008
500	0.013	0.016	0.014	0.009	0.011	0.006	0.008
10	0.015	0.018	0.016	0.011	0.012	0.007	0.008
20	0.019	0.021	0.019	0.013	0.013	0.008	0.010
30	0.024	0.026	0.022	0.016	0.015	0.009	0.011
40	0.033	0.034	0.028	0.022	0.019	0.011	0.009
50	0.051	0.052	0.044	0.033	0.026	0.017	0.013
55	0.064	0.062	0.053	0.043	0.034	0.022	0.017
60	0.077	0.075	0.065	0.053	0.042	0.028	0.024
65	0.091	0.090	0.078	0.067	0.056	0.040	0.032
70	0.105	0.105	0.094	0.083	0.069	0.053	0.045
75	0.120	0.118	0.109	0.100	0.090	0.071	0.061
80	0.132	0.132	0.127	0.121	0.112	0.093	0.080
85	0.146	0.147	0.146	0.143	0.138	0.118	0.105
90	0.159	0.162	0.166	0.166	0.164	0.143	0.128
95	0.166	0.172	0.176	0.178	0.176	0.157	0.143
600	0.173	0.177	0.181	0.183	0.181	0.163	0.152
5	0.181	0.185	0.186	0.187	0.184	0.172	0.167
10	0.191	0.193	0.192	0.189	0.187	0.181	0.185
15	0.196	0.198	0.196	0.192	0.191	0.189	0.195
20	0.206	0.206	0.205	0.205	0.206	0.208	0.221
25	0.219	0.222	0.225	0.227	0.235	0.240	0.255
30	0.227	0.232	0.237	0.239	0.246	0.252	0.265
35	0.233	0.237	0.242	0.246	0.254	0.255	0.266
40	0.240	0.245	0.252	0.257	0.265	0.265	0.274
45	0.245	0.250	0.258	0.265	0.273	0.273	0.278
50	0.248	0.255	0.263	0.266	0.274	0.275	0.285
55	0.251	0.256	0.263	0.267	0.275	0.284	0.304
60	0.252	0.256	0.263	0.274	0.280	0.292	0.325
65	0.250	0.256	0.265	0.274	0.289	0.310	0.340
70	0.247	0.255	0.268	0.279	0.298	0.318	0.345
75	0.237	0.248	0.266	0.283	0.308	0.325	0.348
80	0.223	0.233	0.256	0.276	0.305	0.328	0.350
85	0.200	0.210	0.237	0.261	0.295	0.322	0.350
90	0.163	0.180	0.205	0.227	0.268	0.303	0.338
95	0.130	0.145	0.168	0.189	0.228	0.270	0.309
700	0.097	0.108	0.127	-----	-----	-----	0.262

TABLE V (Continued)

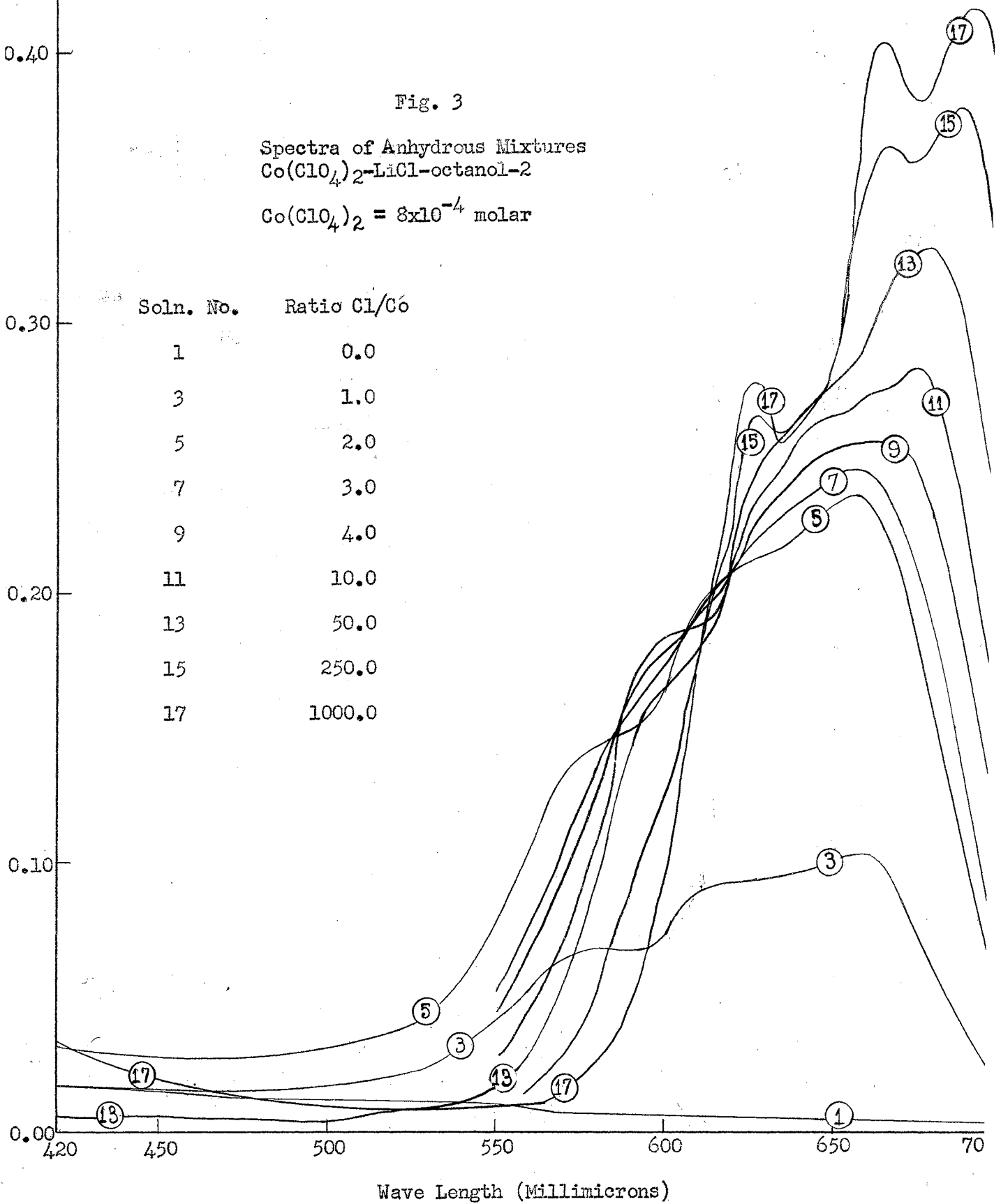
Wave Length	Ratio Cl/Co		
	250.0	500.0	1000.0
420	0.009	0.019	0.033
30	0.008	0.016	0.026
40	0.007	0.014	0.023
50	0.007	0.012	0.019
60	0.006	0.011	0.016
70	0.005	0.009	0.013
80	0.005	0.008	0.012
90	0.005	0.008	0.011
500	0.006	0.008	0.011
10	0.006	0.008	0.010
20	0.007	0.008	0.009
30	0.008	0.010	0.010
40	0.008	0.010	0.010
50	0.011	0.011	0.010
55	0.012	0.011	0.009
60	0.016	0.013	0.010
65	0.022	0.018	0.012
70	0.030	0.024	0.016
75	0.040	0.031	0.020
80	0.054	0.042	0.027
85	0.071	0.055	0.034
90	0.090	0.070	0.048
95	0.106	0.088	0.067
600	0.122	0.108	0.092
5	0.145	0.138	0.129
10	0.180	0.182	0.182
15	0.196	0.200	0.205
20	0.225	0.231	0.238
25	0.262	0.270	0.276
30	0.267	0.273	0.275
35	0.259	0.259	0.256
40	0.265	0.260	0.263
45	0.272	0.270	0.267
50	0.279	0.280	0.280
55	0.312	0.320	0.324
60	0.350	0.367	0.385
65	0.366	0.388	0.404
70	0.364	0.381	0.395
75	0.360	0.372	0.383
80	0.363	0.375	0.384
85	0.374	0.389	0.402
90	0.380	0.403	0.414
95	0.365	0.400	0.416
700	0.323	0.358	0.393

Fig. 3

Spectra of Anhydrous Mixtures
 $\text{Co}(\text{ClO}_4)_2\text{-LiCl-octanol-2}$

$\text{Co}(\text{ClO}_4)_2 = 8 \times 10^{-4}$ molar

Soln. No.	Ratio Cl/Co
1	0.0
3	1.0
5	2.0
7	3.0
9	4.0
11	10.0
13	50.0
15	250.0
17	1000.0



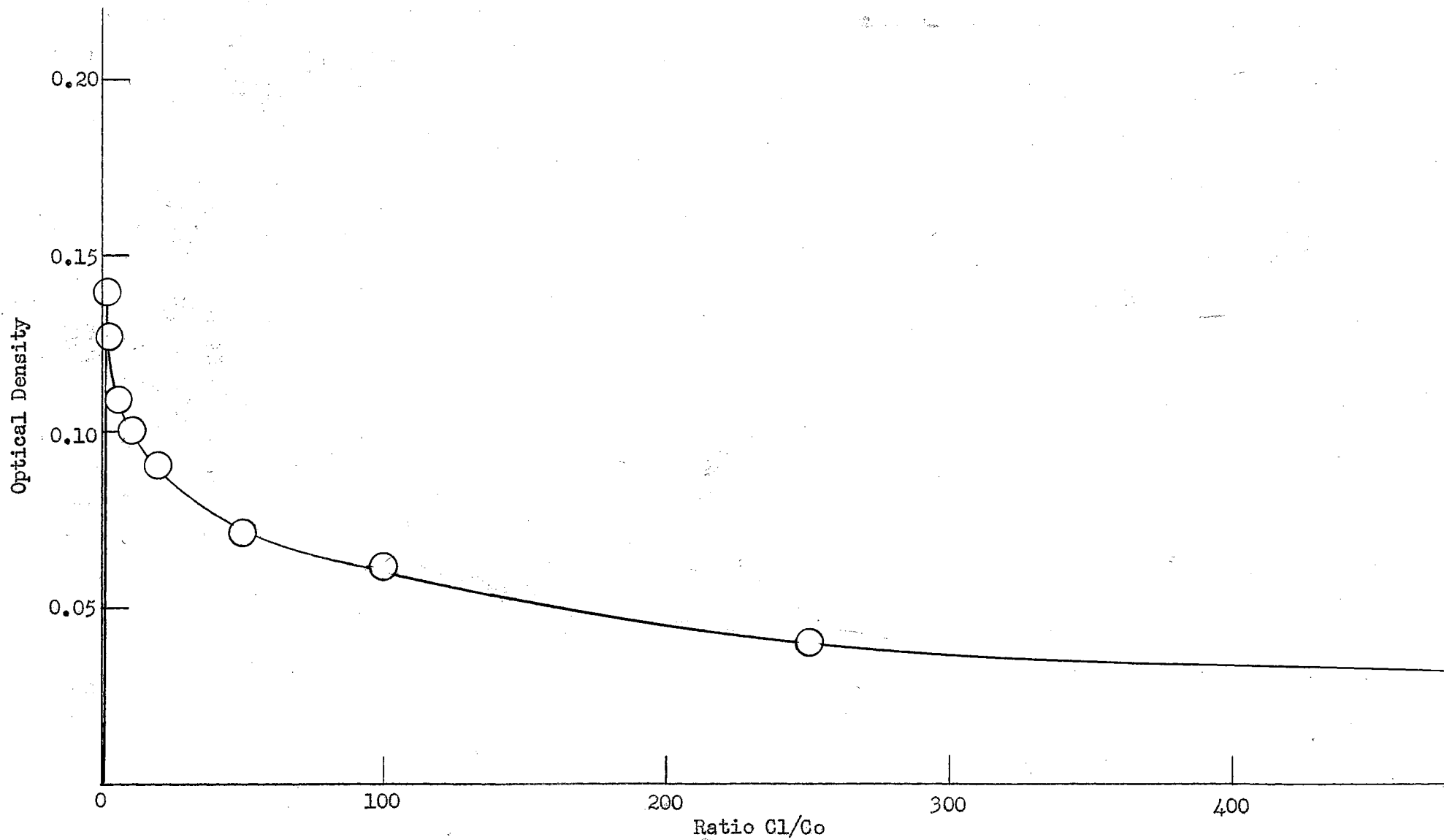


Fig. 4: Saturation Plot for the System $\text{Co}(\text{ClO}_4)_2\text{-LiCl-octanol-2}$.

TABLE VI

Optical Densities for the System: $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$
 Temperature = 30° $\text{Co}(\text{ClO}_4)_2 = 1.6 \times 10^{-3}$ molar

Wave Length	Ratio Cl/Co						
	0.0	0.5	1.0	1.5	2.0	2.5	3.0
420	0.030	0.069	0.088	0.094	0.053	0.096	0.097
30	0.028	0.065	0.081	0.088	0.050	0.090	0.090
40	0.028	0.062	0.077	0.079	0.048	0.083	0.085
50	0.025	0.059	0.075	0.074	0.046	0.077	0.079
60	0.025	0.058	0.073	0.070	0.047	0.073	0.074
70	0.025	0.057	0.070	0.068	0.046	0.070	0.071
80	0.024	0.057	0.069	0.067	0.047	0.067	0.068
90	0.023	0.056	0.069	0.065	0.048	0.064	0.066
500	0.024	0.052	0.069	0.062	0.049	0.064	0.066
10	0.023	0.048	0.069	0.059	0.052	0.065	0.066
20	0.021	0.048	0.071	0.063	0.057	0.068	0.067
30	0.020	0.048	0.074	0.068	0.064	0.072	0.074
40	0.017	0.048	0.080	0.077	0.077	0.086	0.089
50	0.016	0.048	0.090	0.094	0.099	0.105	0.108
55	0.014	0.049	0.097	0.104	0.114	0.123	0.125
60	0.013	0.049	0.105	0.114	0.129	0.137	0.142
65	0.012	0.048	0.110	0.123	0.142	0.152	0.158
70	0.012	0.048	0.116	0.130	0.154	0.166	0.172
75	0.011	0.048	0.117	0.134	0.161	0.176	0.185
80	0.010	0.048	0.115	0.135	0.166	0.179	0.190
85	0.010	0.047	0.113	0.137	0.170	0.193	0.205
90	0.009	0.046	0.113	0.140	0.176	0.201	0.216
95	0.008	0.045	0.115	0.143	0.185	0.211	0.229
600	0.008	0.047	0.123	0.154	0.197	0.223	0.239
5	0.008	0.048	0.130	0.166	0.212	0.239	0.255
10	0.008	0.049	0.137	0.175	0.224	0.250	0.265
15	0.008	0.049	0.140	0.178	0.229	0.255	0.270
20	0.008	0.049	0.140	0.180	0.234	0.262	0.279
25	0.008	0.049	0.141	0.183	0.239	0.268	0.285
30	0.007	0.048	0.141	0.184	0.241	0.274	0.294
35	0.007	0.048	0.141	0.185	0.243	0.277	0.300
40	0.006	0.047	0.142	0.187	0.250	0.284	0.307
45	0.006	0.048	0.144	0.191	0.255	0.291	0.314
50	0.006	0.049	0.148	0.196	0.263	0.298	0.322
55	0.006	0.049	0.150	0.200	0.267	0.302	0.325
60	0.006	0.048	0.148	0.198	0.264	0.299	0.322
65	0.006	0.048	0.140	0.191	0.252	0.290	0.313
70	0.006	0.042	0.128	0.170	0.232	0.272	0.297
75	0.006	0.037	0.111	0.146	0.200	0.244	0.270
80	0.006	0.033	0.093	0.121	0.174	0.214	0.240
85	0.005	0.027	0.078	0.098	0.141	0.182	0.207
90	0.005	0.024	0.062	0.076	0.108	0.137	0.159
95	0.005	0.021	0.049	0.056	0.081	0.108	0.125
700	0.005	0.018	0.039	0.039	0.058	0.080	0.094

TABLE VI (Continued)

Wave Length	Ratio C_1/C_0						
	3.5	4.0	6.0	10.0	20.0	50.0	100.0
420	0.097	0.086	0.123	0.109	0.045	0.016	0.023
30	0.090	0.079	0.115	0.103	0.042	0.016	0.020
40	0.085	0.075	0.108	0.098	0.041	0.015	0.018
50	0.079	0.071	0.100	0.090	0.038	0.013	0.017
60	0.074	0.068	0.094	0.086	0.037	0.012	0.014
70	0.071	0.064	0.090	0.082	0.037	0.012	0.013
80	0.068	0.062	0.086	0.080	0.038	0.013	0.013
90	0.065	0.061	0.083	0.076	0.037	0.012	0.014
500	0.065	0.061	0.080	0.074	0.040	0.015	0.014
10	0.064	0.062	0.080	0.074	0.041	0.016	0.016
20	0.068	0.064	0.081	0.075	0.047	0.022	0.018
30	0.072	0.069	0.085	0.077	0.050	0.022	0.021
40	0.088	0.080	0.093	0.086	0.058	0.024	0.022
50	0.105	0.102	0.112	0.102	0.075	0.035	0.027
55	0.123	0.116	0.125	0.116	0.091	0.046	0.035
60	0.139	0.131	0.141	0.132	0.107	0.061	0.045
65	0.156	0.148	0.161	0.153	0.130	0.082	0.059
70	0.172	0.166	0.183	0.179	0.159	0.109	0.080
75	0.186	0.181	0.201	0.202	0.192	0.140	0.105
80	0.194	0.194	0.221	0.230	0.232	0.184	0.138
85	0.211	0.211	0.248	0.268	0.276	0.233	0.179
90	0.226	0.228	0.271	0.300	0.325	0.284	0.220
95	0.240	0.242	0.286	0.320	0.345	0.309	0.253
600	0.249	0.253	0.297	0.327	0.358	0.325	0.275
5	0.265	0.267	0.306	0.335	0.366	0.344	0.310
10	0.274	0.274	0.313	0.339	0.373	0.363	0.357
15	0.276	0.279	0.319	0.345	0.383	0.383	0.385
20	0.289	0.292	0.335	0.368	0.420	0.433	0.445
25	0.298	0.308	0.356	0.403	0.462	0.490	0.507
30	0.308	0.315	0.368	0.419	0.486	0.517	0.517
35	0.315	0.324	0.382	0.434	0.497	0.425	0.515
40	0.324	0.333	0.390	0.442	0.519	0.540	0.520
45	0.332	0.343	0.405	0.458	0.529	0.550	0.552
50	0.340	0.348	0.408	0.460	0.531	0.560	0.559
55	0.341	0.350	0.410	0.463	0.540	0.588	0.606
60	0.339	0.351	0.412	0.471	0.555	0.620	0.662
65	0.333	0.344	0.410	0.476	0.573	0.649	0.708
70	0.320	0.335	0.409	0.482	0.590	0.668	0.713
75	0.294	0.315	0.392	0.479	0.595	0.672	0.712
80	0.267	0.285	0.365	0.458	0.581	0.671	0.714
85	0.232	0.250	0.333	0.421	0.541	0.648	0.715
90	0.176	0.203	0.275	0.358	0.478	0.608	0.704
95	0.142	0.157	0.221	0.292	0.400	0.529	0.655
700	0.107	0.113	0.163	0.219	0.315	0.430	0.560

TABLE VI (Continued)

Wave Length	Ratio Cl/Co				
	250.0	1.0*	2.0*	100.0*	250.0*
420	0.031	0.052	0.027	0.014	0.025
30	0.026	0.048	0.025	0.012	0.020
40	0.024	0.047	0.025	0.012	0.018
50	0.022	0.047	0.024	0.011	0.018
60	0.018	0.046	0.024	0.009	0.015
70	0.015	0.046	0.024	0.008	0.013
80	0.014	0.046	0.025	0.009	0.013
90	0.015	0.048	0.026	0.010	0.013
500	0.016	0.050	0.029	0.010	0.014
10	0.016	0.053	0.034	0.012	0.014
20	0.017	0.060	0.043	0.014	0.016
30	0.018	0.068	0.056	0.017	0.020
40	0.020	0.082	0.078	0.018	0.019
50	0.022	0.105	0.120	0.023	0.021
55	0.024	0.120	0.149	0.028	0.024
60	0.028	0.137	0.181	0.037	0.029
65	0.036	0.152	0.209	0.048	0.035
70	0.048	0.166	0.240	0.068	0.048
75	0.064	0.175	0.260	0.089	0.066
80	0.083	0.178	0.276	0.119	0.085
85	0.112	0.177	0.290	0.162	0.114
90	0.144	0.176	0.303	0.195	0.146
95	0.178	0.178	0.315	0.226	0.180
600	0.214	0.188	0.334	0.256	0.220
5	0.273	0.203	0.355	0.298	0.278
10	0.356	0.224	0.385	0.355	0.363
15	0.398	0.235	0.403	0.385	0.402
20	0.460	0.240	0.422	0.448	0.462
25	0.545	0.243	0.437	0.506	0.539
30	0.560	0.245	0.447	0.528	0.549
35	0.538	0.247	0.455	0.514	0.525
40	0.540	0.249	0.466	0.530	0.530
45	0.550	0.253	0.477	0.540	0.547
50	0.570	0.258	0.489	0.561	0.566
55	0.645	0.264	0.496	0.612	0.645
60	0.747	0.265	0.498	0.680	0.738
65	0.791	0.255	0.490	0.720	0.788
70	0.785	0.237	0.468	0.720	0.774
75	0.769	0.207	0.428	0.712	0.757
80	0.771	0.174	0.383	0.724	0.763
85	0.796	0.145	0.325	0.734	0.785
90	0.810	0.107	0.255	0.740	0.815
95	0.803	0.077	0.194	0.710	0.800
700	0.728	0.056	0.135	0.615	0.731

*These solutions are anhydrous but have the same cobalt concentration as members of this system.

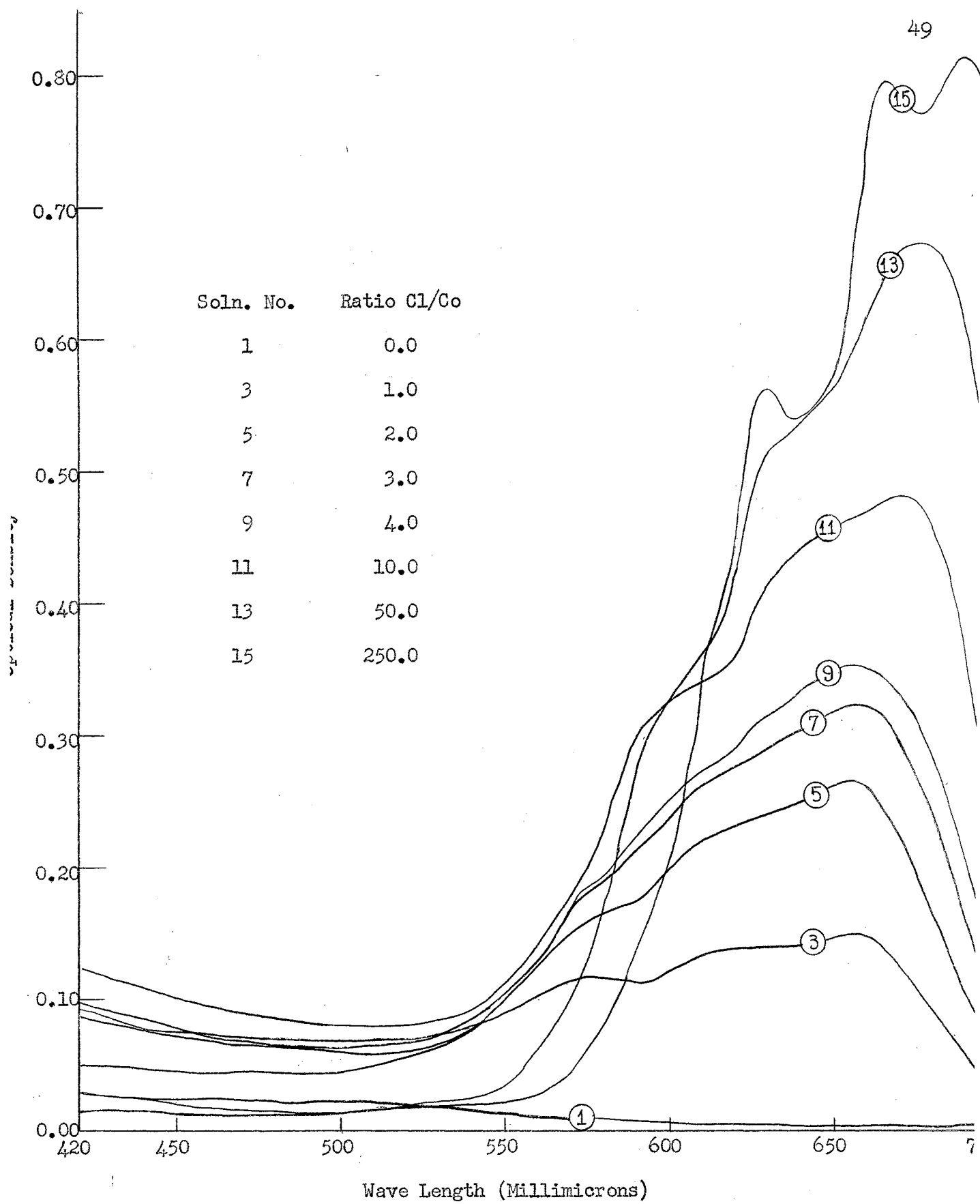


Fig. 5: Spectra of the System $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-octanol-2}$. $\text{Co}(\text{ClO}_4)_2 = 1.6 \times 10^{-3}$ Molar.

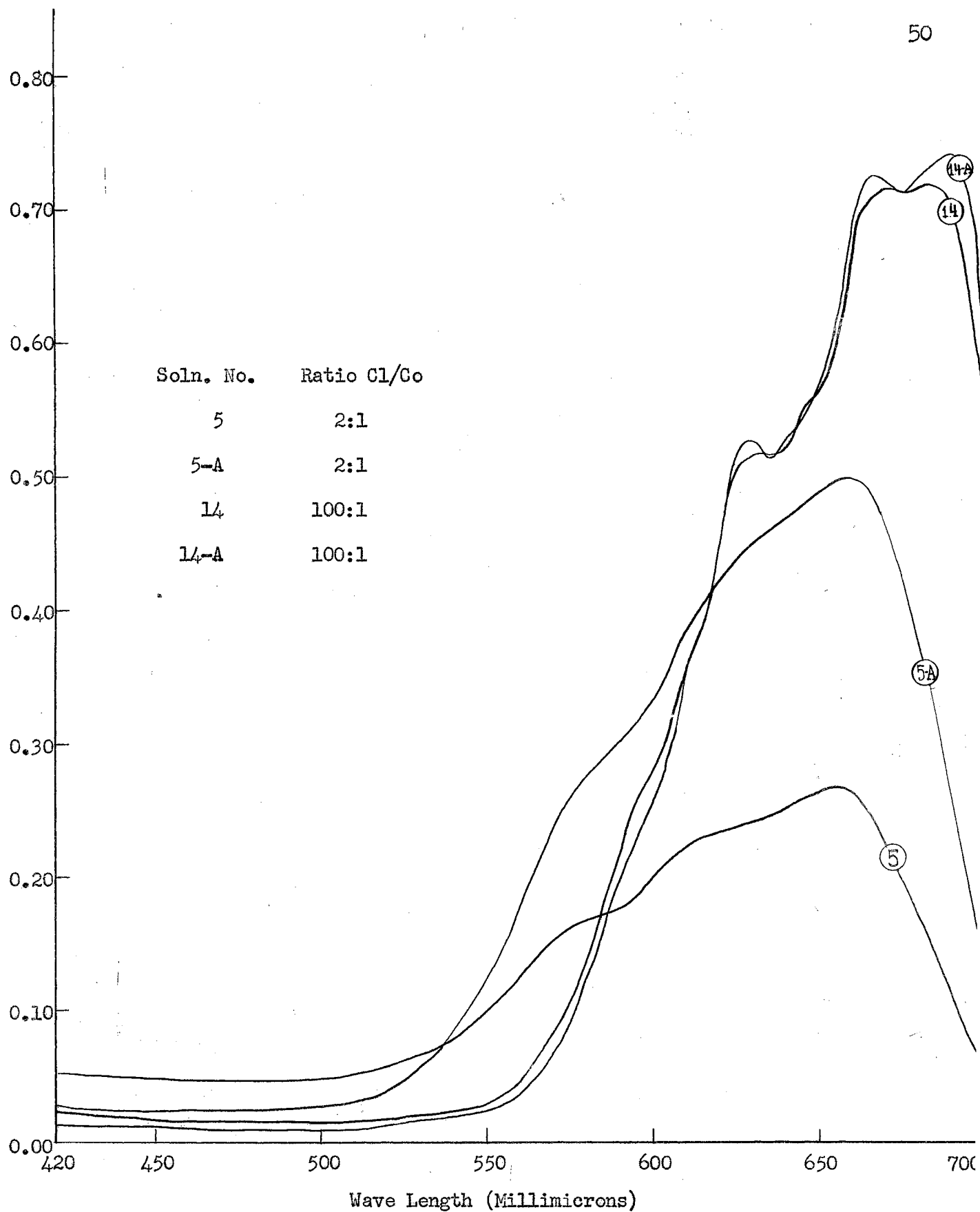


Fig. 6: A Comparison of the Spectra of Mixtures of $\text{Co}(\text{ClO}_4)_2$ -LiCl-octanol-2 in the Presence and Absence of Water. $\text{Co}(\text{ClO}_4)_2 = 1.6 \times 10^{-3}$ Molar. $\text{H}_2\text{O} = 0.5$ Molar in Solutions 5 and 14.

TABLE VII

Optical Densities for the System: $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$ Temperature = 30° $\text{CoCl}_2 = 1.6 \times 10^{-3}$ molar

Wave Length	Ratio $\text{H}_2\text{O/Co}$					
	0.0	1.0	2.0	3.0	4.0	10.0
420	0.001	0.004	0.002	0.013	0.003	0.005
30	0.002	0.001	0.002	0.014	0.004	0.005
40	0.002	0.001	0.002	0.013	0.005	0.005
50	0.002	0.000	0.002	0.012	0.005	0.004
60	0.003	0.001	0.003	0.011	0.005	0.006
70	0.005	0.004	0.005	0.012	0.007	0.007
80	0.006	0.005	0.007	0.014	0.010	0.008
90	0.009	0.009	0.010	0.016	0.012	0.011
500	0.013	0.015	0.022	0.017	0.015	0.016
10	0.021	0.020	0.021	0.026	0.023	0.024
20	0.031	0.030	0.032	0.036	0.032	0.034
30	0.048	0.047	0.048	0.052	0.049	0.051
40	0.079	0.078	0.079	0.082	0.080	0.081
50	0.134	0.133	0.135	0.122	0.132	0.133
55	0.166	0.164	0.167	0.171	0.168	0.168
60	0.200	0.198	0.202	0.204	0.202	0.203
65	0.237	0.234	0.238	0.240	0.238	0.237
70	0.266	0.262	0.266	0.270	0.267	0.265
75	0.286	0.285	0.283	0.284	0.282	0.282
80	0.294	0.292	0.288	0.292	0.290	0.287
85	0.293	0.292	0.288	0.292	0.290	0.289
90	0.294	0.291	0.289	0.293	0.290	0.290
95	0.300	0.297	0.300	0.303	0.301	0.302
600	0.328	0.325	0.326	0.325	0.325	0.326
5	0.336	0.352	0.360	0.363	0.360	0.361
10	0.407	0.403	0.405	0.408	0.406	0.407
15	0.431	0.428	0.428	0.430	0.429	0.426
20	0.439	0.427	0.436	0.438	0.437	0.435
25	0.457	0.457	0.443	0.445	0.444	0.440
30	0.455	0.452	0.445	0.443	0.445	0.448
35	0.469	0.465	0.456	0.459	0.458	0.452
40	0.464	0.462	0.459	0.461	0.460	0.459
45	0.485	0.481	0.471	0.473	0.472	0.470
50	0.490	0.488	0.489	0.490	0.490	0.488
55	0.520	0.518	0.501	0.503	0.502	0.500
60	0.509	0.508	0.498	0.496	0.498	0.500
65	0.508	0.502	0.481	0.484	0.482	0.482
70	0.450	0.448	0.439	0.438	0.439	0.438
75	0.407	0.405	0.374	0.377	0.376	0.371
80	0.345	0.343	0.316	0.318	0.317	0.309
85	0.271	0.271	0.249	0.252	0.251	0.243
90	0.193	0.193	0.170	0.172	0.171	0.165
95	0.130	0.130	0.118	0.120	0.119	0.117
700	0.085	0.085	0.076	0.078	0.077	0.074

TABLE VII (Continued)

Wave Length	Ratio H ₂ O/Co					
	20.0	50.0	100.0	312.5	500.0	600.0
420	0.017	0.011	0.008	0.026	0.069	0.063
30	0.016	0.010	0.008	0.025	0.064	0.050
40	0.015	0.008	0.007	0.023	0.059	0.046
50	0.013	0.008	0.007	0.021	0.056	0.039
60	0.014	0.008	0.008	0.019	0.054	0.037
70	0.014	0.009	0.009	0.021	0.052	0.034
80	0.014	0.011	0.011	0.022	0.048	0.032
90	0.016	0.013	0.014	0.025	0.047	0.030
500	0.021	0.018	0.019	0.026	0.046	0.028
10	0.027	0.025	0.026	0.031	0.047	0.028
20	0.038	0.035	0.036	0.038	0.047	0.028
30	0.056	0.053	0.052	0.051	0.048	0.028
40	0.084	0.084	0.081	0.074	0.052	0.028
50	0.137	0.015	0.132	0.109	0.058	0.029
55	0.170	0.069	0.163	0.131	0.063	0.030
60	0.204	0.204	0.196	0.152	0.068	0.032
65	0.239	0.237	0.226	0.173	0.072	0.033
70	0.265	0.264	0.249	0.189	0.075	0.033
75	0.282	0.277	0.265	0.191	0.076	0.033
80	0.286	0.280	0.267	0.201	0.076	0.033
85	0.287	0.284	0.269	0.191	0.075	0.032
90	0.289	0.285	0.273	0.206	0.075	0.031
95	0.302	0.298	0.285	0.215	0.080	0.033
600	0.326	0.325	0.312	0.221	0.086	0.034
5	0.363	0.362	0.345	0.264	0.093	0.036
10	0.407	0.402	0.381	0.271	0.097	0.038
15	0.424	0.419	0.395	0.289	0.098	0.038
20	0.432	0.433	0.404	0.282	0.099	0.038
25	0.438	0.437	0.409	0.288	0.099	0.038
30	0.441	0.440	0.411	0.288	0.100	0.038
35	0.448	0.449	0.417	0.288	0.101	0.039
40	0.453	0.460	0.423	0.295	0.104	0.040
45	0.465	0.469	0.434	0.291	0.106	0.041
50	0.483	0.478	0.450	0.317	0.108	0.042
55	0.494	0.489	0.461	0.304	0.108	0.041
60	0.494	0.489	0.459	0.319	0.106	0.040
65	0.472	0.462	0.436	0.279	0.099	0.037
70	0.430	0.419	0.391	0.268	0.088	0.033
75	0.359	0.350	0.325	0.204	0.072	0.027
80	0.296	0.284	0.264	0.167	0.059	0.022
85	0.231	0.224	0.203	0.127	0.047	0.017
90	0.155	0.152	0.134	0.085	0.034	0.012
95	0.109	0.105	0.094	0.061	0.026	0.009
700	0.069	0.065	0.059	0.037	0.019	0.008

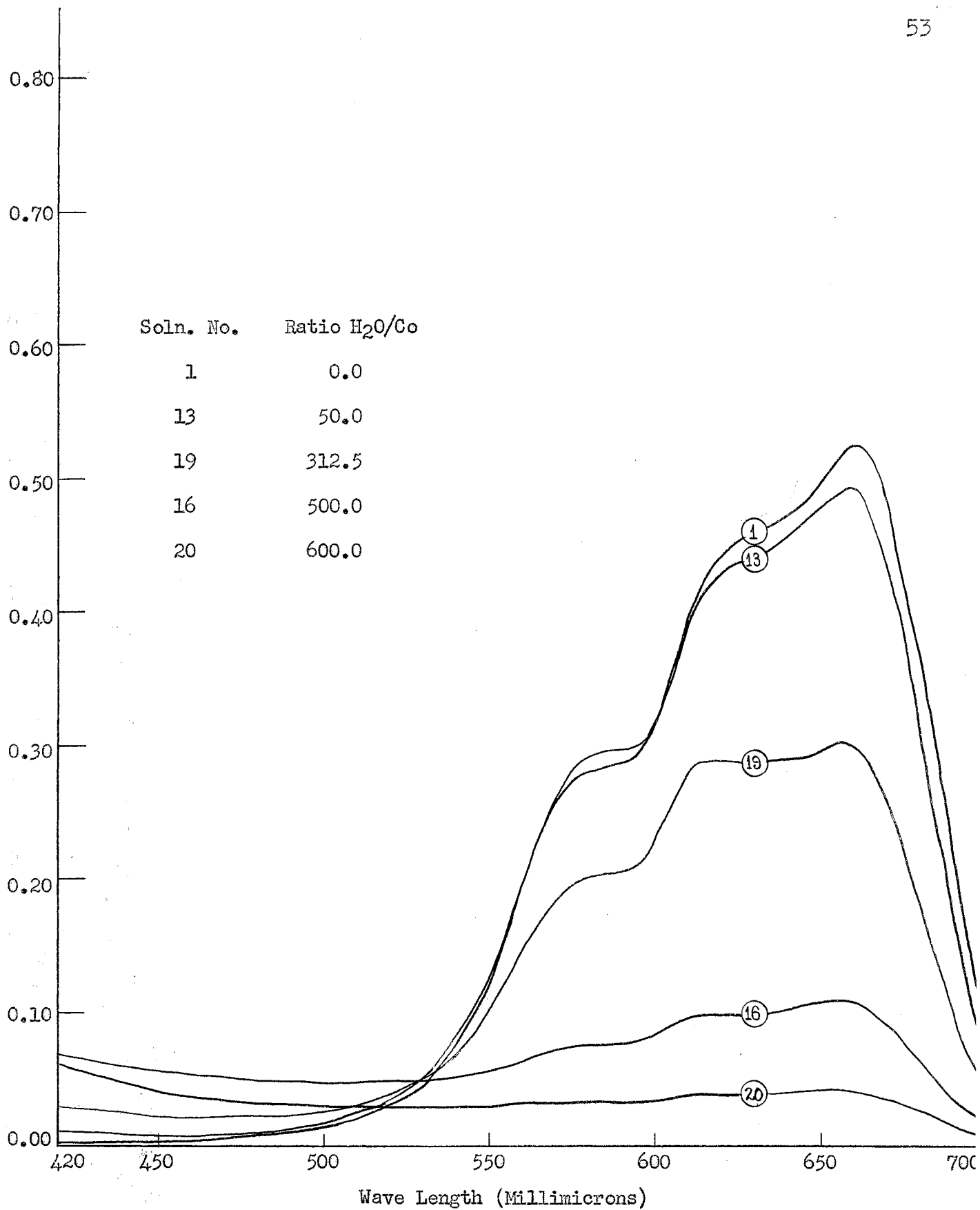


Fig. 7: Spectra of Mixtures of $\text{CoCl}_2\text{-H}_2\text{O-octanol-2}$. $\text{CoCl}_2 = 1.6 \times 10^{-3}$ Molar.

TABLE VIII

Optical Densities for the System: $\text{CoCl}_2\text{-Co}(\text{ClO}_4)_2\text{-2-octanol}$ A = $\text{Co}(\text{ClO}_4)_2 \times 10^4$ molarB = $\text{CoCl}_2 \times 10^4$ molarTemperature = 30°

Wave Length	A: 0 B: 16	A: 2 B: 14	A: 4 B: 12	A: 6 B: 10	A: 8 B: 8
550	0.135	0.116	0.098	0.084	0.071
55	0.171	0.145	0.122	0.102	0.085
60	0.205	0.175	0.147	0.126	0.098
65	0.240	0.204	0.169	0.139	0.111
70	0.268	0.236	0.186	0.152	0.121
75	0.284	0.239	0.198	0.162	0.128
80	0.289	0.243	0.200	0.164	0.129
85	0.290	0.244	0.201	0.164	0.129
90	0.291	0.244	0.200	0.164	0.129
95	0.300	0.252	0.205	0.170	0.132
600	0.326	0.273	0.224	0.180	0.140
5	0.363	0.304	0.250	0.200	0.155
10	0.407	0.337	0.275	0.225	0.174
15	0.427	0.355	0.291	0.234	0.180
20	0.435	0.361	0.296	0.244	0.190
25	0.440	0.366	0.300	0.245	0.190
30	0.449	0.374	0.305	0.247	0.190
35	0.454	0.379	0.310	0.250	0.192
40	0.460	0.384	0.314	0.253	0.194
45	0.471	0.392	0.320	0.258	0.196
50	0.489	0.409	0.332	0.267	0.202
55	0.501	0.418	0.339	0.273	0.207
60	0.502	0.418	0.339	0.272	0.205
65	0.481	0.400	0.325	0.260	0.198
70	0.435	0.359	0.293	0.238	0.179
80	0.310	0.256	0.207	0.170	0.129
90	0.167	0.136	0.112	0.092	0.070
700	0.074	0.060	0.048	0.040	0.033

TABLE VIII (Continued)

Wave Length	A: 10 B: 6	A: 12 B: 4	A: 14 B: 2	A: 16 B: 0
550	0.059	0.056	0.056	0.016
55	0.068	0.059	0.057	0.015
60	0.076	0.063	0.056	0.014
65	0.086	0.068	0.057	0.013
70	0.092	0.071	0.057	0.012
75	0.097	0.073	0.057	0.011
80	0.097	0.072	0.055	0.010
85	0.097	0.072	0.054	0.010
90	0.097	0.071	0.053	0.009
95	0.099	0.073	0.053	0.009
600	0.104	0.075	0.053	0.009
5	0.114	0.081	0.054	0.008
10	0.128	0.087	0.056	0.008
15	0.134	0.090	0.057	0.008
20	0.137	0.091	0.056	0.008
25	0.138	0.092	0.055	0.008
30	0.137	0.092	0.055	0.008
35	0.139	0.093	0.055	0.008
40	0.140	0.093	0.055	0.008
45	0.142	0.094	0.054	0.008
50	0.147	0.096	0.054	0.008
55	0.150	0.097	0.054	0.008
60	0.148	0.096	0.053	0.008
65	0.141	0.092	0.050	0.007
70	0.127	0.083	0.047	0.008
80	0.093	0.061	0.037	0.008
90	0.052	0.041	0.028	0.008
700	0.025	0.039	0.022	0.008

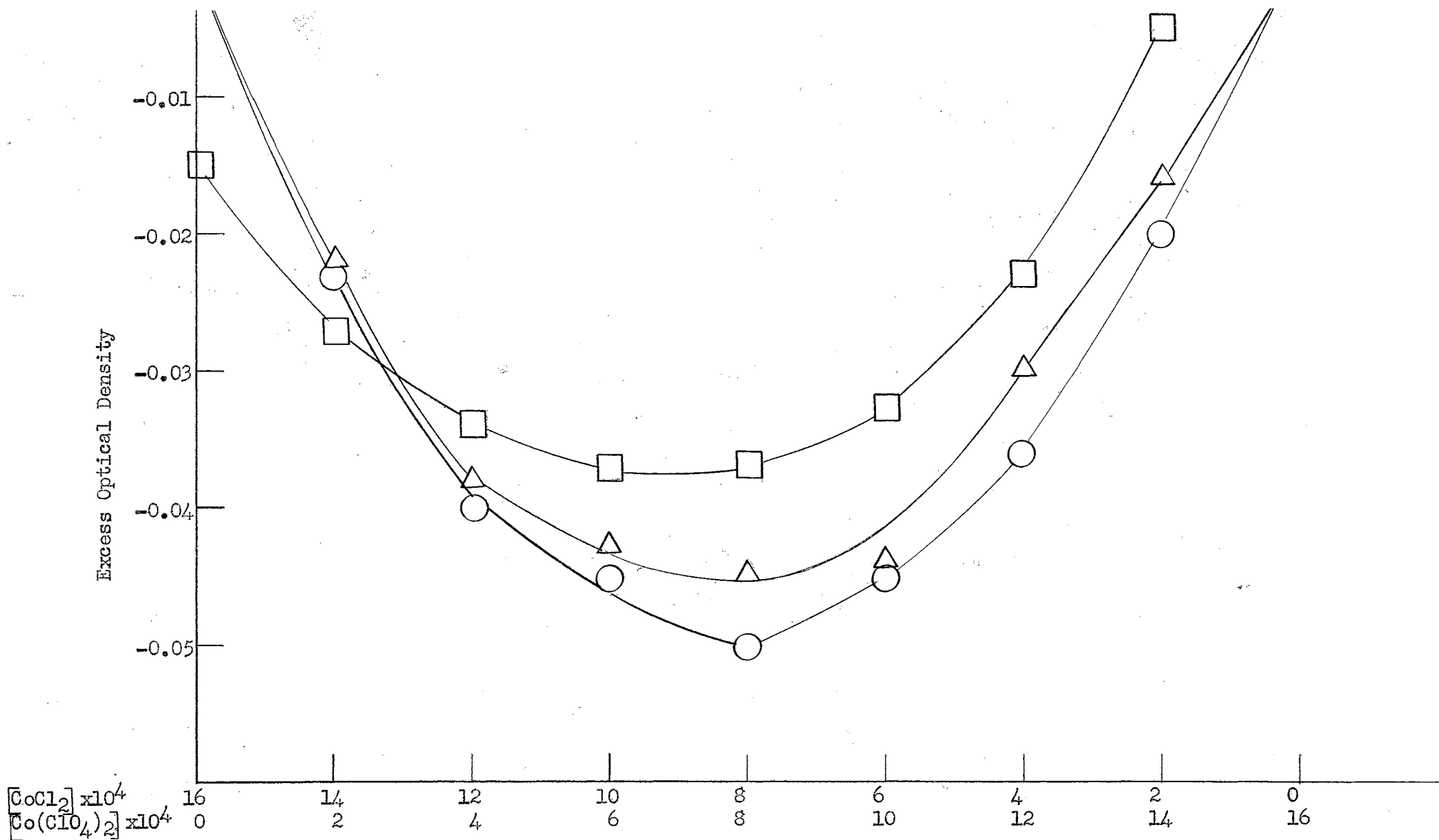


Fig. 8: A Continuous Variation Study for the System $\text{CoCl}_2\text{-Co}(\text{ClO}_4)_2\text{-octanol-2}$.

○ -- 660 millimicrons; △ -- 665 millimicrons; □ -- 585 millimicrons.

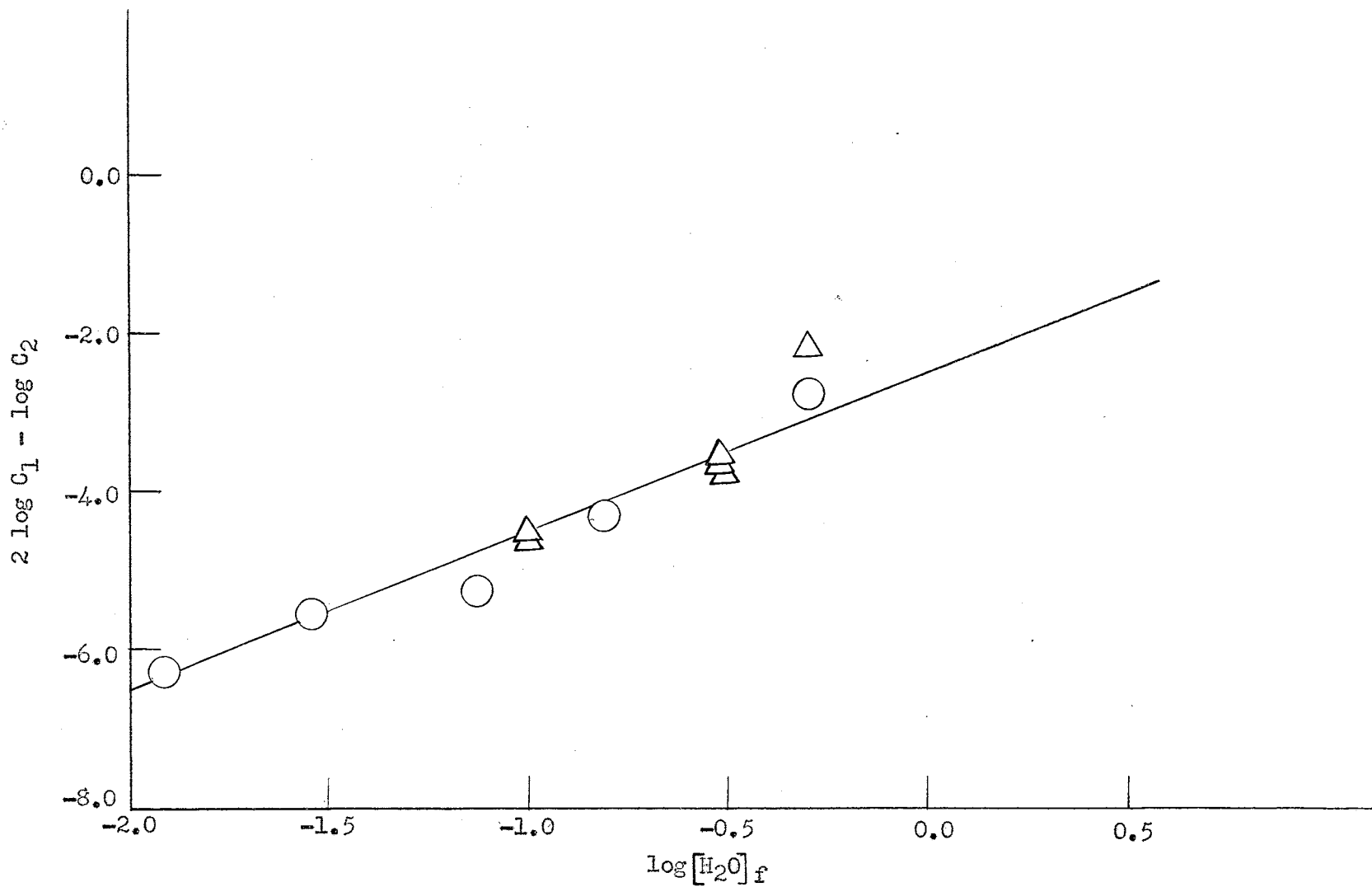


Fig. 9: A Test of the Mass-action Expression for the Reaction $CoCl_2 + nH_2O = CoCl(H_2O)_2^+ + Cl^-$.
 \triangle -- System $Co(ClO_4)_2-LiCl-H_2O$ -octanol-2; \circ -- System $CoCl_2-H_2O$ -octanol-2
 $C_1 = [CoCl(H_2O)_2^+]$; $C_2 = [CoCl_2]$

TABLE IX

K_2 Values for the System
 $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$

Ratio Cl/Co	K_2		
	For 0.5 molar H_2O	For 0.3 molar H_2O	For 0.1 molar H_2O
2.0	45.3	-----	-----
2.5	57.2	4.59×10^2	3.73×10^2
3.0	57.2	3.15×10^2	4.56×10^2
3.5	58.1	3.16×10^2	-----
4.0	55.6	4.76×10^2	-----
6.0	76.4	-----	-----

K_2 Values for the System
 $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$

Ratio $\text{H}_2\text{O/Co}$	K_2
10.0	4.46×10^2
20.0	3.72×10^2
50.0	11.90×10^2
100.0	5.64×10^2
312.5	1.53×10^2

TABLE X

Optical Densities for the System: $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$
Concentration of $\text{CoCl}_2 = 1.6 \times 10^{-3}$ molar
Temperature = 30°
Wave length = 660 millimicrons

Ratio $\text{H}_2\text{O/Co}$	Optical Density
450	0.173
500	0.139
520	0.123
540	0.100
560	0.092
580	0.080
600	0.050
650	0.032

TABLE XI

K_1 Values for the System
 $\text{Co}(\text{ClO}_4)_2 - \text{LiCl} - \text{H}_2\text{O} - 2\text{-octanol}$

$\text{Co}(\text{ClO}_4)_2 = 1.6 \times 10^{-3}$ molar

$\text{H}_2\text{O} = 0.5$ molar

Ratio Cl/Co	K_1
0.25	1.55×10^{-1}
0.50	1.56×10^{-1}
0.75	2.83×10^{-1}
1.00	5.24×10^{-1}
1.25	12.40×10^{-1}

K_1 Values for the System

$\text{CoCl}_2 - \text{H}_2\text{O} - 2\text{-octanol}$

$\text{CoCl}_2 = 1.6 \times 10^{-3}$ molar

Ratio $\text{H}_2\text{O}/\text{Co}$	K_1
450	70.9
500	72.9
520	71.6
540	62.6
560	79.2
580	85.4
600	52.0
650	71.0

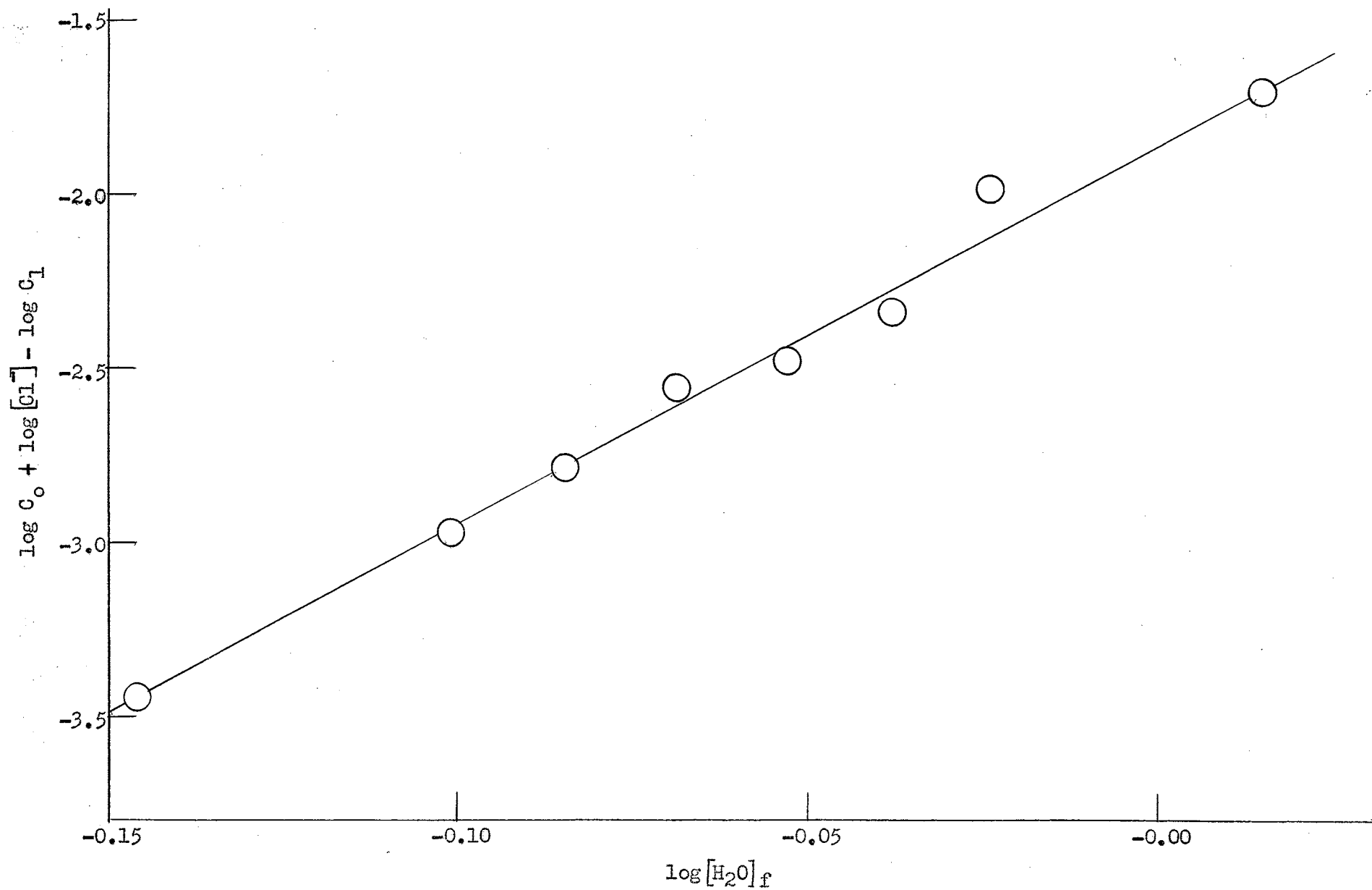


Fig. 10: A Test of the Mass-action Expression for the Reaction $CoCl(H_2O)_2^{\ddagger} + mH_2O = Co(H_2O)_{13}^{\ddagger\ddagger} + Cl^-$
 for the System $CoCl_2-H_2O$ -octanol-2.
 $C_0 = [Co(H_2O)_{13}^{\ddagger\ddagger}]$; $C_1 = [CoCl(H_2O)_2^{\ddagger}]$.

TABLE XII

Optical Densities for the System: $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$ $\text{Co}(\text{ClO}_4)_2 = 1.6 \times 10^{-3}$ molarTemperature = 30°

Wave Length	Ratio Cl/Co							
	$\text{H}_2\text{O} = 0.3$ molar				$\text{H}_2\text{O} = 0.1$ molar			
	2.5	3.0	3.5	4.0	2.5	3.0	3.5	4.0
575	0.237	0.229	0.230	0.242	0.255	0.248	0.243	0.240
580	0.250	0.246	0.247	0.267	0.275	0.275	0.270	0.271
585	0.265	0.267	0.272	0.295	0.295	0.303	0.304	0.310
610	0.346	0.350	0.353	0.372	0.385	0.386	0.389	0.392
620	0.365	0.371	0.378	0.400	0.417	0.410	0.424	0.429
625	0.380	0.390	0.400	0.426	0.436	0.444	0.451	0.459
630	0.387	0.402	0.411	0.437	0.448	0.458	0.468	0.476
635	0.394	0.410	0.422	0.449	0.458	0.468	0.481	0.489
655	0.431	0.446	0.458	0.482	0.493	0.500	0.520	0.530
660	0.430	0.441	0.458	0.480	0.493	0.500	0.521	0.530
665	0.413	0.433	0.450	0.479	0.488	0.495	0.520	0.530
675	0.352	0.385	0.413	0.447	0.433	0.457	0.499	0.521
685	0.266	0.301	0.334	0.368	0.339	0.375	0.423	0.449
690	0.207	0.241	0.271	0.300	0.270	0.304	0.355	0.389

TABLE XIII

Values of K_3 and the Extinction Coefficient of CoCl_3^-
 for the System: $\text{Co}(\text{ClO}_4)_2\text{-LiCl-2-octanol}$

Wave length = 660 millimicrons

Ratio Cl/Co	ξ_3 (calculated)	K_3
2.5	428	287.8
3.0	400	177.4
3.5	407	200.0
4.0	423	168.0
6.0	413	131.6
10.0	427	92.9
20.0	417	59.4
50.0	407	45.5
100.0	448	----
250.0	469	----
500.0	486	----
1000.0	514	----

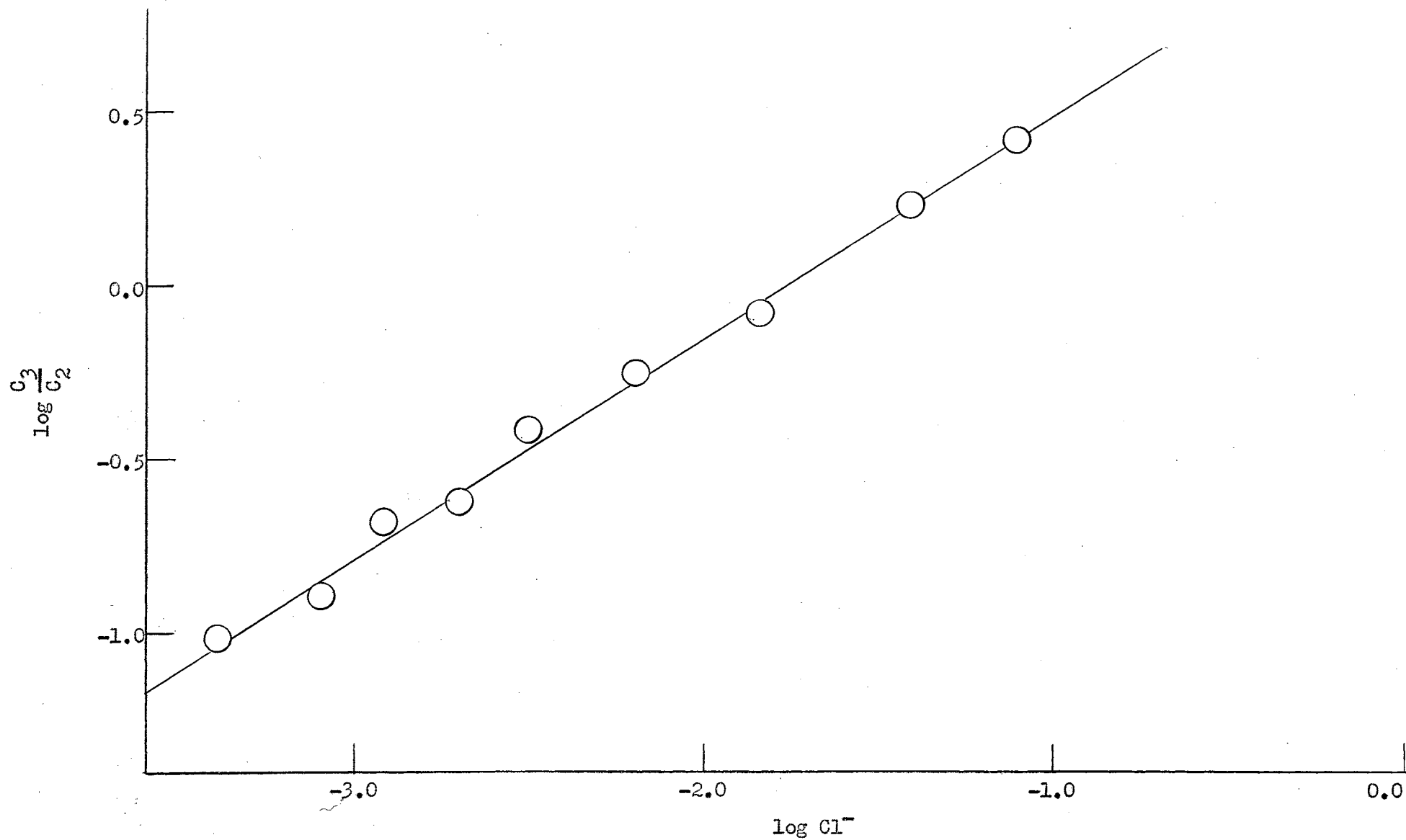


Fig. 11: A Test of the Mass-action Expression for the Reaction $CoCl_2 + Cl^- = CoCl_3^-$ for the system $Co(ClO_4)_2-LiCl$ -octanol-2. $C_2 = [CoCl_2]$. $C_3 = [CoCl_3^-]$.

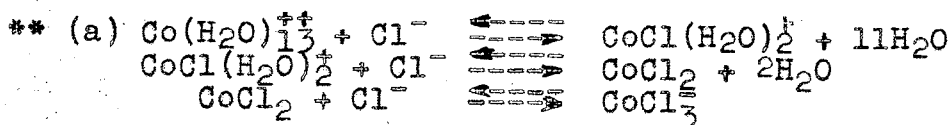
CONCLUSION

Evidence for a number of chloro- and aquo-complexes of cobalt in hydrous and anhydrous 2-octanol has been found in this investigation. These complexes are listed in Table XIV with the system in which they were found to exist, conditions necessary for their formation, and values of equilibrium constants where calculated.

TABLE XIV

Complex	System*	Conditions	Reaction** & Equilibrium Constants	
$\text{Co}(\text{H}_2\text{O})_{13}^{++}$	(1)	Higher water concentrations	(a)	72.
	(2)	Cl/Co ratio less than 1 and $\text{H}_2\text{O} = 0.5$ molar	(a)	1.56×10^{-1}
$\text{CoCl}(\text{H}_2\text{O})_2^{\dagger}$	(1)	Lower water concentrations	(b)	3.16×10^2
	(2)	Cl/Co ratio from 2 to 6	(b)	57.2
		$\text{H}_2\text{O} = 0.5$ molar	(b)	3.76×10^2
		$\text{H}_2\text{O} = 0.3$ molar	(b)	4.10×10^2
	$\text{H}_2\text{O} = 0.1$ molar	(b)		
CoCl^{\dagger}	(4)	Anhydrous		
CoCl_2	(3)	Cl/Co ratio of 1 to 1000	(c)	1.0×10^2
	(1)	Lower water concentrations		
	(2)	Cl/Co ratio of 1 to 250		
	(4)	All regions		
CoCl_3^-	(3)	Cl/Co ratio of 2.5 to 1000	(c)	1.0×10^2
	(2)	Cl/Co ratio of 10 to 1000		
CoCl_4^{--}	(3)	Cl/Co ratio of 100 to 1000		
	(2)	Cl/Co ratio of 100 to 1000		

* (1) $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$; (2) $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$
 (3) $\text{Co}(\text{ClO}_4)_2\text{-LiCl-2-octanol}$; (4) $\text{Co}(\text{ClO}_4)_2\text{-CoCl}_2\text{-2-octanol}$



Although relatively little work was done using the conductance approach because of experimental limitations, some comparison of the results obtained by this method and those obtained by spectrophotometric methods is possible. As has been pointed out, conductance measurements in the system $\text{CoCl}_2\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ showed marked changes in conductance at water-to-cobalt ratios of 2:1 and 10:1. (See Fig. 2). This corresponds closely to the numbers of water molecules coordinated in the complexes $\text{CoCl}(\text{H}_2\text{O})_2^+$ and $\text{Co}(\text{H}_2\text{O})_{13}^{++}$ as determined by spectrophotometric studies in 2-octanol. Although the solvent systems are not the same, it seems quite possible that these complexes may exist in other similar solvents but in different concentration ranges.

It is also quite interesting to note that all of the chloro-complexes which have been positively reported in the literature have been found in this investigation. Since most of the studies of this nature have been made over much narrower concentration ranges than those covered here, it seems likely that the majority of the apparently conflicting findings of other workers are valid but have not been correctly compared.

SUMMARY

The method of continuous variations was used in a study of the system $\text{CoCl}_2\text{-Co}(\text{ClO}_4)_2\text{-2-octanol}$ and indicated the existence of a monochloro-complex of cobalt(II).

Spectrophotometric studies gave qualitative evidence for the existence of the complexes $\text{Co}(\text{H}_2\text{O})_{13}^{++}$, $\text{CoCl}(\text{H}_2\text{O})_2^+$, and CoCl_2 in the systems $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$ and $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$. The best values of the equilibrium constants for the reactions $\text{Co}(\text{H}_2\text{O})_{13}^{++} + \text{Cl}^- \rightleftharpoons \text{CoCl}(\text{H}_2\text{O})_2^+ + 11\text{H}_2\text{O}$ and $\text{CoCl}(\text{H}_2\text{O})_2^+ + \text{Cl}^- \rightleftharpoons \text{CoCl}_2 + 2\text{H}_2\text{O}$ were determined from spectrophotometric data to be 72 and 3.16×10^2 respectively.

Qualitative spectrophotometric evidence was obtained for the existence of the complexes CoCl_2 , CoCl_3^- , and CoCl_4^{--} in the systems $\text{Co}(\text{ClO}_4)_2\text{-LiCl-2-octanol}$ and $\text{Co}(\text{ClO}_4)_2\text{-LiCl-H}_2\text{O-2-octanol}$. The chloride to cobalt ratio was varied from 0 to 250 for the hydrated system. An equilibrium constant for the reaction $\text{CoCl}_2 + \text{Cl}^- \rightleftharpoons \text{CoCl}_3^-$ was determined from data in the anhydrous system to be approximately 1.0×10^2 .

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Master of Science

Thesis: A STUDY OF THE FORMATION OF AQUO- AND CHLORO-COM-
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Major: Chemistry

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THESIS TITLE: A STUDY OF THE FORMATION OF AQUO- AND
CHLORO-COMPLEXES OF COBALT(II) IN
2-OCTANOL AND ETHANOL

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