

SPECTROPHOTOMETRIC STUDY OF COBALT (II) CHLORIDE IN OCTANOL-2

By

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NATURE AND PURPOSE OF PROBLEM

In recent years much attention has been given the field of inorganic salt separation by means of liquid-liquid extraction. Among the important problems in salt separation is the separation of nickel-cobalt (1) mixtures, since these elements often appear together in nature. Due to the differential that exists in the market price of the two metals, it is desirable to find an economical and rapid method of separation.

To gain an understanding of the fundamentals of the extraction of cobalt by organic liquids, it is evident that information concerning the nature of cobaltous complexes in the organic phase is necessary. Since octanol-2 has a high separation factor for the selective extraction of cobalt from aqueous solutions of nickel and cobaltous chlorides, the method of continuous variations is applied to the problem of determining the composition of the molecular species in octanol-2 solutions of cobaltous chloride.

Historical

Although much interest and curiosity has been shown in the color changes of cobaltous chloride in various solvents, little conclusive evidence has been obtained which explains this behavior. It has been generally assumed by most workers that the variety of colors observed is due to complex ion formation. This assumption is not entirely groundless since, in 1904 Bassett and Donnan (2) showed that in a blue aqueous solution of cobaltous chloride the blue color migrated on electrolysis to the anode, proving the blue-colored species had associated with it a negative charge. Further evidence of complex formation came from the measurements of transport numbers by Kohlschutter (3) and electrical and optical measurements by Groh (4). These workers concluded that when either zinc or mercuric chloride is added to an alcoholic solution of cobaltous chloride the solution turns pink due to the fact that zinc and mercuric ions have a stronger tendency to form complexes than does cobaltous ion, thereby reforming the pink cobaltous ion. However, there is another theory which has received some recognition. Instead of explaining the blue color on the basis of complex formation this attributes these color changes to differences in hydration (5).

It is also interesting to note that even the adherents of the complex theory are not in complete agreement as to the probable complex responsible for the blue color shown by these cobaltous compounds in various solvents. Thus Wormser (6) believed, on the basis of his conductivity measurements, that the colored complex was a trichloro

anion in acetone; while Barbinok (7) on the basis of spectrophotometric studies believed a tetrachloro complex was formed in the same solvent.

Recently however, Katzin and Gerbert (8) have shown the work done by Barbinok to be in error because of his incomplete data and have substantiated the results of Wormser that the complex largely responsible for the blue color in acetone is the trichloro entity.

This is in agreement with the conclusion of Job (9) and others (2) that in aqueous solution the blue color developed by the addition of hydrochloric acid or chloride salts to cobaltous chloride is largely due to a trichloro anion. These results do not rule out the possibility of the existence of CoCl_4^{2-} ion since such complexes have been shown to exist in the solid phases which have been obtained from these blue solutions; e.g., Cs_3CoCl_5 (10). Katzin and Gerbert (8) and also Bobstelsky and Stiegler (11) have also obtained spectral evidence for such complexes in solution. Thus it can be simply demonstrated that the addition of a few drops of water to a blue solution of cobaltous chloride will rapidly change the color from blue to pink. Similarly it is observed that in the solid cobaltous compounds, those of highest hydration have a pink color while those of lower hydration are blue. These two points of view may be harmonized since the color is doubtless some function of the solvent coordination as well as chloride-complex ion formation. As a matter of fact, it appears that this is the best way at present of explaining the observation that anhydrous methanol turns pink on the addition of anhydrous cobaltous chloride. This behavior appears anomalous since solutions of cobaltous chloride in other organic solvents are blue. Indeed, Katzin and Gerbert (8) have postulated that the

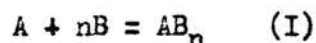
pink solution in methanol results from the cobalt having a coordination number of six whereas the cobalt in the blue state has a lower coordination number, probably four.

Theoretical

The problem of determining the composition of a complex ion by absorption spectrophotometry has been thoroughly investigated. The methods which have been described are applicable under a variety of experimental conditions so that while the choice of any one may not be the best in all cases, the spectrophotometric method is still a powerful tool in the study of colored species in solution. Recently an excellent critical review of the principal methods used in determining the composition of colored complexes has been published (12). The methods best adaptable are the slope ratio method of Harvey and Manning (12), the molar ratio method of Yoe and Jones (13), the unit slope method of Bent and French (14), the method of Edmonds and Birnbaum (15), and the method of continuous variations of Job (16). The principles upon which each of these is based and the conditions best suited for their use are discussed in the paper referred to above.

The method of continuous variations of Job (16), extended by Vosburgh and Cooper (17) and Katzin and Gerbert (8), was selected to study the nature of cobaltous complexes in octanol-2. This method has the advantage of providing information concerning the number of colored compounds which may be formed as well as their compositions. The analysis described in the following section is the extension of Job's method by Vosburgh and Cooper.

The formation of many complex ions can be represented by the simple equation



in which A is a metallic ion and B may either be a molecule such as ammonia or an anion. The coefficient n then can be evaluated by measuring a suitable

property of the system as the proportions of A and B are continuously varied. Molar solutions of A and B are mixed in varying proportions, and the difference (Y) between each measured value and the corresponding value calculated on the assumption that no reaction occurs on mixing is plotted against the composition. The resulting curve should have a maximum if the property measured has a larger value for the complex ion than for either A or B or a minimum if it has a smaller value. Job has shown that the composition at which (Y) is a maximum or minimum bears a simple relationship to n in equation (I) and is independent of the equilibrium constant, provided a single compound is formed.

If the molar concentrations of A and B are not the same, the position of the maximum is a function of the equilibrium constant as well as n . If n is known and the stability of the complex is not too great it is possible to calculate the equilibrium constant of the complex. In this way, for example, Betts and Michels (18) have determined the ionic association of uranyl nitrate and sulfate.

Job noted that the method of continuous variation is not generally applicable to a system in which more than one compound is formed. However, Vosburgh and Cooper and also Katzin and Gerbert have shown that the method could be extended to cover the formation of two or more complexes under special conditions.

Following Vosburgh and Cooper if one adds x liters of B to $(1-x)$ liters of A, (x l), with no appreciable change in volume on mixing, and if c_1 , c_2 , and c_3 are the concentrations of A, B, and AB_n respectively, then for any mixture the following equations hold:

$$c_1 = M(1-x) - c_3 \quad (1)$$

$$c_2 = Mx - nc_3 \quad (2)$$

$$c_1 c_2^n \stackrel{\sim}{=} K c_3 \quad (3)$$

The conditions for a maximum in the c_3 vs. x curve is

$$\frac{dc_3}{dx} = 0 \quad (4)$$

Differentiation of equations (1), (2) and (3) and combination of the resulting differential equations with equations (1) and (4) gives

$$n = \frac{x}{1-x} \quad (5)$$

A determination of the values of x for which c_3 is a maximum allows the calculation of n in equation (I) by equation (5). It is now necessary to show that a maximum (or minimum) in the absorption of monochromatic light when x is varied coincides with the maximum of c_3 . If e_1 , e_2 and e_3 are the extinction coefficients of A, B and AB_n at a given wave length, the optical density, E , is

$$E = d(e_1 c_1 + e_2 c_2 + e_3 c_3) \quad (6)$$

where d is the length of the path of the light through the solution.

If one lets Y be the difference between E of equation (6) and the optical density the solution would have had if there had been no reaction on mixing the solutions of A and B, then

$$Y = d [e_1 c_1 + e_2 c_2 + e_3 c_3 - e_1 M(1-x) - e_2 Mx] \quad (7)$$

By differentiation of equation (7) with respect to x it can be shown that Y is a maximum when c_3 is a maximum if $e_3 > e_1$, or a minimum when c_3 is a maximum if $e_3 < e_1$.

Similarly if two complexes are formed:



and the concentration of the second complex is c_4 , then the set of equations describing the system become

$$c_1 = M(1-x) - (c_3 + c_4) \quad (8)$$

$$c_2 = Mx - (nc_3 + (n+q)c_4) \quad (9)$$

$$c_1 c_2^n \stackrel{\sim}{=} Kc_3 \quad (10)$$

$$c_3 c_2^q \stackrel{\sim}{=} K'c_4 \quad (11)$$

The condition for a maximum in c_3 can be shown to be

$$n = \frac{x}{1-x} + \frac{q(q+n)}{M(1-x)} c_4 \quad (12)$$

and the condition for a maximum in c_4 :

$$(n+q) = \frac{x}{(1-x)} - \frac{nq}{M(1-x)} c_3 \quad (13)$$

If the stability of the two complex ions is such that when c_3 is a maximum c_4 is small, n can be determined, provided that the maximum in c_3 can be found experimentally. Similarly, it can be shown that $(n+q)$ can be determined from the composition corresponding to a maximum in c_4 provided that c_3 is small.

The use of optical density for the analysis of complex ions is much more complicated if more than one compound is formed. However, if the extinction coefficient of B is zero, which is often the case, the optical density of any of the solutions is given by

$$E = d(e_1 c_1 + e_2 c_2 + e_3 c_3 + e_4 c_4) \quad (14)$$

and the difference, Y, is given by

$$Y = d [e_1 c_1 + e_3 c_3 + e_4 c_4 - eM(1-x)] \quad (15)$$

Differentiation of equation (15) and combination with

$$\frac{dc_1}{dx} = -M - \frac{dc_3}{dx} - \frac{dc_4}{dx} \quad (16)$$

gives

$$dY/dx = d [(e_3 - e_1) dc_3/dx + (e_4 - e_1) dc_4/dx] \quad (17)$$

In general the maximum (or minimum) value of Y will not coincide with the maximum in either c_3 or c_4 , since it is not necessary for either dc_3/dx

or dc_4/dx to be zero when dY/dx is zero. Furthermore, the value of x at which dY/dx is zero should vary with extinction coefficients and therefore with the wave length used.

Vosburgh and Cooper have called attention to some useful special cases in the application of equation (17). If the wave length can be chosen so that $e_4 = e_1$, and $e_3 \neq e_1$, the maximum in Y corresponds to the maximum in c_3 . Also, if the wave length is such that $e_3 = e_4$ the same is approximately true, provided that the complex ions are highly stable. The condition for a maximum Y is then

$$dc_3/dx + dc_4/dx = 0 \quad (18)$$

When c_4 and dc_4/dx are small, as they must be when c_3 is a maximum (if compound AB_n is highly stable), the maximum in Y corresponds approximately to the maximum in c_3 .

It can further be shown that a somewhat different and useful Y function is a maximum when c_4 is a maximum, provided that e_4 is considerably larger than e_3 . Beyond the point of maximum AB_n concentration, as more B is added, AB_{n+q} is formed from AB_n . If $e_4 = e_3$, this reaction causes no change in light absorption, but if e_4 is enough larger than e_3 , the optical density of the solution will continue to increase after c_3 is a maximum in spite of the continuous dilution of the solution as B is added. The function Y' is defined as the difference between the actual optical density and the density calculated on the assumption that all A has been converted to AB_n , but that latter does not react further with B . If it is assumed further that the complex ions are so stable that when considerable AB_{n+q} is present there is no appreciable A left uncombined, the condition for maximum Y' can be shown to be

$$(e_4 - e_3) dc_4/dx = 0$$

and since $e_4 - e_3$ is finite, dc_4/dx must be equal to zero and c_4 must either be a maximum or minimum.

Experimental

A. Apparatus

Spectrophotometric measurements were made with the Beckman model DU quartz Spectrophotometer using correx glass cells of 1.000 cm. thickness.

B. Materials

Cobalt perchlorate hexahydrate was prepared from "reagent" grade cobaltous carbonate and "Chemically Pure" grade perchloric acid by carefully neutralizing the acid with the carbonate until a slight amount of solid carbonate remained. The solution after filtration was evaporated until rose crystals of the hexahydrate appeared. This was recrystallized twice. Several attempts then were made to prepare the anhydrous salt. The moist crystals formed from the original preparation were dried at a temperature of about 50°C for twelve hours in an oven, and the product on analysis was found to be the hexahydrate. Further heating at about 80°C yielded the tetrahydrate. Heating to a still higher temperature in an oven resulted in the slow decomposition of the cobalt perchlorate tetrahydrate to a black solid believed to be Co_3O_4 .

It was then decided to attempt the dehydration under vacuum at constant temperature. The apparatus used for this treatment was the conventional vapor-jacketed vacuum drying pistol. The temperature was changed by one- or two-degree increments through the proper selection of boiling liquids.

Using the tetrahydrate obtained from air drying of the hexahydrate and starting at a temperature of 110°C, the temperature was gradually raised to the decomposition temperature which was found to be about 143°C

under a pressure of less than 1 mm Hg. No observable change in color was noticed until a temperature of 129°C was reached, and at this point the light purple color could be seen to turn a slightly darker purple. This deepening of color could be seen to become more and more pronounced as the temperature was increased until in the range 138-143°C no further change could be detected in the appearance of the sample. The darkening in the color, however, was not produced by an admixture of black Co_3O_4 and rose tetrahydrate. All samples were dried for not less than 24 hours to assure that slow decomposition was not taking place.

The product formed at 138°C was found to have consistently the same composition on the basis of analyses for cobalt and perchlorate. For example the results of analyses on three separate preparations gave formula weights of 299.3, 299.3, and 299.4. The formula weight of $\text{Co}(\text{ClO}_4)_2$ is 257.8 so that the formula assigned to this product was $\text{Co}(\text{ClO}_4)_2 \cdot 2.30 \text{H}_2\text{O}$. A search of the literature showed that either anhydrous cobaltous perchlorate does not exist or has not been prepared in amounts or of purity sufficient for characterization (19) (20) (21). Analyses for cobalt were made by precipitation with *o*-nitroso- β -naphthol and ignition to Co_3O_4 . Analyses for perchlorate were made by precipitation of potassium perchlorate in anhydrous ethanol.

The lithium chloride was "Chemically Pure" grade and was dried at a temperature of 110°C for several hours.

The octanol-2, obtained from Eastman Kodak Company, was ketone-free as well as anhydrous. No further purification was made on the alcohol.

C. Procedure

Individual stock solutions of the two salts LiCl and $\text{Co}(\text{ClO}_4)_2$ were made carefully by rapid weighing to minimize the tendency of these substances to pick up water. The two solutions were made up to be of equal molality as required by the continuous variation method. Three series of these stock solutions were prepared: (1) Molality equal to 4.25×10^{-3} . This solution was found to be too dilute since the maximum light absorption was found to be only of the order of 30%. (2) Molality equal to 38.5×10^{-3} . This solution also proved unsatisfactory since it was too concentrated to transmit light over all of the spectrum studied. (3) Molality equal to 12.7×10^{-3} . This solution had a maximum absorption of around ninety per cent, thereby permitting the desired details of the absorption curves to be studied and increasing the accuracy of the measurements.

Fifteen separate solutions were prepared from the stock solutions by weighing out a definite quantity of each into a small calibrated flask; the total quantity of the component solutions was kept constant at 5.09 ± 0.01 g. throughout. In this manner the fraction x , defined by $x = \frac{\text{g. LiCl solution}}{5.09 \text{ g.}}$ is varied from $x = 0$, corresponding to pure cobaltous perchlorate solution, to $x = 1$, corresponding to pure lithium chloride solution. Since the stock solutions contain equal numbers of formula weights of the salts per gram, the fraction x is also the mol fraction of lithium chloride in the mixture.

The absorption spectra of these solutions were determined in the visible region of the spectrum from 400 μ to 700 μ as a function of x . These data and their significance will be discussed in the following section.

Discussion of Results

The absorption spectrum of cobaltous perchlorate from 400 μ to 700 μ was obtained at several different concentrations in order to determine whether or not the Beer-Lambert Law held at certain wave lengths. The results indicated that the law was followed as can be seen from the curves in Figure I computed from the data given in Table I. Curve (e) in Figure II is the spectrum of pure lithium chloride.

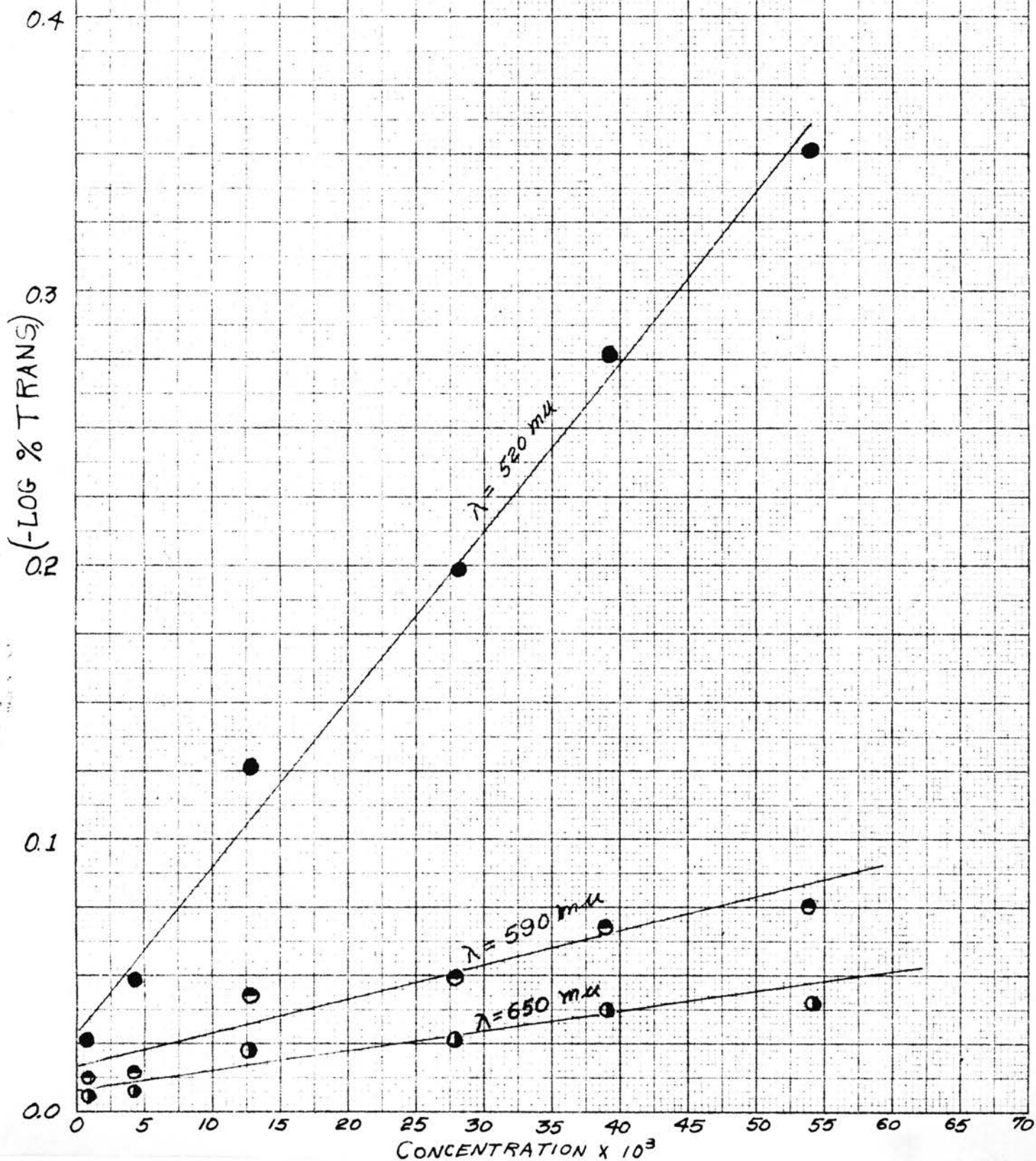
Curves (a) to (k) in Figure II are plots of the spectrum for various mixtures of cobaltous perchlorate and lithium chloride in octanol-2. These different mixtures of the two salts are identified by their x value which is, as pointed out before, equal to the mole fraction of lithium chloride. A glance at Figure II enables one to locate three well defined absorption maxima, the principal one being located between 650 to 670 μ and two less distinct absorptions at 570 to 580 μ and at 460 to 480 μ . A closer study of the curves also shows a slight wiggle around 610 to 620 μ . The significance of these absorption maxima will be discussed later. Table II gives in tabular form the same information shown in Figure II. Table III is similar to Table II differing only in the concentrations.

It is obvious from the curve for pure lithium chloride that its absorption in the visible region is negligible, so we may assume that its extinction coefficient, e_2 , is zero. By making this assumption, our calculations are considerably simplified. However, in the case of pure cobaltous perchlorate the absorption is too great to assume its extinction coefficient to be zero. It is now possible to define our simplified Y function

$$Y = d(e_1c_1 + e_3c_3 - e_1M(1-x))$$

FIGURE I

Pure $\text{Co}(\text{ClO}_4)_2$ IN OCTANOL-2



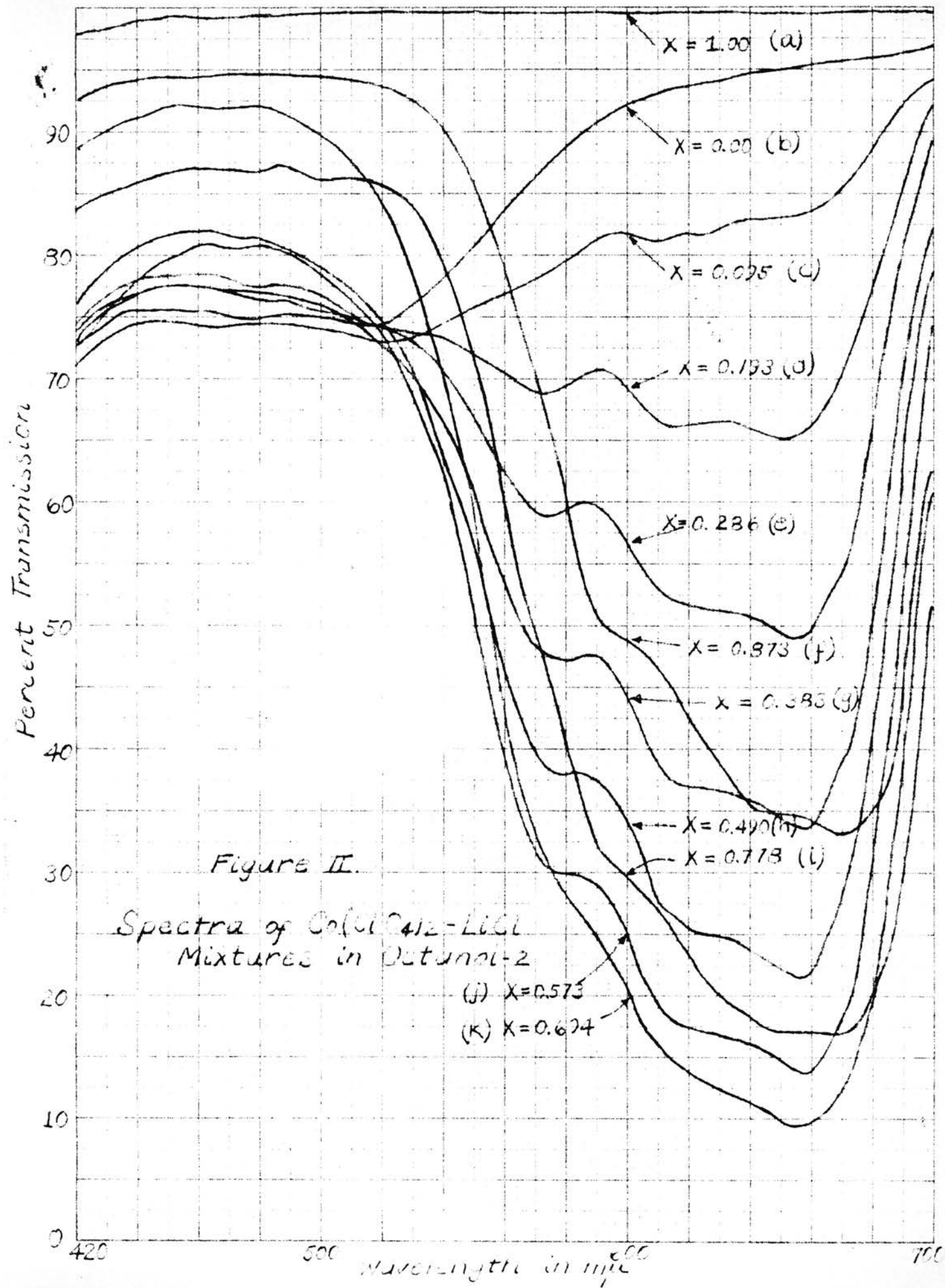


Table I

Values of Percent Transmission for Pure $\text{Co}(\text{ClO}_4)_2$

Molality	Wave Lengths (in μ)		
	520	590	650
1.005×10^{-3}	94.0	97.1	98.5
4.25×10^{-3}	89.1	96.7	98.2
12.7×10^{-3}	74.4	90.6	94.8
28.2×10^{-3}	63.2	89.5	94.1
38.0×10^{-3}	52.2	85.2	91.6
54.0×10^{-3}	44.2	83.8	91.0

Table II (cont.)

<u>X</u>	520	510	500	490	480	470	460	450	440
0.00	74.4	74.3	75.0	75.0	74.9	75.0	75.1	75.3	75.4
.0955	72.9	73.2	73.7	74.0	74.2	74.0	74.1	74.2	73.9
.193	74.0	74.9	75.3	76.0	76.4	76.8	76.9	77.3	77.0
.286	74.0	75.2	76.3	77.1	77.2	77.7	78.0	78.2	77.8
.383	72.4	74.1	75.5	76.3	76.8	76.8	77.2	77.3	76.6
.490	74.3	76.8	78.8	80.0	80.7	81.0	81.4	81.1	80.2
.574	73.2	76.1	78.1	79.7	80.2	80.2	80.8	80.5	79.4
.584	74.4	76.8	78.5	79.6	80.4	80.9	80.9	80.9	80.0
.619	74.8	77.8	80.0	81.3	82.1	82.5	82.8	82.5	81.7
.6495	74.3	77.3	78.8	80.3	80.7	80.6	80.5	79.9	79.1
.6935	84.1	87.2	89.3	90.6	91.6	91.6	91.8	91.6	91.0
.722	86.3	89.5	91.5	93.0	93.7	93.9	94.2	94.1	93.9
.779	84.9	86.0	85.7	86.9	86.5	86.5	86.5	86.4	85.8
.8725	93.2	93.8	94.3	94.4	94.5	94.3	94.3	94.3	93.9
.881	94.8	96.0	96.1	96.5	96.7	96.6	96.7	96.7	96.3
.952	97.1	97.8	98.1	97.8	98.0	97.9	97.7	97.6	97.1
1.00	99.8	99.8	99.8	99.7	99.5	99.4	99.3	99.3	99.0

<u>X</u>	430	420	410	400
0.00	74.3	72.7	69.7	66.2
.0955	72.8	70.6	67.5	64.0
.193	75.8	73.8	70.6	67.2
.286	76.3	74.2	71.1	67.5
.383	75.4	72.7	69.7	66.0
.490	78.7	75.8	72.8	69.3
.574	77.8	74.9	72.1	68.1
.584	78.3	75.9	73.1	69.4
.619	79.9	77.4	74.4	70.9
.6495	77.2	74.8	72.1	68.4
.6935	89.9	88.4	86.6	84.6
.722	93.1	92.3	91.3	89.7
.779	84.7	83.3	81.7	79.3
.8725	93.4	92.3	91.4	89.8
.881	96.0	95.5	95.2	94.6
.952	96.9	96.9	96.2	96.2
1.00	98.4	97.8	92.0	91.2

Table III

Values of Percent Transmission of $\text{Co}(\text{ClO}_4)_2\text{-LiCl}$ -Mixtures

$$M = 4.25 \times 10^{-3}$$

Wave Length	X Value					
	0.00	.098	.194	.292	.39	.515
700	99.3	99.7	97.8	97.8	96.7	97.8
690	99.1	99.3	97.2	96.8	95.1	95.5
680	98.8	99.2	96.6	95.3	92.8	91.3
670	98.8	98.8	95.7	93.7	90.0	86.8
660	98.7	98.4	91.1	92.5	87.8	83.7
650	98.2	97.8	94.8	92.3	87.6	83.3
640	98.1	98.4	94.6	92.7	87.8	83.9
630	98.0	97.9	94.3	92.5	87.9	84.3
620	97.8	97.7	94.3	92.3	87.8	84.3
610	97.3	97.8	94.1	92.1	87.7	84.4
600	97.1	97.2	93.9	92.6	88.6	86.2
590	96.7	96.9	93.7	92.6	89.2	87.5
580	96.0	96.3	93.2	92.1	88.9	87.3
570	95.4	95.6	92.5	91.7	88.3	85.3
560	94.2	94.9	91.9	91.3	88.3	88.5
550	92.9	93.8	90.9	91.1	89.2	90.0
540	91.7	92.6	90.1	90.8	89.2	91.2
530	90.3	91.4	89.2	90.1	89.1	91.8
520	89.1	90.6	88.6	89.8	88.8	91.9
510	88.4	89.9	87.9	88.9	88.7	92.4
500	88.2	89.7	87.8	89.2	88.6	92.2
490	88.1	89.8	87.7	89.2	87.8	92.8
480	87.9	89.5	87.4	89.1	88.5	92.3
470	87.2	89.5	87.3	88.9	88.3	92.1
460	86.9	89.0	87.1	88.8	88.1	92.0
450	86.9	89.0	86.8	88.5	87.9	92.2
440	86.3	88.7	86.4	88.2	87.7	91.7
430	85.8	87.8	85.6	87.3	86.9	91.0
420	84.7	86.7	84.5	86.4	86.2	90.1
410	83.1	85.2	83.2	85.3	84.8	88.8
400	81.4	83.8	81.7	---	82.3	87.4

Table III (cont.)

Wave Length	X				
	.578	.685	.793	.872	1.00
700	96.8	95.3	94.7	96.3	98.8
690	93.7	91.5	89.1	92.9	
680	87.7	83.8	82.3	87.9	
670	81.7	75.7	75.1	83.9	
660	77.6	70.7	71.1	81.2	
650	77.2	70.1	70.8	81.0	99.0
640	78.4	71.3	72.1	82.0	
630	78.8	72.0	72.9	82.7	
620	78.9	72.3	73.7	83.2	
610	79.3	73.2	74.3	83.9	
600	81.8	75.9	77.0	85.3	99.0
590	83.8	79.3	79.7	87.0	
580	83.8	79.5	80.7	88.1	
570	84.2	80.3	81.8	89.1	
560	85.9	83.4	84.7	91.0	
550	88.1	87.0	88.4	93.5	99.0
540	90.7	90.2	91.2	95.0	
530	91.9	92.3	93.0	96.1	
520	92.3	93.1	93.7	96.8	
510	92.7	93.7	94.7	96.8	
500	92.8	93.8	94.3	96.7	99.0
490	93.0	94.2	94.3	96.7	
480	93.1	93.9	94.2	96.7	
470	92.2	93.8	94.0	96.3	
460	92.8	93.5	93.8	96.0	
450	92.7	93.5	93.2	95.5	99.0
440	92.4	93.2	92.7	95.5	
430	91.9	92.5	91.9	94.5	
420	91.1	91.8	91.2	93.9	
410	89.9	90.6	90.1	93.3	
400	88.7	89.3	88.8	92.6	98.0

Table IV
Values of Y'

X	Wave Lengths		
	640	660	670
0.00	-2.516	-2.120	-2.931
.0955	-2.213	-1.818	2.629
.193	-1.87	-1.469	2.300
.286	-1.514	-1.114	1.956
.383	-1.123	- .703	1.567
.490	- .674	- .240	1.140
.584	- .335	+ .102	- .828
.619	- .079	+ .203	- .570
.722	+ .159	.618	- .282
.779	+ .181	.611	- .193
.8725	.123	.539	- .234
.881	.122	.530	- .252
.952	.086	.491	- .297
1.00	0.00	0.00	0.00

Plots of \underline{Y} against \underline{x} at four different wavelengths are shown in Figure III. Two points of interest immediately present themselves. First, the composition at which the maximum occurs has an \underline{x} value between 0.72 and 0.74 mole fraction of lithium chloride. The average value of \underline{x} for which \underline{Y} has a maximum is 0.725. In an earlier section it was shown that if only one complex is formed from two reactants, \underline{n} is defined by the equation

$$n = \frac{x}{1-x}$$

If the average value of \underline{x} is substituted in the above equation, we obtain a value of 2.64 for \underline{n} .

Second, the position of the maximum appears to vary slightly with wavelength, which indicates, as was pointed out earlier in the theory of the method of continuous variations, that more than one complex is present.

Since we have evidence for the formation of more than one compound, it is now convenient to define a simplified \underline{Y}' function

$$Y' = d [e_3c_3 + e_4c_4 - e_3M(1-x)]$$

The last term in this expression was calculated from data obtained on a sample of pure anhydrous cobaltous chloride dissolved in octanol-2. The extinction coefficient for the cobaltous chloride was calculated at each of the wavelengths for which the \underline{Y}' functions were evaluated. In the neighborhood of 650 m μ the values were approximately constant at 200. Figure IV is a plot of \underline{Y}' against \underline{x} for three different wavelengths. It can be seen from these curves that the maxima again have values of \underline{x} close to 0.75 from which the value of \underline{n} is calculated as 3.0. This is the theoretical value for the CoCl_2^- entity although the agreement may be fortuitous.

Figure III

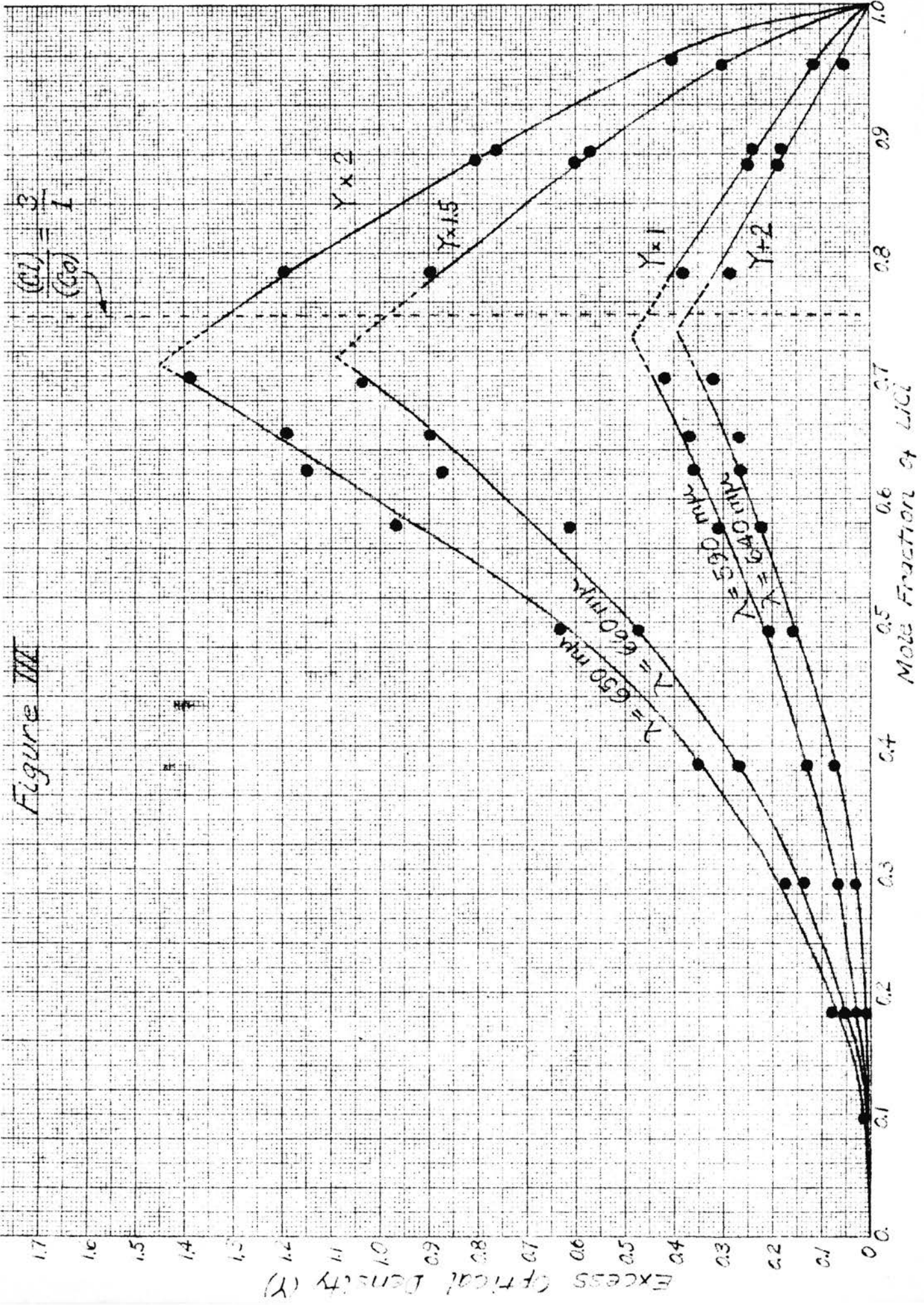


FIGURE IV

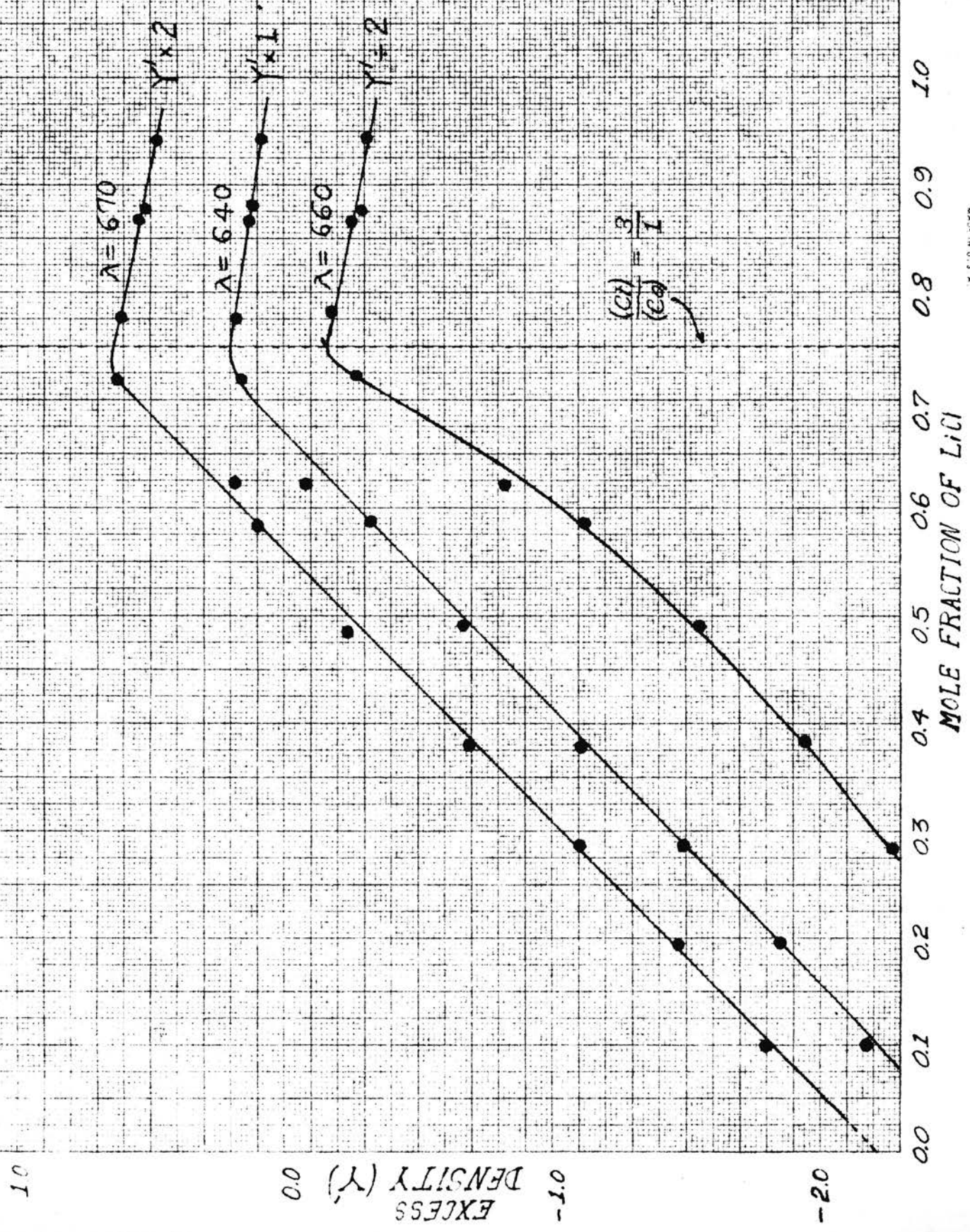
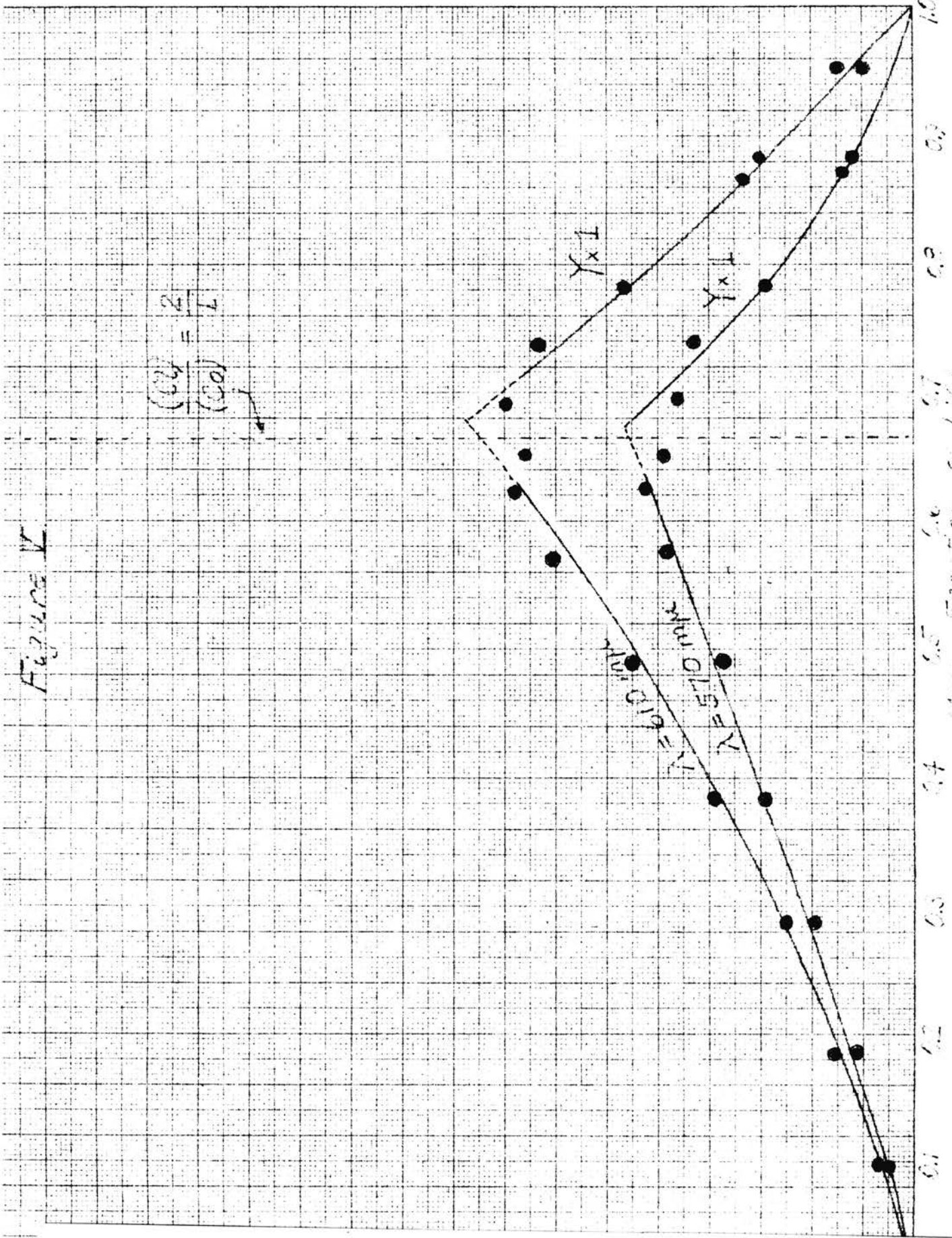


FIGURE V

$$\frac{(90)}{(90)} = \frac{2}{1}$$



The results obtained using either Y or Y' in the neighborhood of $\lambda = 640 - 670 \text{ m}\mu$ point to these absorptions as due to CoCl_3^- with possibly some contribution by CoCl_2 .

Plots of Y for wavelengths of 610 and 570 are included in Figure V. These wavelengths have been shown from studies of cobaltous chloride (8) in methanol to correspond to CoCl_2 . Our work confirms this on the basis of the position of maximum Y in Figure V. Even when the uncertainties in the extrapolation of the curves in locating the positions of the maxima are considered, the differences between the curves of Figure IV and Figure V are apparent. The slight irregularity or wiggle in the curves of Figure II in the vicinity of $\lambda = 460-480$ may be due to CoCl^+ (8), but application of the variation method was not possible at this wavelength.

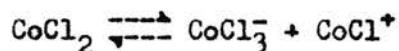
It should be noted that the portion of the curves in Figure IV lying to the right of $\underline{x} = 0.75$ has a quite small slope which causes the maximum in Y' to be only slightly above the value of Y' at $\underline{x} = 1$. This small slope combined with the experimental scatter of the points increases the uncertainty in the position of the maximum greatly.

A small slope in \underline{Y}' is to be expected if the extinction coefficients of CoCl_2 and CoCl_3^- are not greatly different since the change in \underline{Y}' would then presumably be due to the increase in the colored form, CoCl_3^- , and corresponding decrease in CoCl_2 . This assumes, of course, that the complex CoCl_3^- is stable.

The results of this investigation are not altogether convincing. On the basis of the order appearance of the various absorption peaks as one passes continuously from $\underline{x} = 0$ to $\underline{x} = 1$, one can assign to CoCl_2 the peaks at 575 and 615 $\text{m}\mu$ (in agreement with Katzin and Gerbert) which make their appearance as soon as lithium chloride is added to cobaltous perchlorate. The peak at

655 μ is probably also due to this entity although CoCl_3^- is strongly absorbing in this wave length region. The absorption at 595 is believed to be due to CoCl_3^- also. Whether the higher complex, CoCl_4^{2-} , contributes to these absorptions was not ascertained.

The analysis of these spectra by the method of continuous variations is further complicated by the possibility of disproportionation of CoCl_2



The extent to which this occurs is not known.

Reference to the fundamental equation (13) relating the formula of the complex to the value of x for which a maximum appears in the concentration of the complex shows that if two complexes are formed, *viz.*, CoCl_2 and CoCl_3^- , the maximum in \underline{Y} which corresponds to a maximum in C_4 occurs when

$$\left(\frac{x}{1-x} \right) = (q+n) + \frac{nq}{M(1-x)} C_3$$

The value of $\frac{x}{1-x}$ is then seen to be theoretically greater than the stoichiometric value $(q+n)$ by a function of C_3 . This is not in close agreement with our results since our ratio of $\frac{x}{1-x}$ actually was somewhat less than $(q+n) = 3$. The close agreement, however, between the observed and theoretical ratios for CoCl_3^- suggests that this is the principle stable colored species in the solution. The results might have been improved had the ionic strength of the solutions been maintained constant since activities enter into the equilibrium equations rather than concentrations.

Summary

The modified method of continuous variations was employed to study the system of cobaltous perchlorate, lithium chloride and octanol-2.

The visible absorption spectra for mixtures of $\text{Co}(\text{ClO}_4)_2$, LiCl and octanol-2 were obtained at fifteen different ratios of the two salts.

These data are interpreted as showing the existence of CoCl_2 and CoCl_3^- in the solutions.