A SPECTROPHOTOMETRIC STUDY OF THE AQUO COMPLEXES OF COBALT (II), COPPER (II), NICKEL (II) CHLORIDES AND PERCHLORATES IN I-BUTANOL

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1959

Submitted to the faculty of the Graduate School of the
Oklahoma State University in partial fulfillment of the
requirements for the degree of
MASTER OF SCIENCE
June, 1963

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ACKNOWLEDGEMENT

The author wishes to express appreciation to Dr. Tom E. Moore for his advice during this investigation. He also wishes to thank the Atomic Energy Commission under whose sponsorship this investigation was made possible.

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INTRODUCTION

The color of aqueous solutions of the salts of the first transition series metals is characteristic and familiar, but it is well known that alcoholic solutions of the same salts may have drastically different colors. Basically, this is due to differences within the solvation sphere of the metal. Addition of water to an anhydrous alcohol solution may thus be expected to cause a shift in the color toward that of the aqueous solution.

Evidence has been found for the existence of aquo complexes or hydrated species in hydrous alcohol solutions of salts. This evidence comes from study of such systems through a variety of techniques. In the Author's laboratory, for example, there are studies of aquo complexing involving calorimetry, electrical conductance, and electrical transport in addition to the spectrophotometric study to be described.

Since the salts of interest give highly colored species in both aqueous and nonaqueous solutions, it seemed feasible to study the hydration of such salts in solvent mixtures by spectrophotometry. A necessary assumption, therefore, is that both the non-hydrated forms and the aquo complexes have characteristic absorptions such that Beer's law is followed.

A better understanding of the conditions for the formation and stability of aquo complexes of transition metal salts in organic solvents is of direct importance in connection with liquid-liquid extraction processes in ion association systems, for the non-aqueous phases are almost always hydrous and the extracted metal probably exists as an aquo complex in most cases.

LITERATURE SURVEY

Recent interest in transition metal salt solutions in alcohols and other nonaqueous solvents containing varying amounts of water has caused a great increase in the number of papers relating to the subject of this thesis. These studies are best shown by listing in tabular form and are summarized in Table I where there is given the system studied, method applied and the conclusion of the study. Only the work most closely related to the thesis will be discussed in greater detail.

The absorption spectra of metallic ions are distinctly different according to the degree of solvation. Jones et al.(1) found that for the rare earth salts alcohol solutions containing small amounts of water showed some features of the aqueous system as well as the features of the pure alcohol system.

In general, there are two schools of thought regarding the reasons for the difference in color of a salt observed in different solvents; one holding that there is merely a change in the co-ordination number of the metal, and the other believing that stable complexes are formed between the metal and solvent of the system (2). One must realize that there may be interactions within a given system where both explanations are required to give an adequate description of the color changes. Bjerrum (3) draws attention to a powerful method for the study of complexes, known as the "method of corresponding solutions," by which the results of optical measurements can be used to determine the formation curves for complexes in solution. The applicability and limitations of the corresponding solution principle have been discussed by Woldbye (6) and Sullivan and Hindman (7). The method in principle is applicable at all wavelengths where absorption occurs (3). However, Schukarev and Lobaneva (10) believe that Bjerrum's method requires that all measurements of the absorption coefficients be carried out for the wavelength of absorption of the highest complex.

Subsequent workers have studied a variety of systems using the method of corresponding solutions (3, 4, 5). In particular the formation of aquo ions in nonaqueous solutions has received considerable attention from several authors since the color changes which occur upon the addition of water apparently are caused by changes in solvation of the central metal ions (5, 8, 9, 11, 12, 26).

Several other methods have also been applied to the study of aquo complex formation among transition metal salts. Thus, Larson and Iwanoto (9) combined electrochemical and infrared measurements to determine the average formation constants of aquo copper complexes in nitromethane and compared them to the previously determined constants of Jørgensen (5) and Minc and Libús (12). Goodrich (15) found by calorimetric studies that the reaction of water with n-butanol solutions of $CoCl_2$ and $NiCl_2$ took place in a stepwise fashion. Yates et al. (34), McManamey (37), and Libús (39) have used liquid-liquid extraction to investigate the degree of hydration of salts in nonaqueous solutions. Katzin and Ferraro (35) have used the wet residue method in a phase study of the $CoCl_2$-H_2O-acetone system to show the existence of $CoCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 3H_2O$ over a narrow range of water activity. These, in general, illustrate most of the different methods that have been utilized in studying aquo complexes, particularly in nonaqueous solutions.

Attempts have been made by several authors to deduce the structure of complexes from spectral data and magnetic studies (17, 18, 51, 52). Cotton et al. (16, 42, 43) have recently correlated the magnetic properties and the absorption spectra of tetrahedral halide complexes of Co, Ni, and Mn with their electronic structure. Ferguson (13, 14) has also attempted to relate the electronic structure of tetrahedral and octahedral complexes of cobalt with their crystal spectra.

TABLE I

INVESTIGATION OF THE AQUO COMPLEXES

Ref.	Author	System	*Method	Conclusions
1	Jones Anderson	rare earth salts in alcohol-water	(b)	Spectra of alcohol solutions containing water showed features of both aqueous and alcohol solutions.
4	Bjerrum Jørgensen	didymium chloride MeOH-water	(b)	Addition of water changes characteristics of the absorption spectrum. Spectrophotometric measurements can be used to measure affinity of water molecules and alcohol molecules to the metal salt.
5	Jørgensen	$Co(NO_3)_2$, $Ni(NO_3)_2$ $Cu(NO_3)_2$- water-EtOH	(b)	Average formation constants of the aquo complexes of Co^{++}, Ni^{++} and Cu^{++} are 1.08, 0.82 and 0.19 mole/liter respectively.
8	Katzin	$Co(NO_3)_2$, $Ni(ClO_4)_2$ water - EtOH	(b)	Change in spectrum due to cation-anion interaction and not a water-alcohol replacement.
9	Larson Iwanoto	$Cu(ClO_4)_2$-water nitromethane	(a), (b)	Average formation constants obtained agree closely with constants previously obtained (5, 12).
10	Shchukarev Lobaneva	$CoBr_2$-LiBr EtOH	(b)	Change in spectra upon addition of ligand.

TABLE I (Continued)

Ref.	Author	System	*Method	Conclusions
11	Beaver et al.	$Co(ClO_4)_2$, $CoCl_2$-$LiCl_2$-H_2O- 2-octanol, Ni^{++}- H_2O-2-octanol	(b)	Stoichiometric reaction with two water molecules with $CoCl_2$. Both Co^{++} and Ni^{++} may be polymerized in 2-octanol.
12	Minc/ Libus	$Cu(NO_3)_2$-water- EtOH	(a), (e)	Cu^{++} show a preferential solvation in aqueous solution.
13 14	Ferguson	Crystals of Cobalt Salts; $CoPy_2Cl_2$, $CoCl_2 \cdot 6H_2O$, Cs_3CoCl_5	(b)	Correlated absorption spectra with electronic structure.
15	Goodrich	Cobalt, Nickel, Copper, Chlorides and perchlorates-water-butanol	(d)	Reaction occurred in stepwise fashion.
16	Cotton			
42 43	Goodgame, L. Goodgame, M.	Ni, Co, Mn Halides in various solvents	(f), (b)	Correlated magnetic studies and absorption spectra to electronic structure.
19	Ashkinazi Kostyukova	$Cu(ClO_4)_2$-water- MeOH, EtOH, PrOH and BuOH	(b)	Different shift in spectra from a change in the solvent.

TABLE I (Continued)

Ref.	Author	System	*Method	Conclusions
20	Wormser	$CoCl_2$-LiCl Acetone-H_2O	(a)	Water molecules co-ordinate themselves to the central atom of each complex.
21	Jorgensen Bjerrum	$Co(NO_3)_2$-H_2O-EtOH	(b)	Explained disagreement with Katzin & Gebert (8).
22	Weicksel Lynch	$CuCl_2$-dioxane-water	(c)	These complexes were identified: $CuCl_2.2H_2O$-dioxane $CuCl_2.2H_2O$-2 dioxane
23	Katzin	Co^{++}, Ni^{++}, Cu^{++} nitrates-*t*-BuCH	(b)	Absorption in *t*-Butanol is vastly different from the nitrates in water.
24	Katzin Gebert	$CoCl_2$-MeOH	(b)	Absorption at 510 mu due to the hexahydrated Co^{++}ion. Blue color is presumed to be $CoCl_2$.2 solvent.
25	Katzin Gebert	$Co(NO_3)_2$ $Co(ClO_4)_2$-water-MeOH, BuOH *iso*-BuOH, PrOH, EtOH, *iso*-PrOH and several others	(b)	When excess water is added, the hexahydrated species formed.
26	Pominov Ulganov	$CuCl_2$-EtOH-water	(b)	2 Moles of water were present in the water-alcohol envelop of the copper ion.

TABLE I (Continued)

Ref.	Author	System	*Method	Conclusions
27	Mischenko Pominov	$CoCl_2$, $NiCl_2$, EtOH-water	(b)	Maximum co-ordination number is 6.
28	Bako Tananiko	$Co(NO_3)_2$-water-<u>iso</u>-amyl	(b)	Absorption decreases in addition of water. Product is $Co(H_2O)_n^{++}$ or $CoCl_3(H_2O)_n^-$ where n is 5 or 3, respectively.
29	Sergeeva Dement'ev	$CuCl_2$-water-EtOH	(b)	Addition of alcohol to aqueous system causes a displacement of the absorption maximum and increase in optical density.
30 31	Minc Libus	Cu^{++}, Co^{++} nitrates-H_2O-EtOH, <u>iso</u>-PrOH, PrOH	(b)	Change in spectra caused by the change in the composition of the solvation cation layers.
32	Minc Libus	$Cu(NO_3)_2$-water-EtOH	(b)	Extinction maximum at 790 and 910 mu. Cu shows a preferential solvation in aqueous solutions.
33	Katzin Ferraro	$Cu(NO_3)_2$-water-MeOH	(d)	Transition of tetrasolvated neutral molecule to the hexasolvated entity.
34	Yates, et al.	$LiCl_2$, $CuCl_2$, $ZnCl_2$, $Ni(ClO_4)_2$ and $Co(ClO_4)_2$-water-2-octanol	(g)	Perchlorates had extremely high hydration numbers in comparison with corresponding chlorides.

TABLE I (Continued)

Ref.	Author	System	*Method	Conclusions
35	Katzin Ferraro	$CoCl_2$-water-acetone	(c)	Showed that $CoCl_2.3H_2O$ and $CoCl_2.4H_2O$ existed over narrow range of water activity.
37	McManamey	$Co(NO_3)_2$, $Zn(NO_3)_2$-H_2O-, Butanol, Hexanol, Heptanol, $CoCl_2$, $NiCl_2$-H_2O-BuOH	(g)	Determined the apparent hydration number of the salts by solvent extraction.
38	Minc Jastrzebska	$Cu(NO_3)2$-H_2O-MeOH	(a)	Gradual change in the potential shows a slow replacement of water for MeOH in the solvating sphere around the Cu^{++} ion.
39	Libús, W. Siekierska Libús, Z.	Co, Ni, Cu nitrates-H_2O-butyl, amyl, <u>iso</u>-amyl and octyl alcohols	(g)	Partition coefficient depends upon the kind and number of the co-ordinated ligands.
40	Libus, W.	$CoCl_2$, $CuCl_2$-water-, EtOH, PrOH, <u>iso</u>-PrOH	(b)	Rapid changes in absorption occur when water is present in a 0 to 50% mixture and slow changes occur after this value.
41	Pominov	$CuCl_2$-H_2O-EtOH, MeOH	(b)	Degree of hydration depends upon concentration in aqueous EtOH solutions.

TABLE I (Continued)

*Methods

(a) Electrometric
(b) Spectrophotometric
(c) Phase studies
(d) Calorimetric
(e) Pycnometric
(f) Magnetic studies
(g) Extraction studies

EXPERIMENTAL

A. Reagents

Nickel chloride was recrystallized from C.p.-grade hydrated salt. The anhydrous $CoCl_2$ was prepared by drying the dihydrate in a vacuum oven at 120° for several hours. Anhydrous Reagent grade $CuCl_2$ was purchased from the Fisher Scientific Company.

Anhydrous silver perchlorate, used in making cobalt, copper and nickel perchlorates was prepared by drying Reagent-grade silver perchlorate in an oven at 90° for several hours.

Anhydrous butanol was prepared from Fisher's Reagent-grade *n*-butanol by first refluxing with a small amount of magnesium turnings and iodine and then distillation according to the method of Lund, Hakon and Bjerrum (44).

B. Preparation of Stock Solutions

Anhydrous solutions of cobalt chloride and copper chloride were prepared by weighing the respective anhydrous salt and dissolving it in the butanol. Heating the solution aids in dissolving the salt. The anhydrous nickel chloride solution was prepared by adding nickel dihydrate to the butanol, heating the solution under a reduced pressure, and stripping off the excess water present as an azeotrope, b.p. = 92°. All the solutions were stored in glass bottles with polyethylene screw caps.

Anhydrous solutions of cobalt, copper and nickel perchlorate in butanol were prepared by the metathesis of anhydrous silver perchlorate with stoichiometric quantities of cobalt, copper and nickel chlorides dissolved in butanol. The perchlorate solutions were carefully decanted into glass bottles which were then sealed to keep out moisture. Any residual AgCl was removed by centrifugation.

Tervorrow (45) showed by determining the quantity of silver chloride precipitated in such a preparation that the reaction may be considered as quantitative.

All equipment used in the preparation of the stock solutions were oven-dried and other necessary precautions were taken to insure anhydrous solutions.

The stock solutions prepared were:

Nickel Chloride	-	0.112	Molar
Copper Chloride	-	0.0196	"
Cobalt Chloride	-	0.0873	"
Nickel Perchlorate	-	0.0628	"
Copper Perchlorate	-	0.118	"
Cobalt Perchlorate	-	0.0957	"

All other solutions were prepared by proper dilution of the stock solutions.

C. Analytical Procedures

The determination of water in the butanol solutions was made by a Karl Fischer titration (46) using a dead-stop endpoint. The concentrations of the salt solution were determined by aqueous ethylene diaminetetraacetate (EDTA) titration using the methods described by Flaschka (47). Butanol solutions could be similarly titrated after first solulibilizing with ethanol.

D. Apparatus

The spectrophotometric studies were carried out employing either the Beckman Model DU quartz spectrophotometer or the Beckman Model DK-1 recording quartz spectrophotometer. Corex cells of 5 cm, 2 cm, and 1 cm path length were used in this study. Also a 0.9 cm quartz wedge was used on extremely optically dense solutions.

E. Procedure

The optical density of the salt solutions was measured using anhydrous butanol as the reference solution. Addition of water to anhydrous samples was facilitated by using a micro buret fitted to a micrometer graduated in one ten-thousandth milliliter divisions. Water was added either directly to a sample or to aliquot of the sample so as to increase the water concentration. The cells were fitted with either rubber or glass stoppers to exclude the moisture from the air being absorbed during the measurements.

TREATMENT OF DATA

The method used to determine the extent of aquo complex formation in the systems of metallic ions investigated in this research was developed by Bjerrum (3). The method is called the "Method of Corresponding Solutions," for reasons which will become apparent.

For a series of reactions in which complexes are formed in a stepwise manner (3, 4, 6) i.e.

$$\begin{aligned} &M + A \rightleftharpoons MA \\ &MA + A \rightleftharpoons MA_2 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \qquad (1) \\ &MA_{N-1} + A \rightleftharpoons MA_N \end{aligned}$$

it is possible to determine the free ligand concentration and consequently the equilibrium constants by measuring the amount of light absorption of the system.

This method is applicable when (a) a ligand's own absorption is negligible in comparison to that of the complex and (b) measurements are carried out in a salt medium at high concentration of a neutral salt so that the law of mass action holds and Beer's law applies to the individual complexes (3, 6, 7).

It is possible to develop an expression for the formation function which depends only on the concentration of the free ligand (3).

Using the following notation:

(A) = Concentration of free ligand

(MA_n) = Concentration of molecular type MA_n

N = Maximum co-ordination number

$C_M = \sum_0^N (MA_n)$ Total concentration of central group

$C_A = (A) + \sum_0^N n\,(MA_n)$ Total ligand concentration

$\bar{n} = \frac{C_A - (A)}{C_M} = \frac{\sum_0^N n\ (MA_n)}{\sum_0^N (MA_n)}$ The formation function of the system - the average number of ligands bound to the central group

$K_n = \frac{(MA_n)}{(MA_{n-1})\ (A)}$ Consecutive complexity constant corresponding to the equilibrium $MA_{n-1} + A \rightleftharpoons MA_n$

$K_{av} = (K_1 \cdot K_2 \ldots . K_N)^{1/N}$ The average formation constant

$K_N = K_1 \cdot K_2 \ldots . K_N = \frac{(MA_N)}{(M)\ (A)^N}$ Gross complexity constant

Substituting the consecutive complexity constants into the summation for the formation constant, we have

$$\bar{n} = \frac{\sum_0^N n\, \beta_n\, (A)^n}{\sum_0^N \beta_n\, (A)^n}, \quad \beta_n = K_1 K_2 \ldots K_n \qquad (2)$$

which upon expansion gives

$$\bar{n} = \frac{\beta_1 (A) + 2\beta_2 (A)^2 + 3\beta_3 (A)^3 + \ldots . + N\beta_N (A)^N}{1 + \beta_1 (A) + \beta_2 (A)^2 + \ldots\ldots\ldots\ldots + \beta_N (A)^N} \qquad (3)$$

K_o being 1.

This equation shows that the formation function is dependent upon the concentration of the free ligand only. Therefore, it is possible for two solutions with different total concentration to have the same percentage distribution of complexes, and hence be "corresponding solutions."

Also, it can be shown that corresponding solutions have the same concentration of free ligand (Appendix A). Therefore, equating the free ligand concentrations we obtain

$$\bar{n} = \frac{C_{A_1} - (A)}{C_{M_1}} = \frac{C_{A_2} - (A)}{C_{M_2}} \qquad (4)$$

$$\bar{n} = \frac{C_{A_1} - C_{A_2}}{C_{M_1} - C_{M_2}} = \frac{\Delta C_A}{\Delta C_M} \qquad (5)$$

$$\text{and } (A) = \frac{C_{M_1} C_{A_2} - C_{M_2} C_{A_1}}{C_{M_1} - C_{M_2}} \qquad (6)$$

Normally, the use of activities instead of concentration is necessary; however, Wrewsky (48) has shown that, at least for ethanol, over a wide range of water concentration the ratio of the activity coefficient of water to the activity of alcohol is essentially unity; this allows the use concentration values. Consequently, the *n*th consecutive complexity constant can be written for the salt-water-butanol system using cobalt as an example: (4, 5)

$$K_n = \frac{(\mathrm{Co}\ (H_2O)_n^{++})}{(\mathrm{Co}\ (H_2O)_{n-1}^{++})\ (H_2O)} \qquad (7)$$

The concentration symbol $(\mathrm{Co}\ (H_2O)_n\ )$ signifies that n molecules of water are associated with the cobalt and that N-n molecules of butanol are to be considered as a part of the complex, also.

From the N consecutive formation constants K_n, K_{av} is then found as the root mean value

$$K_{av} = (K_1 \cdot K_2 \cdots\cdots K_N)^{1/N} \qquad (8)$$

For the exchange of related ligands such as 1-butanol and water, it is probable that the ratios of successive constants are governed largely by the availability of coordination sites. Bjerrum (4) and Jørgensen (5) have shown that $\bar{n}$ is then given appropriately by

$$\bar{n} = \frac{N \cdot K_{av} \cdot (H_2O)}{1 + K_{av}\ (H_2O)} \qquad (9)$$

from which it is seen that the K_{av} is the reciprocal water concentration when the system has reached the midpoint of formation, i.e. $\bar{n} = \frac{N}{2}$

$$K_{av} = \left[\frac{1}{(H_2O)}\right]_{\bar{n} = \frac{N}{2}} \qquad (10)$$

In order to find corresponding solutions optically, the apparent molar extinction coefficients $\bar{E}_1$ and $\bar{E}_2$ for each salt at two different concentrations are plotted against the wavelength. Let us consider a series of aquo complexes of metal M. Then one has for the total concentration of M

$$C_M = (M) + (M.H_2O) + (M.2H_2O) + \dots\dots \qquad (11)$$

and for the molar absorbance

$$D = \bar{E}C_M = E^o(M) + E'(M.H_2O) + E''(M2H_2O) + \dots\dots (12)$$

Dividing through by the total concentration of M, one has

$$\bar{E} = E^o(M)/C_M + E'(M.H_2O)/C_M + E''(M.2H_2O)/C_M + \dots (13)$$

Since by definition of corresponding solutions the concentration ratios for two different total concentrations of M are the same for each aquo complex; e.g., $(M.H_2O)_1/C_{M_1} = (M.H_2O)_2/C_{M_2}$, etc., it follows that $\bar{E}_1 = \bar{E}_2$ at any given wavelength for two corresponding solutions.

Be measuring the optical density for a pair of solutions at different wavelengths, it is possible to obtain an adjustment curve (3, 4, 5, 6). The adjustment curve can then be used to find corresponding solutions and to calculate the average number of bound ligands. The average number of bound ligands and the appropriate free ligand concentration enables one to construct the formation curve, and then it is possible for one to calculate the average complexity constant from equation (10) (3, 4, 5).

DISCUSSION OF RESULTS

A. Nickel Chloride-Water-Butanol System

By dilution of the 0.112 M nickel chloride solution, a second stock solution was prepared and found to be 0.050 Molar (47). The optical densities were obtained over the range from 620 to 820 millimicrons in 20 millimicron intervals. The corresponding extinction coefficients are listed in Table II. The spectra of the nickel chloride-water-butanol system are shown in Figure 1. The spectra presented there are for various water-to-salt molar ratios and show the changes in the spectra caused by the addition of water.

Several observations can be made from studying Figure 1. At a wavelength of approximately 790 millimicrons, the anhydrous system shows an absorption maximum which decreases with increasing water concentration. This maximum also shifts by approximately 60 millimicrons toward the shorter wavelengths at a H_2O:salt ratio of 30:1. Also, a second absorption maximum can be detected around 685 millimicrons, and this shifts to about 650 millimicrons but does not decrease in intensity as rapidly.

A shift as much as 60 millimicrons cannot be accounted for as merely due to the exchange of water molecules for alcohol molecules because a similar concentration of nickel perchlorate (Figure 5) has a shift of only 20 millimicrons. Consequently, the shift of 60 millimicrons is likely caused by the exchange of a water molecule for a chloride in the solvation sphere or hydration sheath surrounding the metal ion (49).

In Figure 2, the curves representing the excess optical density were actually obtained from the Beckman DK-1 spectrophotometer using the anhydrous salt solution in each case as a reference solution. The maximum excess optical density is plotted since this varied only slightly in wavelength with increasing ratios of H_2O:salt. Similar curves could be obtained, also, by subtracting the optical density of the anhydrous solution from the values obtained for the solutions containing water given in Table II.

Examining Figure 2, it is possible to distinguish breaks in the curve for the nickel chloride-water-butanol system at mole ratios of water to salt of 4:1 and possibly 6:1 or 8:1. This may be considered indicative of the fact that over a limited range of water-to-salt molar ratios, the absorption is due to a relatively stable 4:1 complex. Goodrich (15) found in his calorimetric studies some evidence also for the existence of a 4:1 hydrate in solution. The excess optical density levels off after reaching a molar ratio of approximately 18:1.

From the data given in Table II, the necessary information can be obtained to construct the adjustment curves shown in Figure 3. Corresponding solution calculations are given for two different wavelengths in Tables III and IV. Using the method of calculation described in the section on Treatment of Data, a formation curve (see Figure 4) was constructed for the nickel chloride-water-butanol system.

The formation curve seems to approach the value of $\bar{n}$ equal to six (27). Since $\bar{n}$ also measures the average ligand (or hydration in this case) number, this would indicate that the maximum hydration number of nickel is 6. This is reasonable in view of the established coordination chemistry of nickel and the position of the absorption bands in the spectum.

The average formation constant (K_{av}) was calculated under the assumptions that $N=6$ and that only alcohol molecules are replaced by water, as described in the section dealing with the Treatment of Data. It was found that K_{av} is equal to 1.85 liter/mole. Jørgensen (5) found K_{av} for the nickel ion in ethanol to be 0.82 liter/mole. Although this difference is fairly large, it may be accounted for on the basis that in the ethanol solutions, the competition of water and ethanol molecules for sites in the solvation sheath would be more nearly equal than that of water and butanol since the former pair of molecules more nearly resemble each other (49). Furthermore, the extra length and size of the butanol may permit easier substitution of the water into the solvation sphere in the butanol system. It is not at all established, however, that chloride ions are not involved.

B. The Nickel Perchlorate-Water-Butanol System

A second stock solution was prepared by dilution of 0.0628 molar nickel perchlorate and was found to be 0.0324 molar by EDTA titration (47). The optical density of the solutions of varying water concentration was measured in the range from 620 millimicrons to 820 millimicrons in 20 millimicron intervals. The extinction coefficients were calculated (see Table V) and the spectra of the nickel perchlorate-water-butanol system are exhibited in Figure 5. The curves, again, are for varying water-to-salt molar ratios.

Examining Figure 5, it is quite obvious that the maximum absorption peak at 740 millimicrons shifts to approximately 720 millimicrons with increase in water concentration. The spectrum at the highest H_2O/salt ratio becomes essentially that of an aqueous solution which has an absorption maximum at 715 millimicrons (DK-1 measurements). This small shift in wavelength is much less than the shift observed for nickel chloride (see Figure 1). This suggests that in this case there is only a substitution of the water molecules for butanol molecules within the solvation sheath (49). The perchlorate ion probably does not directly affect the hydration of the metal ion because it cannot attach itself strongly to the metal ion because of its large size, i.e., does not enter into complex formation with the metal (34).

There appears to be a second absorption maximum present around 660 millimicrons. It does not shift toward shorter wavelength but instead increases in optical density with increasing water concentration. The excess absorbance peak in this region remains constant at H_2O/salt ratios above 6.

Upon examining Figures I and 5, it is seen that the nickel chloride-water-butanol spectrum becomes essentially that of the nickel perchlorate-water-butanol system at the highest water concentration. This identity would substantiate the suggested substitution of water molecules for chloride ions in the hydration sheath in the nickel chloride-water-butanol system. It is likely that there occurs also the progressive replacement of solvent butanol by water.

It seems reasonable to attribute the increase in absorption of both the nickel chloride and the nickel perchlorate-water-butanol systems at 660 millimicrons with increasing water concentration to the formation of a hydration structure. As mentioned earlier, the excess optical density of the nickel perchlorate-water-butanol system (see Figure 2) shows a relatively rapid leveling off at water-to-salt ratios of above 6:1. This is indicative of the comparative ease with which water enters the hydration sphere of the metal ion. The excess optical density curve refers to a wavelength of 620 millimicrons and again was measured differentially on the Beckman DK-1. A similar curve could of course be obtained using the data in Table V.

Since the curve levels off at a molar ratio of 6:1, this would indicate the presence of only the 6 hydrated nickel ion absorbing at the highest water concentrations.

Using the data in Tables VI and VII, it is possible to construct the adjustment curves for the nickel perchlorate-water-butanol system (see Figure 6), and from the corresponding solution principle, the average number of bound water molecules can then be obtained (see Tables VI and VII).

Based upon the data in Tables VI and VII, the formation curve was plotted (see Figure 4). It is seen from the graph that the average hydration number increases continually, reaching values even in excess of 12, and does not appear to be approaching any limiting value. Yates et al. (34) also found exceptionally high hydration values for cobalt and nickel perchlorates upon extraction by 2-octanol. Perhaps this may include complexes having both first and higher solvation layers occupied by water molecules.

Consequently, since the formation curve did not level off, it was not possible to calculate the average formation constant of the system.

C. Copper Chloride-Water-Butanol System

By dilution from the 0.0196 molar copper chloride stock solution, a second stock solution was prepared and the concentration (0.0118 molar) determined by EDTA titration (47).

The optical density of solutions of varying water concentration were again obtained with the Beckman DU spectrophotometer in 25 or 30 millimicron intervals from 700 millimicrons to 950 millimicrons. The optical densities were as usual converted to extinction coefficients (see Table VIII).

From the data given in Table VIII, the spectral curves illustrated in Figure 7 were obtained for the copper chloride-water-butanol system. Examination of the spectra shows a maximum absorption around 910 millimicrons (32). This maximum shifts toward shorter wavelengths with the addition of water and appears at about 890 millimicrons at the highest water concentration. The maximum, interestingly, first increases and then decreases as the water concentration is increased. It is possible that the small shift in absorption maximum is caused by water molecules interchanging with alcohol molecules in the solvation sphere while the chlorides remain attached to the copper ion. Such replacement may be kinetically slow as suggested by Minc (30). The excess optical density of the absorption maximum (Figure 8) shows first an increase and then a decrease.

Although it is still possible to construct adjustment curves (see Figure 9) and obtain from the corresponding solutions the apparent hydration number (see Table 9), the sign of the average number of bound ligands varies from a positive value to a negative value. This system, therefore, does not appear to lend itself to the usual Bjerrum procedure.

The adjustment curves furthermore exhibit a maximum which is not found in the adjustment curves of any of the other systems. Consequently, the average formation constant cannot be calculated from the formation curve data. Goodrich (15) similarly has observed that this system behaves abnormally (see Figure 20) based upon calorimetric studies of the enthalpy of hydration.

D. Copper Perchlorate-Water-Butanol System

From a 0.118 molar stock solution of copper perchlorate, a 0.0588 molar stock solution was prepared by dilution and checked by EDTA analysis.

Optical densities were measured for solutions of varying water concentration at 25 to 30 millimicron intervals over the range from 700 to 920 millimicrons. The extinction coefficients were calculated and are tabulated in Table XI.

An examination of Figure 10, showing the spectra in the copper perchlorate-water-butanol system, reveals that the absorption maximum which occurs at 800 millimicrons does not shift with the increase in water concentration, although it does decrease in intensity. This decrease is believed to be caused by changes in solvation within the metal-ion solvation sphere (30, 31).

From the graph of the excess optical density taken at maximum absorption (see Figure 8), it is possible to distinguish breaks at molar ratios of H_2O/Salt of 10:1 and 25:1. This may be indicative of abrupt changes in the hydration numbers of the aquo complexes. There does not appear to be any tendency for the excess optical density to level off as it did for nickel chloride.

Using the data in Tables XII, XIII, and XIV, the adjustment curves for the copper perchlorate-water-butanol system were constructed (see Figure 11), and the average number of bound ligands calculated.

As shown in Figure 12, the $\bar{n}$ curve for the copper perchlorate-water-butanol system appears as a two-step wave. The first step indicates a value of N equal to 4 and the second gives $N \geqslant 8$. This means that $Cu(ClO_4)_2$ like $Ni(ClO_4)_2$ is more highly hydrated than the corresponding chlorides. Several authors (26, 22) conclude that there are only two waters present in the solvation sheath of Cu Cl_2 in hydrous ethanol or dioxane, while McManamey (37) arrives at an apparent hydration number of 5.3 for copper nitrate in butanol and pentanol.

Calculation of the average formation constant with N equal to 4 gives a value of 4.04 liter/mole. Using the maximum N value as 8, the average formation constant is 0.605 liter/mole. Jørgensen (5) reports the value of the average formation function for the copper ion to be 0.19 liter/mole in ethanol.

E. The Cobalt Chloride-Water-Butanol System

Stock solutions were prepared in the usual way by diluting 0.0873 molar cobalt chloride solution. The optical densities of the solutions were measured at 20 millimicron intervals over the range from 540 millimicrons to 700 millimicrons. The extinction coefficients were then calculated (see Table XV). Spectra in the cobalt chloride-water-butanol system are shown in Figure 13. It was found that cobalt chloride solutions had such intense color that the use of a 0.9 cm wedge in the 1 cm cells was necessary.

The spectra in Figure 13 show the absorption maximum at 660 millimicrons as the only distinct absorption peak in the visible. However, at 620 millimicrons, there appears to be a second absorption maximum of lesser intensity. The addition of water to the samples causes a progressive decrease in the absorption maximum but no apparent shift of the peak at 660 millimicrons. However, the small absorption peak at 620 millimicrons seems to shift toward shorter wavelengths, the order of the shift being only about 10 to 15 millimicrons with no peak at 510-530 millimicrons characteristic of aquo ions.

Although this small shift and decrease in the optical density may possibly be caused by the substitution of a water molecule for a butanol molecule in the solvation sheath surrounding the metal ion (28, 30, 31), this is probably only partially correct, for as in the case of $NiCl_2$ and certainly $CuCl_2$ the molecules contain relatively firmly bound chlorides as a part of a coordinate group.

Figure 14 shows that there is a steady decrease in excess optical density in the cobalt chloride-water-butanol system with increasing water concentration. This is in marked contrast to the cobalt perchlorate system where the excess optical density decreases but little compared to the cobalt chloride solution. Furthermore, the curves do not exhibit the definite breaks at low water/salt ratios such as were present in the previous systems studied. There is only a slight tendency for the excess optical density to level off after reaching a water/salt ratio of 20:1.

From the data in Tables XVI and XVII, the adjustment curves were obtained in the usual way (see Figure 15) for the cobalt chloride-water-butanol system, and from the adjustment curve (see section on Treatment of Data), the formation curve of aquo complexes for the cobalt chloride-water-butanol system were also obtained (Figure 16).

From Figure 16, it seems that there may be present an aquo complex of 8 moles of water per mole of salt. However, McClure et al. (36) believe that the formation of an 8 coordinated configuration is not likely for cobalt. However, McManamey (37) arrived at an apparent hydration number of 7 for cobalt nitrate in butanol, based upon extraction studies.

Assuming the average number of bound ligands to be 8, the average formation constant was estimated. The average formation constant, defined here as before to be the reciprocal water concentration at $\bar{n} = N/2$, was found to have a value of 9.55 liter/mole. This constant is high in comparison with the constant given for cobalt nitrate complexes in ethanol by Jørgensen (5), who found the value of the average formation constant to be 1.08 liter/mole. It is probable, however, that the method is inapplicable to $CoCl_2$ in butanol.

F. The Cobalt Perchlorate-Water-Butanol System

The optical density of the $Co(ClO_4)_2$ solutions was measured over the range from 460 to 600 millimicrons at 20 millimicron intervals. Extinction coefficients are given in Table XVIII, and a graph of the spectra of the cobalt perchlorate-water-butanol system is shown in Figure 17.

An absorption maximum occurs at approximately 515 millimicrons, and the intensity decreases with increasing water concentration. The absorption maximum did not appear to shift as much as was observed with nickel perchlorate solutions. The decrease in intensity probably arises again from the substitution of water molecules for octahedrally disposed alcohol molecules.

The excess optical density graph (see Figure 18) indicates two breaks occurring at ratios of 6:1 and 14:1. The excess optical density was measured at 520 millimicrons.

From the data in Table XIX, adjustment curves were obtained and are shown in Figure 19. The formation curve was also determined from Table XVIII, using the appropriate values.

Upon examination of the formation curve for the cobalt perchlorate-water-butanol system, one notes that there is a gross deviation from the "normal" features of the curve. The curve drops sharply after reaching a maximum value at a molar ratio of 6:1. Consequently, no reliable formation constant could be obtained by the corresponding solution method.

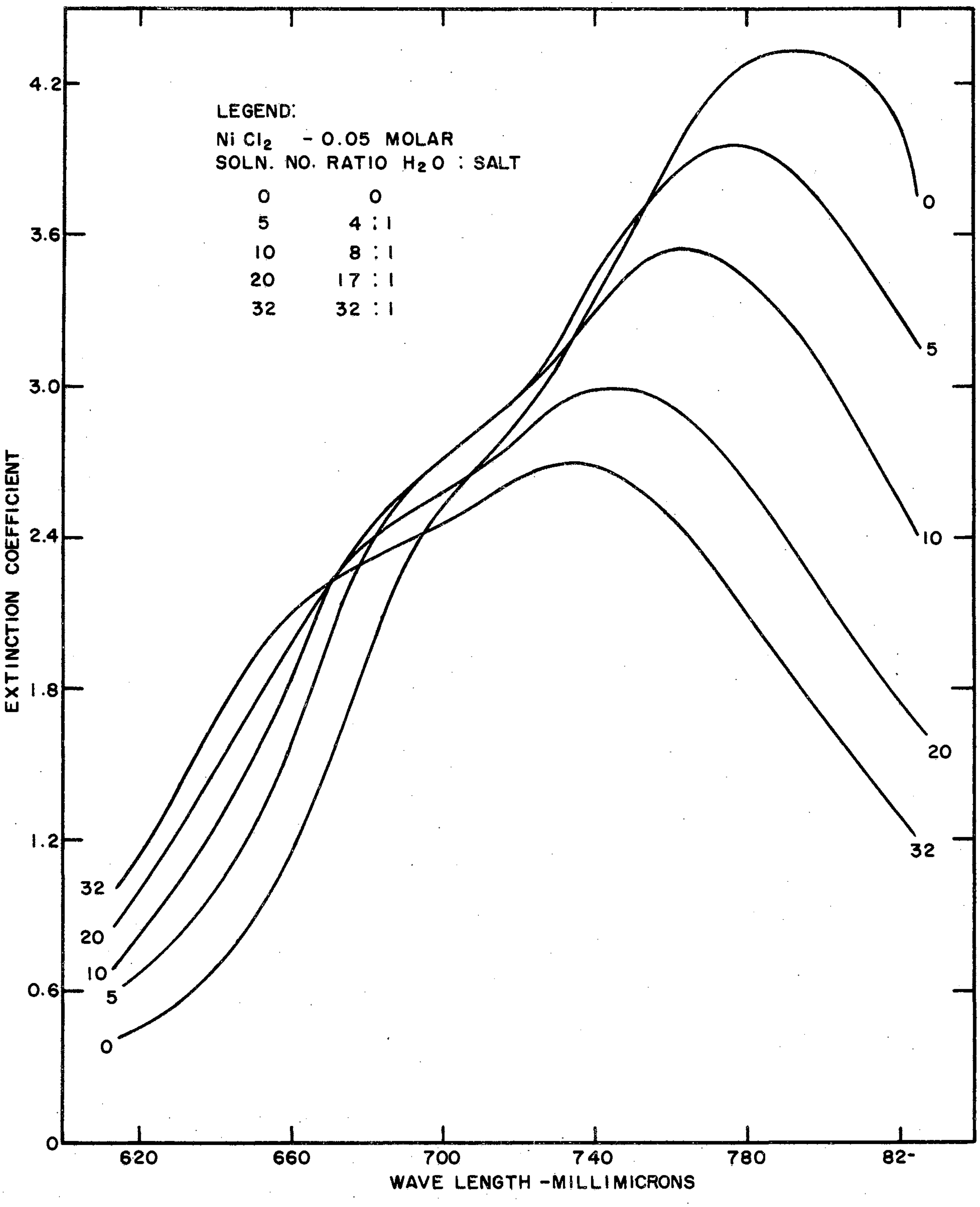

FIGURE I

SPECTRA OF THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

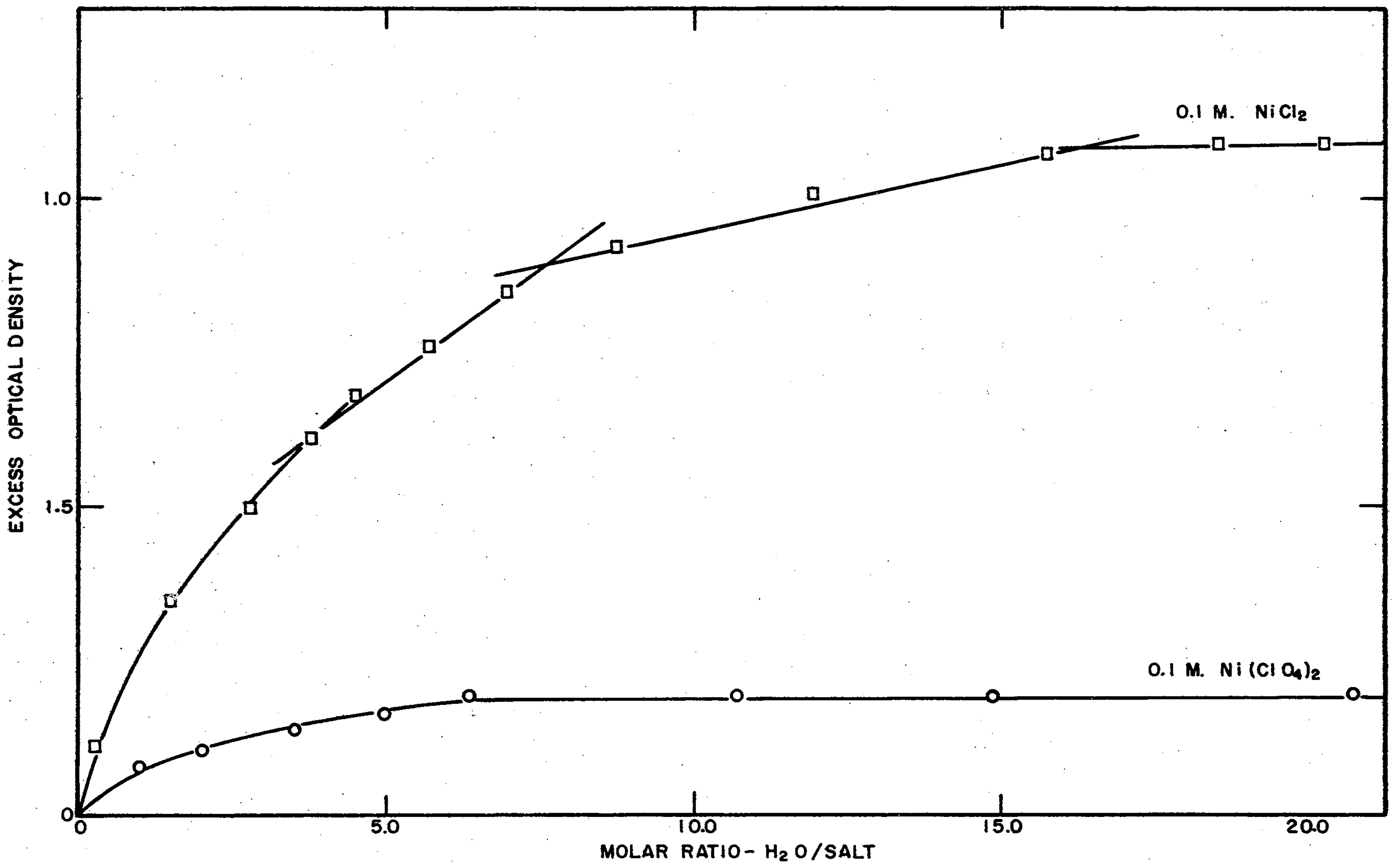

FIGURE 2

EXCESS OPTICAL DENSITY FOR THE NICKEL CHLORIDE, NICKEL PERCHLORATE-WATER-BUTANOL SYSTEMS

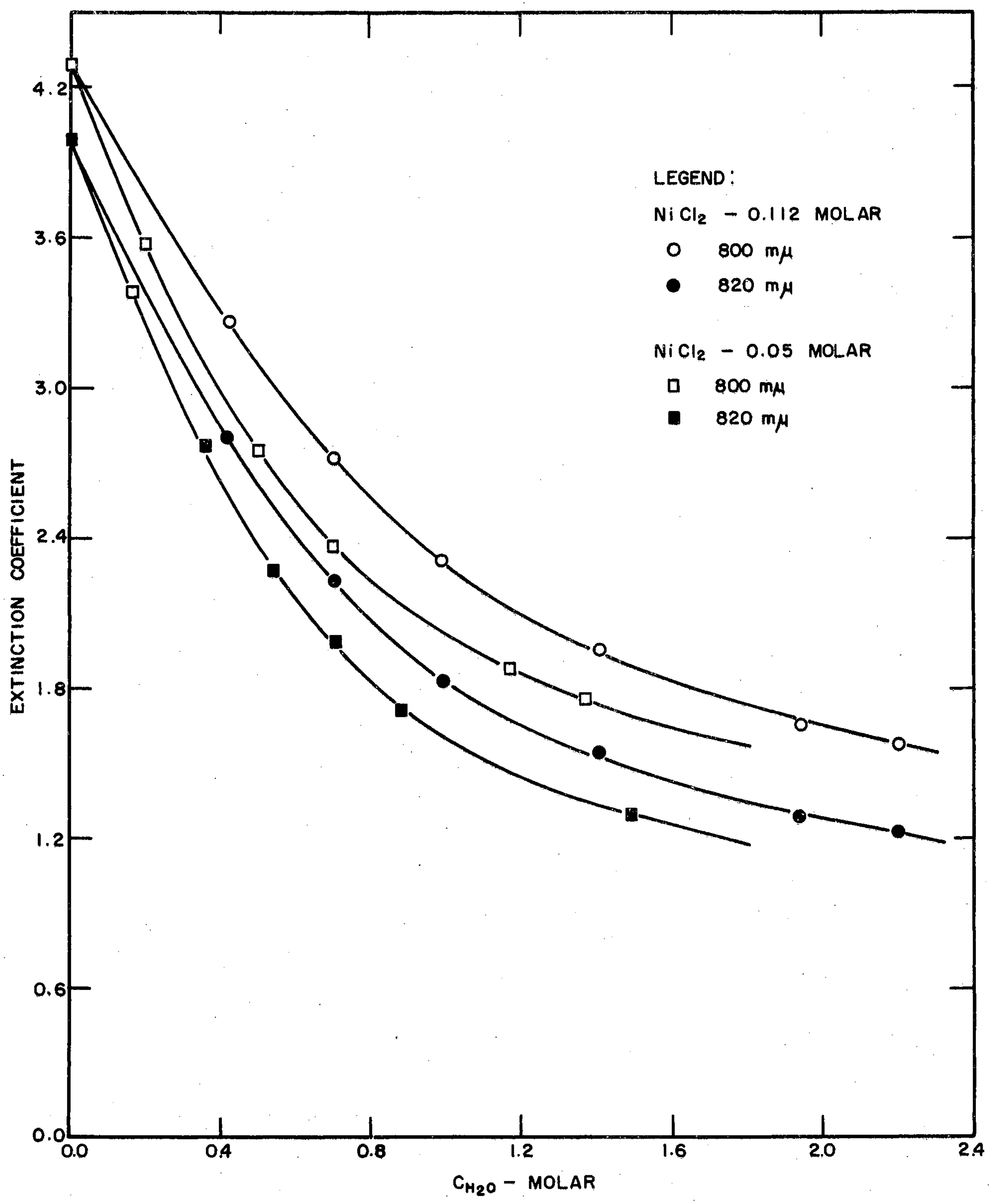

FIGURE 3

ADJUSTMENT CURVES FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

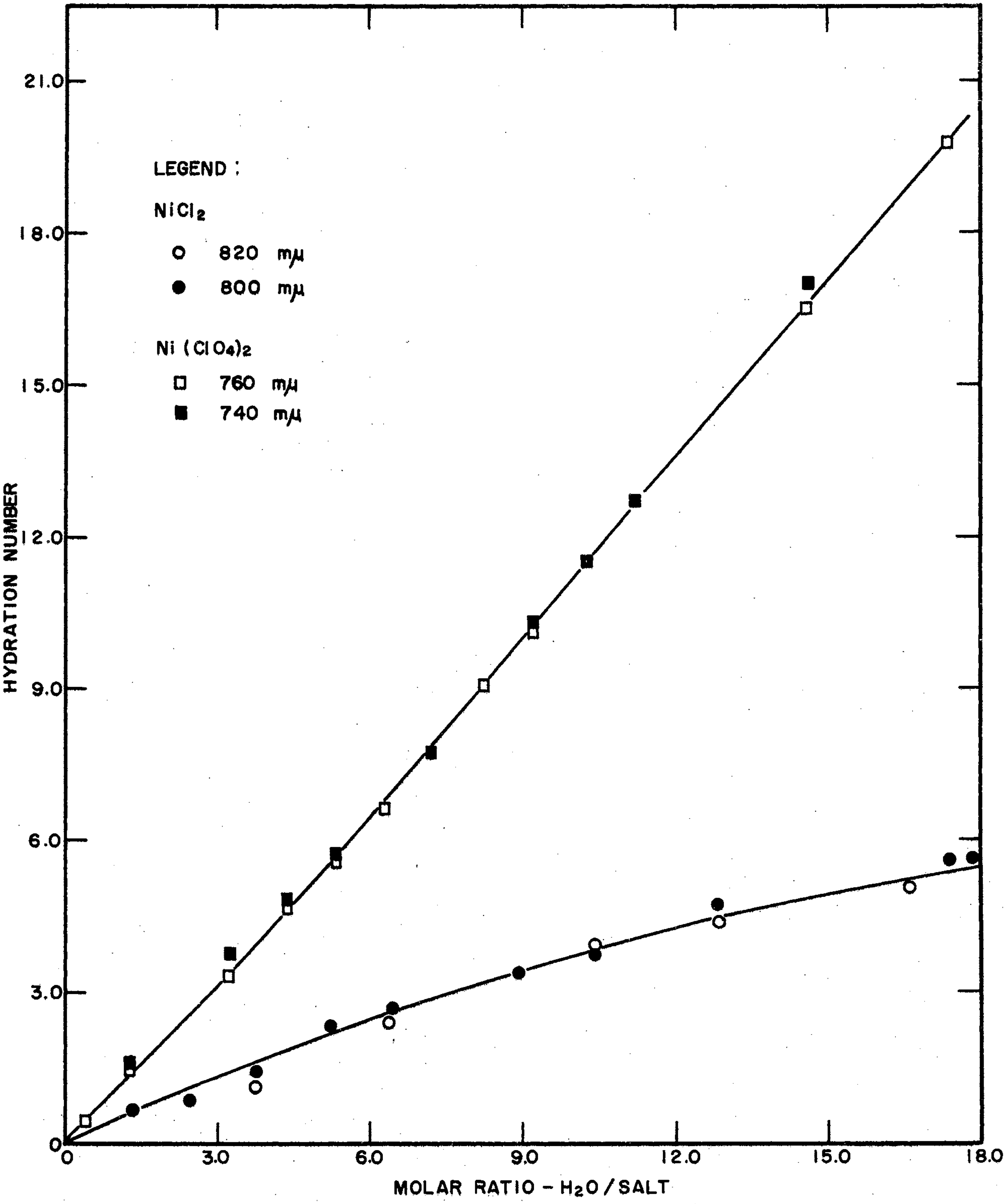

FIGURE 4

FORMATION CURVES FOR THE NICKEL CHLORIDE, NICKEL PERCHLORATE-WATER-BUTANOL SYSTEM

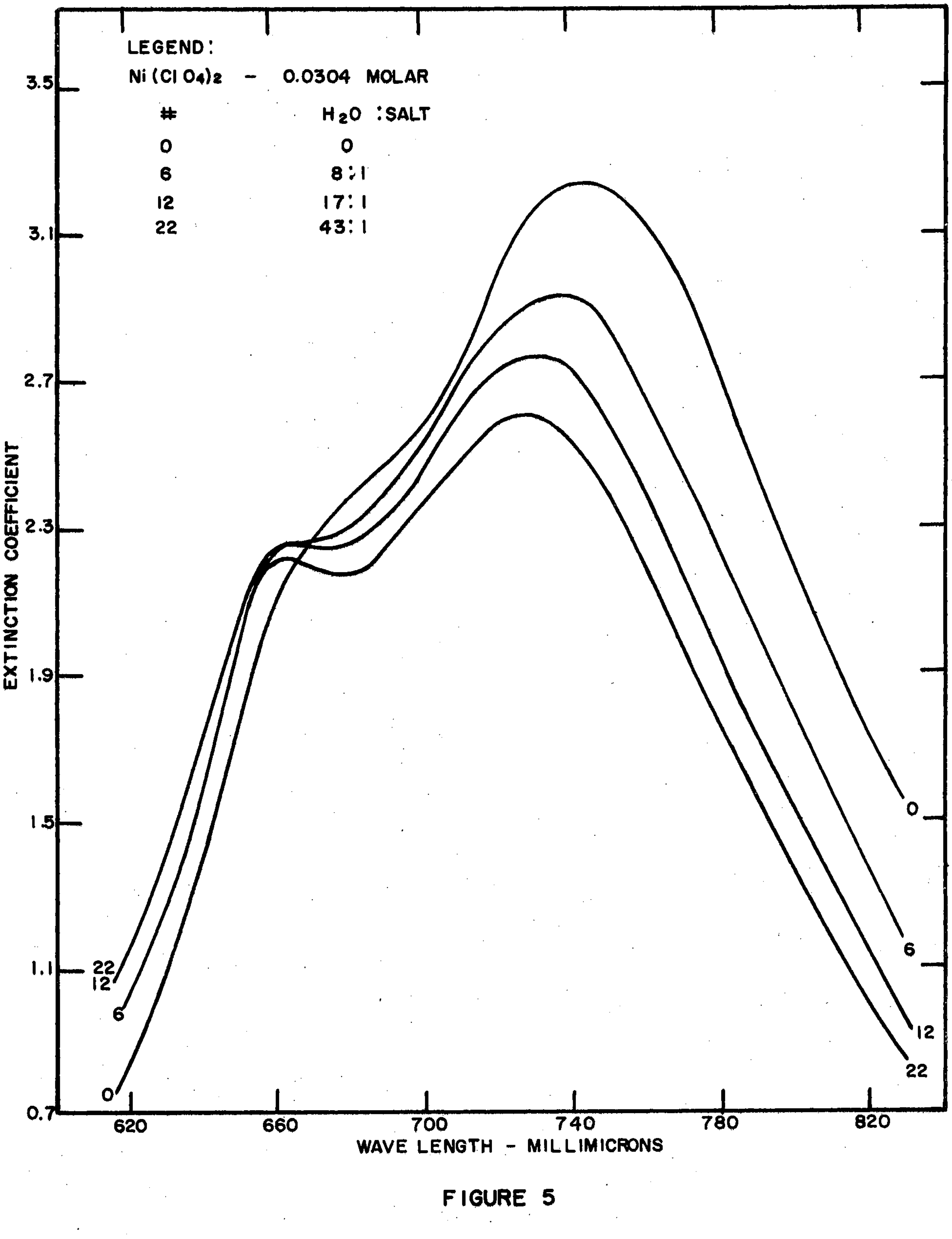

FIGURE 5

SPECTRA OF THE NICKEL PERCHLORATE-WATER-BUTANOL SYSTEM

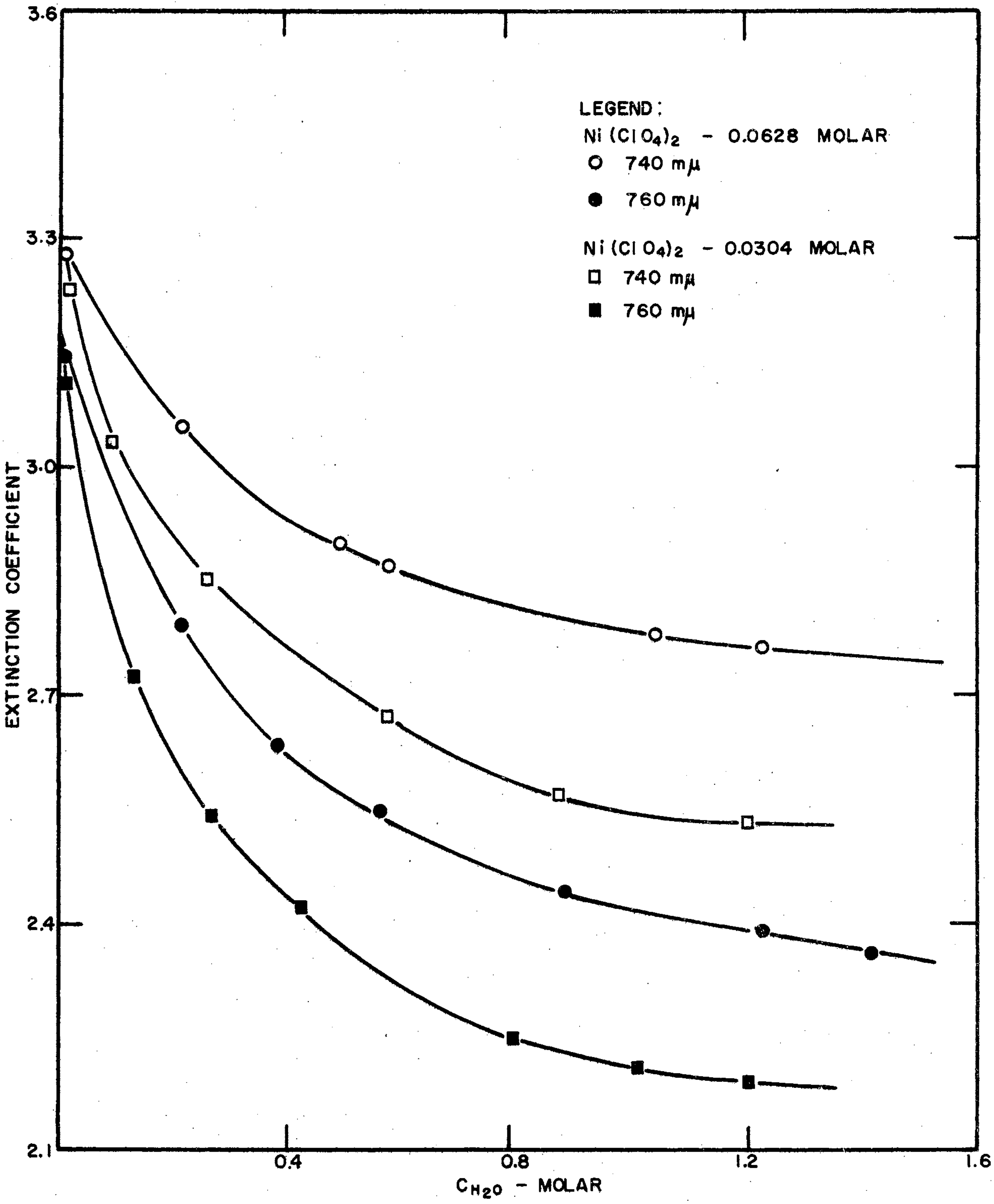

FIGURE 6

ADJUSTMENT CURVES FOR THE NICKEL PERCHLORATE - WATER-BUTANOL SYSTEM

TABLE II

EXTINCTION COEFFICIENT FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.05M

Sample No.	Water Molar	Molar Ratio	Wavelength 410	430	620	640	660	680
Anh.	0	0	10.3	12.6	0.450	0.680	1.15	1.92
1	0.042	0.839	10.7	12.2	0.480	0.750	1.25	2.00
2	0.084	1.69	10.9	11.9	0.540	0.840	1.37	2.10
3	0.126	2.52	10.9	11.5	0.570	0.890	1.44	2.20
4	0.167	3.36	11.0	11.0	0.615	0.965	1.50	2.25
5	0.209	4.19	11.0	10.5	0.650	1.02	1.58	2.34
6	0.250	5.03	10.9	10.2	0.680	1.06	1.69	2.37
7	0.292	5.87	10.9	9.80	0.720	1.11	1.70	2.38
8	0.333	6.71	10.8	9.50	0.750	1.16	1.76	2.41
9	0.374	7.55	10.6	8.90	0.795	1.22	1.81	2.43
10	0.416	8.39	10.5	8.70	0.820	1.25	1.85	2.43
11	0.457	9.22	10.4	8.40	0.850	1.29	1.87	2.44
12	0.498	10.0	10.3	8.10	0.870	1.33	1.92	2.46
13	0.540	10.9	10.1	7.85	0.920	1.37	1.96	2.47
14	0.580	11.7	10.0	7.48	0.920	1.40	1.97	2.47
15	0.622	12.6	9.75	7.20	0.870	1.35	1.94	2.39
16	0.663	13.4	9.50	6.92	0.870	1.36	1.94	2.39
17	0.704	14.2	9.50	6.72	0.870	1.40	1.95	2.40
18	0.744	15.1	9.40	6.58	0.920	1.43	2.00	2.40
19	0.785	15.9	9.25	6.38	0.950	1.44	1.99	2.39
20	0.826	16.8	9.12	6.15	0.985	1.48	2.04	2.39
21	0.887	18.0	8.90	5.80	1.00	1.53	2.06	2.39
22	0.948	19.3	8.80	5.80	1.01	1.51	2.05	2.39
23	1.01	20.5	8.68	5.57	1.03	1.55	2.06	2.37
24	1.07	21.8	8.50	5.32	1.03	1.55	2.07	2.35
25	1.17	23.9	8.40	5.23	1.04	1.56	2.06	2.34
26	1.19	24.3	8.35	5.18	1.04	1.55	2.06	2.32
27	1.25	25.9	8.20	4.98	1.05	1.58	2.07	2.31
28	1.31	27.1	8.10	4.80	1.07	1.60	2.09	2.30
29	1.37	28.4	8.00	4.72	1.10	1.64	2.12	2.31
30	1.43	29.7	7.90	4.58	1.11	1.64	2.12	2.30
31	1.49	30.9	7.90	4.60	1.12	1.65	2.12	2.31
32	1.57	32.6	7.75	4.40	1.12	1.66	2.12	2.30

TABLE II

EXTINCTION COEFFICIENT FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.05M

Sample No.	Wavelength 700	720	740	760	780	800	820
Anh.	2.53	2.86	3.34	3.93	4.30	4.32	4.03
1	2.58	2.89	3.36	3.91	4.25	4.21	3.87
2	2.65	2.92	3.41	3.92	4.21	4.15	3.76
3	2.67	2.95	3.42	3.91	4.14	3.98	3.57
4	2.70	2.97	3.44	3.88	4.08	3.88	3.43
5	2.71	2.96	3.44	3.85	3.96	3.71	3.28
6	2.71	2.98	3.43	3.80	3.85	3.56	3.10
7	2.71	2.96	3.40	3.74	3.75	3.48	3.01
8	2.72	2.98	3.39	3.64	3.65	3.32	2.85
9	2.71	2.96	3.35	3.60	3.55	3.21	2.75
10	2.71	2.96	3.28	3.55	3.44	3.09	2.58
11	2.70	2.94	3.30	3.50	3.38	3.02	2.55
12	2.70	2.94	3.26	3.44	3.27	2.89	2.40
13	2.70	2.94	3.25	3.35	3.16	2.76	2.27
14	2.69	2.91	3.21	3.32	3.10	2.73	2.25
15	2.60	2.85	3.12	3.19	2.97	2.56	2.07
16	2.58	2.81	3.09	3.15	2.93	2.54	2.06
17	2.57	2.81	3.06	3.10	2.85	2.43	1.97
18	2.57	2.81	3.04	3.05	2.78	2.36	1.88
19	2.57	2.80	3.03	3.02	2.77	2.35	1.81
20	2.56	2.80	3.00	2.93	2.63	2.19	1.75
21	2.54	2.79	2.95	2.87	2.56	2.13	1.72
22	2.52	2.77	2.92	2.81	2.48	2.04	1.62
23	2.51	2.75	2.90	2.80	2.46	2.04	1.62
24	2.51	2.75	2.88	2.76	2.45	2.02	1.62
25	2.50	2.71	2.83	2.69	2.36	1.94	1.53
26	2.48	2.70	2.81	2.67	2.32	1.90	1.50
27	2.47	2.70	2.80	2.65	2.31	1.88	1.49
28	2.46	2.70	2.76	2.58	2.23	1.81	1.41
29	2.46	2.70	2.75	2.55	2.17	1.76	1.37
30	2.46	2.68	2.74	2.54	2.15	1.75	1.37
31	2.46	2.66	2.72	2.50	2.10	1.68	1.33
32	2.45	2.65	2.70	2.48	2.12	1.70	1.33

TABLE III

ADJUSTMENT CURVE DATA FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

800 Millimicrons

Sample No.	0.05 M C_{H_2O}	$\overline{E}_{800}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\overline{n}$	0.112 M C_{H_2O}	$\overline{E}_{800}$	Molar Ratio
Anh.	0	4.32					0	4.31	0
1	0.042	4.21	0.10	0.04	0.062	0.64	0.143	4.01	1.28
2	0.084	4.15	0.22	0.05	"	0.81	0.286	3.63	2.56
3	0.126	3.98	0.34	0.09	"	1.45	0.427	3.27	3.83
4	0.167	3.88	0.43	0.14	"	2.26	0.568	3.03	5.11
5	0.209	3.71	0.55	0.16	"	2.58	0.708	2.72	6.39
6	0.250	3.56					0.848	2.54	7.67
7	0.292	3.48	0.78	0.21	"	3.39	0.987	2.31	8.95
8	0.333	3.32	0.89	0.23	"	3.71	1.12	2.16	10.2
9	0.375	3.21					1.26	1.99	11.5
10	0.416	3.09	1.11	0.29	"	4.69	1.40	1.95	12.8
11	0.458	3.02					1.53	1.82	14.1
12	0.499	2.89					1.67	1.83	15.3
13	0.540	2.76					1.80	1.75	16.6
14	0.581	2.73	1.60	0.34	"	5.48	1.94	1.67	17.9
15	0.622	2.56					2.07	1.58	19.2
16	0.663	2.54					2.20	1.58	21.7
17	0.704	2.43					2.34	1.53	23.0
18	0.745	2.36					2.47	1.52	24.3
19	0.786	2.35							
20	0.826	2.19							
21	0.887	2.13							
22	0.948	2.04							

TABLE III

ADJUSTMENT CURVE DATA FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

800 Millimicrons

Sample No.	0.05 M C_{H2O}	 $\overline{E}_{800}$
23	1.01	2.04
24	1.07	2.02
25	1.17	1.94
26	1.19	1.90
27	1.25	1.88
28	1.31	1.81
29	1.37	1.76
30	1.43	1.75
31	1.49	1.68
32	1.57	1.70

TABLE IV

ADJUSTMENT CURVE DATA FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

820 Millimicrons

	0.05 M						0.112 M		
Sample No.	C_L	$\bar{E}_{820}$	C_L^*	ΔC_L	ΔC_M	$\bar{n}$	C_L	$\bar{E}_{820}$	Molar Ratio
Anh.	0	4.03					0	4.05	0
1	0.042	3.87					0.143	3.66	1.28
2	0.084	3.76					0.286	3.18	2.56
3	0.126	3.57	0.36	0.07	0.062	1.13	0.427	2.81	3.83
4	0.167	3.43					0.568	2.56	5.11
5	0.209	3.28	0.56	0.15	"	2.42	0.708	2.24	6.39
6	0.250	3.10					0.848	2.08	7.67
7	0.292	3.01	0.78	0.21	"	3.40	0.987	1.83	8.95
8	0.333	2.85	0.88	0.24	"	3.87	1.12	1.71	10.2
9	0.375	2.75					1.26	1.55	11.5
10	0.416	2.58	1.13	0.27	"	4.35	1.40	1.54	12.8
11	0.458	2.55					1.53	1.54	14.1
12	0.499	2.40					1.67	1.42	15.3
13	0.540	2.27	1.49	0.31	"	5.0	1.80	1.36	16.6
14	0.581	2.25					1.94	1.29	17.9
15	0.622	2.07					2.07	1.21	19.2
16	0.663	2.06					2.20	1.22	20.4
17	0.704	1.97					2.34	1.17	21.7
18	0.745	1.88					2.47	1.16	23.0
19	0.786	1.81					2.60	1.15	24.3

TABLE IV

ADJUSTMENT CURVE DATA FOR THE NICKEL CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

820 Millimicrons

	0.05 M	
Sample No.	C_L	$\bar{E}_{820}$
20	0.826	1.75
21	0.887	1.72
22	0.948	1.62
23	1.01	1.62
24	1.07	1.62
25	1.17	1.53
26	1.19	1.50
27	1.25	1.49
28	1.31	1.41
29	1.37	1.37
30	1.43	1.37
31	1.49	1.33
32	1.57	1.33

TABLE V

EXTINCTION COEFFICIENT FOR NICKEL PERCHLORATE WATER-BUTANOL SYSTEM

Temp. 25° C

0.03 M

			Wavelength				
Sample No.	Water Molar	Molar Ratio	620	640	660	680	700
Anh.	0.021	0.692	0.839	1.41	2.11	2.37	2.57
1	0.055	1.83	0.938	1.51	2.17	2.35	2.57
2	0.090	2.97	0.97	1.56	2.19	2.32	2.55
3	0.125	4.11	1.00	1.60	2.22	2.30	2.55
4	0.159	5.24	1.02	1.64	2.25	2.29	2.55
5	0.193	6.38	1.06	1.72	2.29	2.33	2.55
6	0.227	7.52	1.12	1.73	2.31	2.32	2.55
7	0.262	8.66	1.16	1.76	2.32	2.33	2.55
8	0.313	10.4	1.20	1.78	2.25	2.35	2.56
9	0.364	12.1	1.12	1.71	2.25	2.27	2.48
10	0.416	13.8	1.13	1.73	2.25	2.27	2.48
11	0.467	15.5	1.14	1.74	2.25	2.25	2.47
12	0.518	17.2	1.15	1.75	2.25	2.25	2.47
13	0.568	18.9	1.15	1.73	2.24	2.25	2.45
14	0.618	20.6	1.15	1.73	2.22	2.22	2.42
15	0.702	23.4	1.15	1.74	2.22	2.21	2.42
16	0.788	26.3	1.15	1.74	2.22	2.19	2.40
17	0.872	29.1	1.15	1.73	2.21	2.17	2.39
18	0.956	32.0	1.15	1.73	2.21	2.17	2.37
19	1.03	34.8	1.15	1.75	2.21	2.17	2.37
20	1.10	37.7	1.15	1.75	2.21	2.17	2.37
21	1.20	40.5	1.15	1.75	2.21	2.17	2.37
22	1.29	43.4	1.15	1.75	2.21	2.17	2.37

TABLE V

EXTINCTION COEFFICIENT FOR NICKEL PERCHLORATE WATER-BUTANOL SYSTEM

Temp. 25° C　　　　　　　　　　　　　　　　　　0.03 M

Sample No.	Wavelength					
	720	740	760	780	800	820
Anh.	2.95	3.23	3.11	2.70	2.24	1.74
1	2.93	3.13	2.93	2.50	2.03	1.58
2	2.88	3.03	2.80	2.35	1.91	1.46
3	2.86	2.96	2.72	2.27	1.83	1.38
4	2.84	2.91	2.64	2.22	1.76	1.39
5	2.84	2.91	2.62	2.19	1.73	1.31
6	2.83	2.89	2.58	2.14	1.70	1.28
7	2.81	2.85	2.53	2.09	1.66	1.25
8	2.80	2.81	2.48	2.04	1.61	1.21
9	2.77	2.78	2.45	2.01	1.56	1.18
10	2.73	2.77	2.42	1.98	1.54	1.16
11	2.72	2.73	2.40	1.94	1.52	1.13
12	2.72	2.72	2.37	1.92	1.49	1.10
13	2.69	2.67	2.35	1.89	1.46	1.08
14	2.65	2.62	2.30	1.84	1.43	1.05
15	2.65	2.60	2.27	1.82	1.41	1.02
16	2.62	2.58	2.25	1.79	1.39	1.00
17	2.62	2.57	2.22	1.76	1.36	0.99
18	2.60	2.57	2.22	1.76	1.36	0.99
19	2.58	2.55	2.21	1.74	1.34	0.99
20	2.58	2.55	2.19	1.74	1,34	0.99
21	2.58	2.53	2.19	1.73	1.33	0.99
22	2.58	2.52	2.17	1.73	1.33	0.99

TABLE VI

ADJUSTMENT CURVE DATA FOR THE NICKEL PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

740 Millimicrons

Sample No.	0.0304 M						0.0628 M		Molar Ratio
	C_{H_2O}	$\bar{E}_{740}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{740}$	
Anh.	0.021	3.23	0.008	0.013	0.0324	0.402	0.021	3.28	.334
1	0.055	3.13	0.030	0.052	"	1.60	0.082	3.19	1.313
2	0.090	3.03					0.143	3.16	2.29
3	0.125	2.96	0.081	0.123	"	3.80	0.204	3.05	3.27
4	0.159	2.91	0.115	0.154	"	4.75	0.269	2.99	4.25
5	0.193	2.91	0.140	0.185	"	5.72	0.325	2.96	5.23
6	0.227	2.89					0.387	2.94	6.21
7	0.262	2.85	0.198	0.250	"	7.72	0.448	2.90	7.19
8	0.313	2.81	0.216	0.292	"	9.04	0.508	2.88	8.16
9	0.364	2.78	0.236	0.332	"	10.2	0.568	2.87	9.15
10	0.416	2.77	0.255	0.374	"	11.5	0.629	2.85	10.1
11	0.467	2.73	0.285	0.414	"	12.7	0.699	2.83	11.2
12	0.518	2.72					0.769	2.83	12.4
13	0.568	2.67					0.838	2.82	13.5
14	0.618	2.62	0.355	0.553	"	17.0	0.908	2.79	14.6
15	0.702	2.60					0.987	2.80	16.0
16	0.788	2.58	0.380	0.680	"	21.0	1.06	2.77	17.3
17	0.872	2.57	0.380	0.744	"	23.0	1.12	2.77	18.6
18	0.956	2.57	0.410	0.814	"	25.1	1.22	2.75	19.9
19	1.03	2.55	0.435	0.886	"	27.4	1.32	2.74	21.5
20	1.10	2.55					1.41	2.71	23.1
21	1.20	2.53							
22	1.29	2.52							

TABLE VII

ADJUSTMENT CURVE DATA FOR THE NICKEL PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

760 Millimicrons

	0.0304 M						0.0628 M		
Sample No.	C_{H_2O}	$\bar{E}_{760}$	$C^{*}_{H_2O}$	ΔC_L	ΔC_M	π	C_{H_2O}	$\bar{E}_{760}$	Molar Ratio
Anh.	0.021	3.11	0.009	0.012	0.0324	0.37	0.021	3.19	0.334
1	0.055	2.93	0.036	0.046	"	1.42	0.082	3.03	1.31
2	0.090	2.80					0.143	2.94	2.29
3	0.125	2.72	0.095	0.109	"	3.37	0.204	2.79	3.27
4	0.159	2.64	0.118	0.151	"	4.66	0.269	2.73	4.25
5	0.193	2.62	0.145	0.180	"	5.56	0.325	2.68	5.23
6	0.227	2.58	0.174	0.213	"	6.58	0.387	2.63	6.21
7	0.262	2.53					0.448	2.59	7.19
8	0.313	2.48	0.215	0.293	"	9.04	0.508	2.58	8.16
9	0.364	2.45	0.242	0.326	"	10.0	0.568	2.55	9.15
10	0.416	2.42					0.629	2.53	10.1
11	0.467	2.40					0.699	2.50	11.2
12	0.518	2.37					0.769	2.46	12.4
13	0.568	2.35					0.838	2.44	13.5
14	0.618	2.30	0.376	0.532	"	16.4	0.908	2.44	14.6
15	0.702	2.27					0.987	2.44	16.0
16	0.788	2.25	0.423	0.637	"	19.6	1.06	2.41	17.3
17	0.872	2.22					1.12	2.42	18.6
18	0.956	2.22	0.456	0.768	"	23.7	1.22	2.39	19.9
19	1.03	2.21	0.480	0.841	"	25.9	1.32	2.37	21.5
20	1.10	2.19					1.41	2.36	23.1
21	1.20	2.19							
22	1.29	2.17							

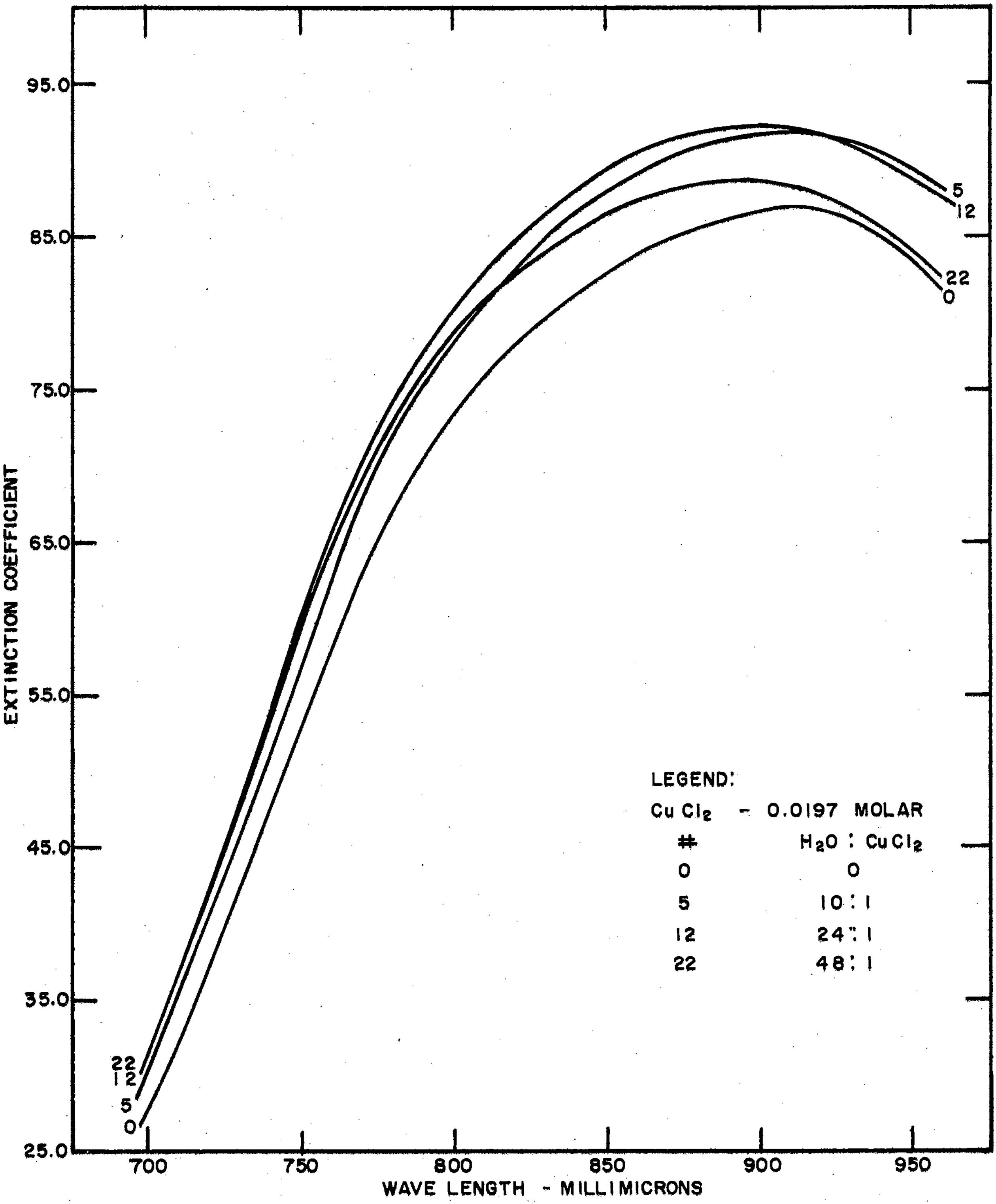

FIGURE 7

SPECTRA OF THE COPPER CHLORIDE-WATER-BUTANOL SYSTEM

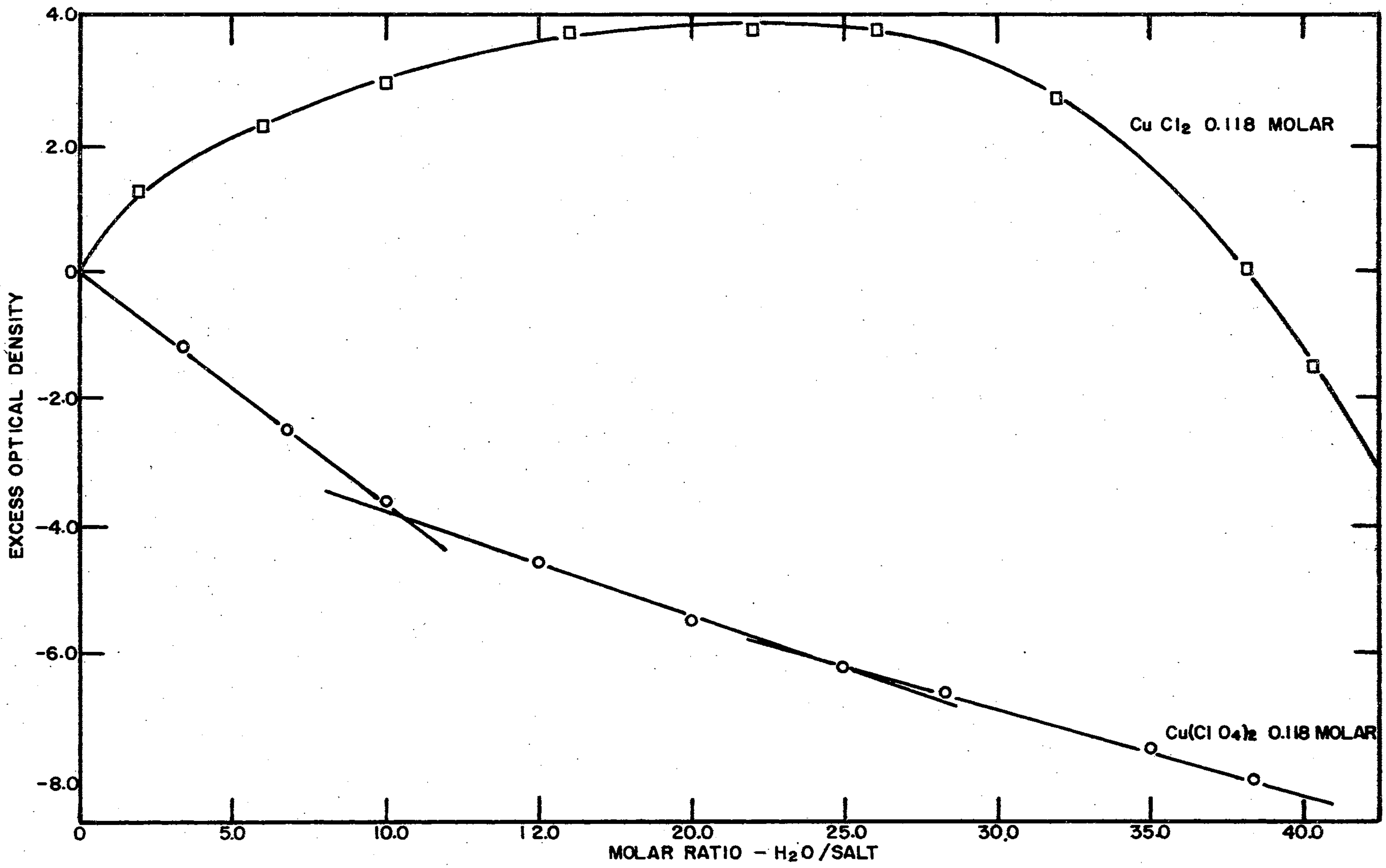

FIGURE 8

EXCESS OPTICAL DENSITY FOR THE COPPER CHLORIDE, COPPER PERCHLORATE-WATER-BUTANOL SYSTEMS

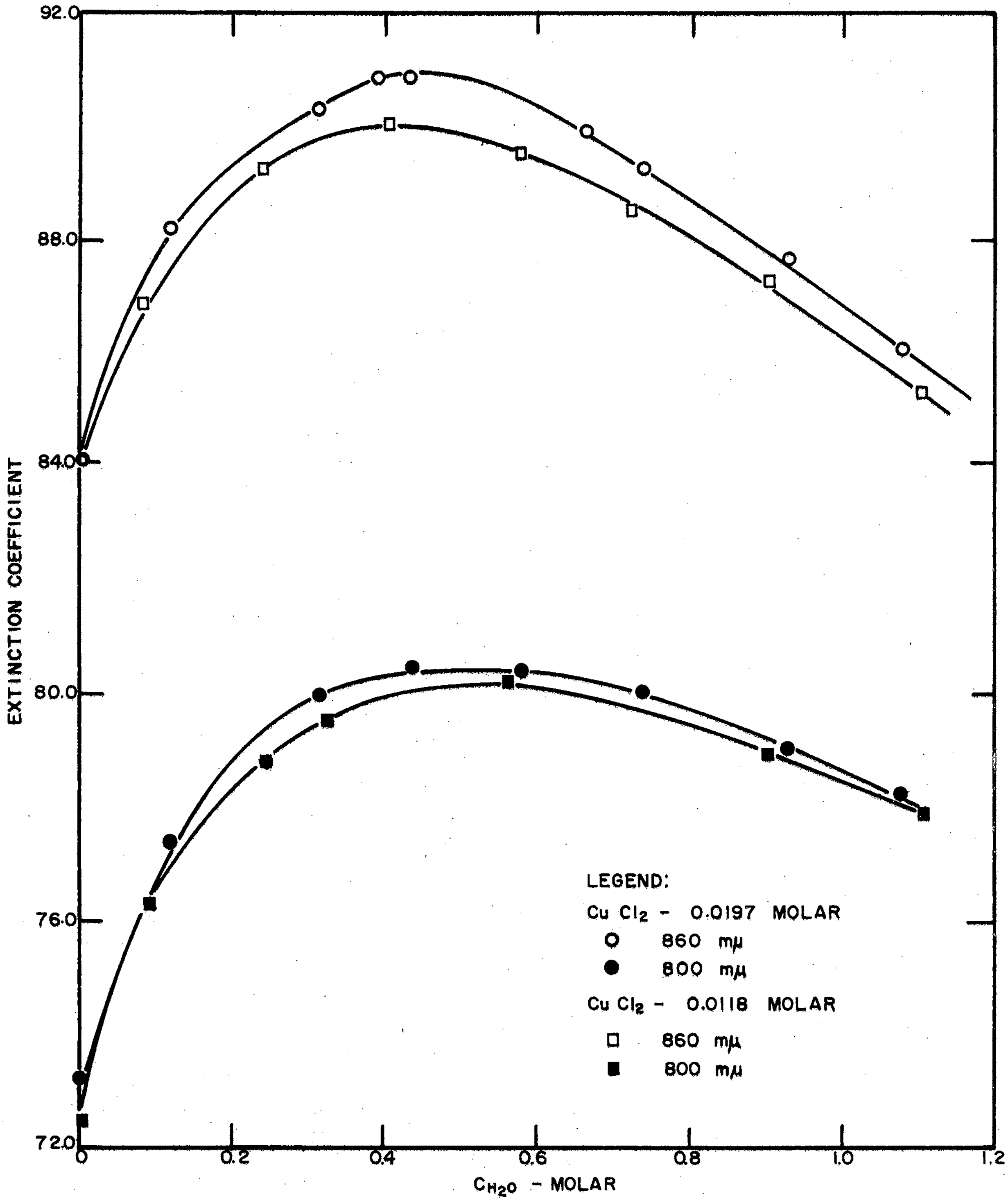

FIGURE 9

ADJUSTMENT CURVES FOR THE COPPER CHLORIDE - WATER - BUTANOL SYSTEM

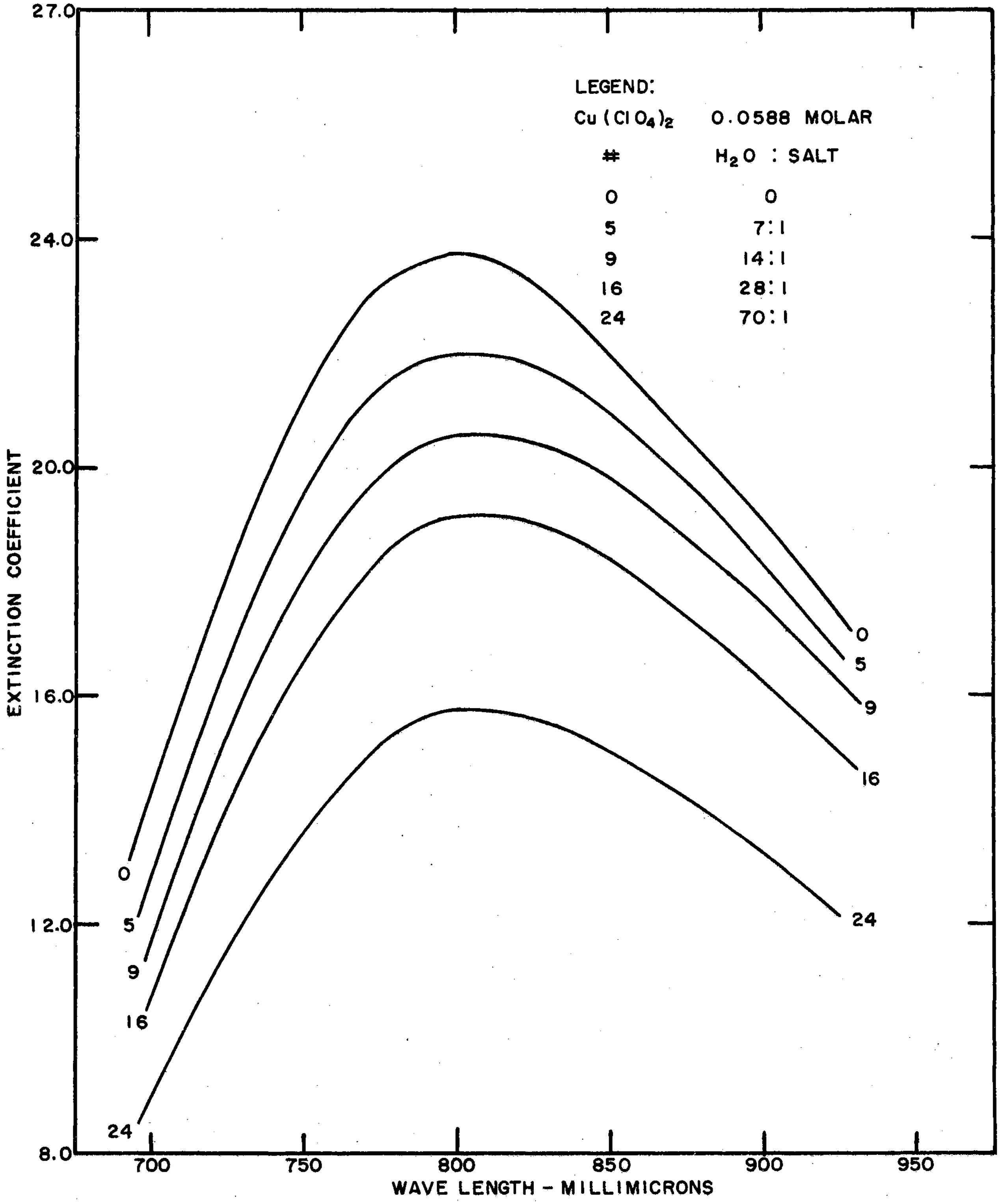

FIGURE 10

SPECTRA OF THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

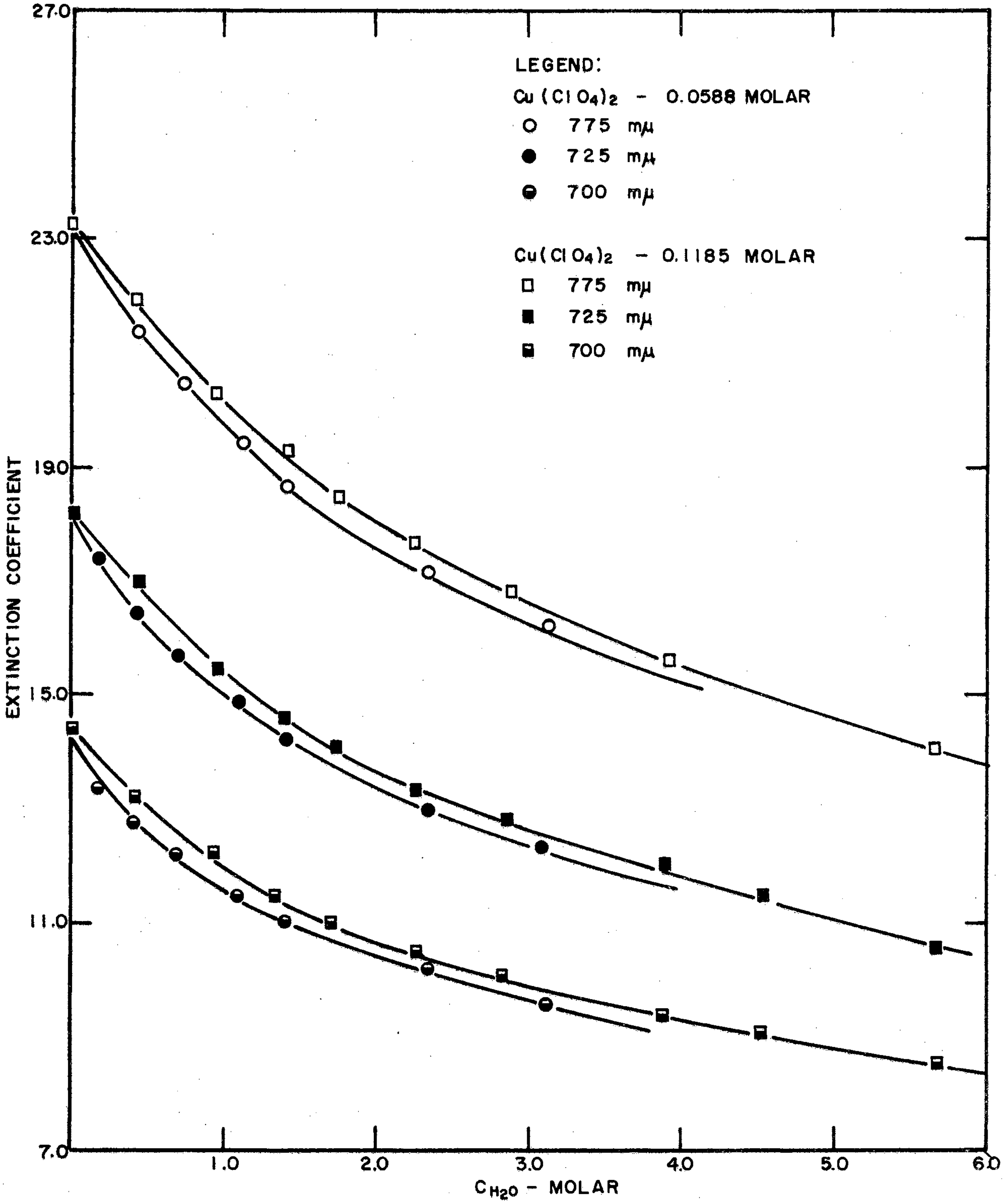

FIGURE 11

ADJUSTMENT CURVES FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

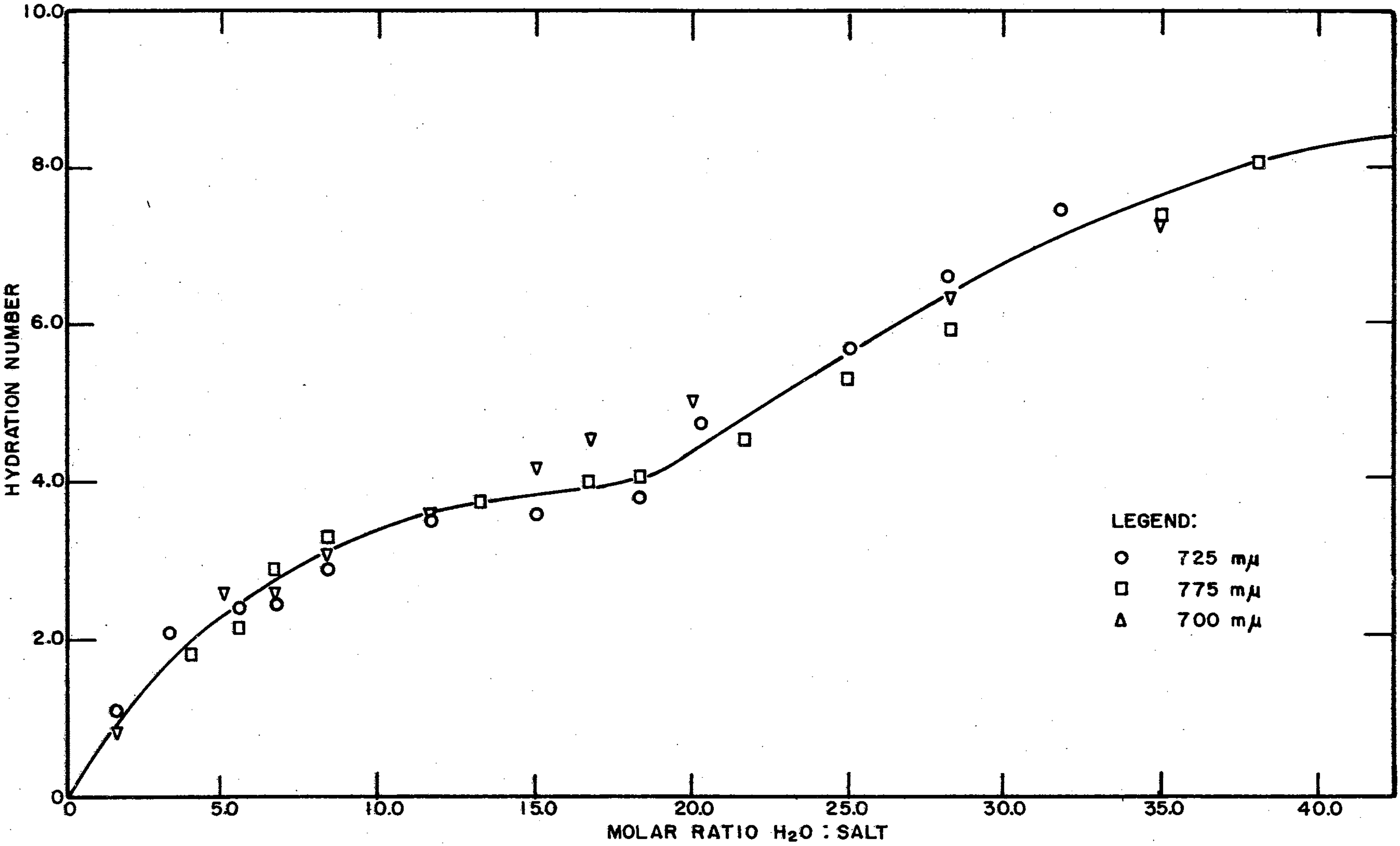

FIGURE 12

FORMATION CURVE FOR THE COPPER PERCHLORATE-WATER-BUTANOL-SYSTEM

TABLE VIII

EXTINCTION COEFFICIENT FOR COPPER CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.0197 M

Sample No.	Water Molar	Molar Ratio	Wavelength 700	725	750	775	800	830
Anh.			27.6	39.8	53.0	64.4	73.2	79.9
1	0.0395	2.01	28.5	41.1	54.2	65.7	74.6	81.5
2	0.079	4.02	29.0	41.6	55.4	67.0	75.9	83.4
3	0.118	6.03	29.6	42.3	56.2	68.5	77.3	84.1
4	0.151	8.04	30.0	42.7	56.9	69.5	78.2	84.8
5	0.197	10.1	30.2	43.2	57.7	70.3	78.7	85.4
6	0.236	12.1	30.6	43.6	58.1	70.8	79.2	85.7
7	0.073	14.1	30.7	44.0	58.9	71.4	79.6	86.1
8	0.314	16.1	31.2	44.5	59.3	71.8	80.0	86.6
9	0.354	18.1	31.6	44.8	59.5	71.8	80.0	87.1
10	0.392	20.1	31.6	45.1	59.4	72.4	80.5	87.1
11	0.431	22.1	31.6	45.1	59.6	72.4	80.5	87.2
12	0.470	24.1	31.6	45.4	60.1	72.4	80.6	87.5
13	0.509	26.1	31.7	44.8	60.2	72.4	80.5	87.2
14	0.542	28.1	31.8	45.2	60.1	72.4	80.5	87.2
15	0.587	30.2	31.8	45.0	59.8	72.5	80.4	87.1
16	0.625	32.2	31.9	45.0	59.8	72.4	80.4	87.1
17	0.664	34.2	31.8	45.0	59.6	72.4	80.4	87.1
18	0.703	36.2	31.8	45.0	59.6	72.4	80.2	86.6
19	0.741	38.2	31.8	44.8	59.6	72.4	80.0	86.1
20	0.780	40.2	31.7	44.8	59.6	72.4	80.0	86.1
21	0.856	44.2	31.7	44.8	59.6	71.8	79.5	85.1
22	0.933	48.2	31.6	44.7	59.3	71.4	79.0	84.6
23	1.01	52.3	31.6	44.4	59.1	70.8	78.8	84.1
24	1.08	56.3	31.4	43.8	58.2	70.3	78.2	83.5

TABLE VIII

EXTINCTION COEFFICIENT FOR COPPER CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.0197 M

	Wavelength			
Sample No.	860	890	920	950
Anh.	84.1	86.6	87.1	83.5
1	85.9	88.2	88.6	86.0
2	87.6	89.6	90.2	87.6
3	88.2	90.2	90.4	88.2
4	88.9	90.7	91.0	88.6
5	89.4	91.6	91.6	89.2
6	89.6	91.2	91.2	88.6
7	90.0	91.6	91.5	89.2
8	90.4	91.6	91.6	88.9
9	90.7	91.6	91.6	89.2
10	90.7	91.7	91.5	88.6
11	90.7	91.7	91.5	88.6
12	90.7	91.6	91.6	88.6
13	90.2	91.6	91.3	88.2
14	90.0	91.5	91.2	88.2
15	89.9	91.4	90.7	87.6
16	89.6	91.0	90.4	87.6
17	89.9	91.0	90.2	87.1
18	89.6	90.8	90.0	86.6
19	89.2	90.0	89.6	86.1
20	89.2	90.0	89.6	86.1
21	88.6	89.6	88.6	85.6
22	87.6	88.6	87.6	84.1
23	86.9	87.9	86.6	83.4
24	86.1	86.8	85.6	82.6

TABLE IX

ADJUSTMENT CURVE DATA FOR THE COPPER CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

860 Millimicrons

	0.0197 M		0.0118 M						
Sample No.	C_{H_2O}	$\bar{E}_{860}$	C_{H_2O}	$\bar{E}_{860}$	$C^*_{H_2O}$	ΔC_M	ΔC_L	$\bar{n}$	Molar Ratio
Anh.		84.1		84.1					
1	0.395	85.9	0.021	85.4					1.68
2	0.079	87.6	0.041	86.3					3.35
3	0.118	88.2	0.061	86.3					5.03
4	0.150	88.9	0.082	86.9	0.064	(-).0079	+.018	(-).434	6.70
5	0.197	89.4	0.123	87.3	0.080	"	+.043	(-).184	10.1
6	0.236	89.6	0.164	87.9	0.102	"	+.062	(-).127	13.4
7	0.274	90.0	0.204	88.6	0.140	"	+.064	(-).123	16.8
8	0.314	90.4	0.245	89.1	0.178	"	+.067	(-).118	20.1
9	0.354	90.7	0.286	89.4	0.202	"	+.084	(-).0942	23.5
10	0.393	90.7	0.326	89.4	0.202	"	+.124	(-).0637	26.8
11	0.432	90.7	0.367	89.4					30.2
12	0.470	90.7	0.407	89.9	0.250	"	+.157	(-).0503	33.5
13	0.509	90.2	0.490	89.6	0.682	"	(-).192	+ .0406	40.2
14	0.542	90.0	0.568	89.4	0.723	"	(-).155	+ .051	46.9
15	0.587	89.9	0.648	88.8					53.6
16	0.626	89.6	0.728	88.6	0.830	"	(-).118	+ .067	60.3
17	0.664	89.9	0.808	88.1	0.883	"	(-).075	+ .105	67.0
18	0.703	89.6	0.908	87.3	0.968	"	(-).060	+ .132	75.4
19	0.741	89.2	1.00	86.4	1.05	"	(-).038	+ .208	83.8
20	0.780	89.2	1.10	85.2					92.2
21	0.856	88.6	1.20	83.9					100.
22	0.933	87.6							
23	1.00	86.9							
24	1.08	86.1							

TABLE X

ADJUSTMENT CURVE DATA FOR THE COPPER CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 800 Millimicrons

	0.01967 M		0.0118 M		
Sample No.	C_{H_2O}	$\bar{E}_{800}$	C_{H_2O}	$\bar{E}_{800}$	Molar Ratio
Anh.		73.2		72.3	
1	0.040	74.6	0.021	74.2	1.68
2	0.079	75.9	0.041	75.2	3.35
3	0.118	77.3	0.061	75.0	5.03
4	0.151	78.2	0.082	76.2	6.70
5	0.197	78.7	0.123	76.5	10.1
6	0.236	79.2	0.164	77.5	13.4
7	0.273	79.6	0.204	78.2	16.8
8	0.314	80.0	0.245	78.8	20.1
9	0.354	80.0	0.286	79.5	23.5
10	0.392	80.5	0.326	79.6	26.8
11	0.431	80.5	0.367	80.1	30.2
12	0.470	80.6	0.407	80.1	33.5
13	0.509	80.5	0.490	80.1	40.2
14	0.542	80.5	0.568	80.4	46.9
15	0.587	80.4	0.648	80.1	53.6
16	0.625	80.4	0.728	80.1	60.3
17	0.664	80.4	0.808	79.6	67.0
18	0.703	80.2	0.908	78.8	75.4
19	0.741	80.0	1.01	78.0	83.8
20	0.780	80.0	1.11	77.2	92.2
21	0.856	79.5	1.2	76.3	100.
22	0.933	79.0			
23	1.01	78.8			
24	1.08	78.2			

TABLE XI

EXTINCTION COEFFICIENT FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

0.0588 M

Sample No.	Wavelength 700	725	750	775	800	830	860
Anh.	14.4	18.2	21.2	23.1	23.8	22.9	21.3
1	14.0	17.8	20.8	22.8	23.4	22.8	21.2
2	13.6	17.4	20.6	22.4	23.0	22.6	21.1
3	13.4	17.2	20.2	22.1	22.8	22.3	21.0
4	13.1	16.8	19.9	21.8	22.4	22.1	20.7
5	12.9	16.5	19.5	21.4	22.1	21.8	20.5
6	12.7	16.3	19.2	21.1	21.8	21.4	20.3
7	12.5	15.9	18.9	20.7	21.4	21.2	20.0
8	12.3	15.6	18.5	20.5	21.1	20.9	19.7
9	12.1	15.4	18.4	20.2	20.7	20.6	19.5
10	11.9	15.3	18.2	19.9	20.6	20.4	19.4
11	11.7	15.0	17.8	19.5	20.3	20.1	19.0
12	11.5	14.9	17.6	19.5	20.1	19.9	18.8
13	11.4	14.6	17.3	19.2	19.9	19.6	18.6
14	11.2	14.4	17.2	18.9	19.7	19.5	18.4
15	11.1	14.3	17.0	18.7	19.5	19.2	18.2
16	10.9	14.0	16.7	18.4	19.1	18.9	17.8
17	10.7	13.6	16.4	18.1	18.7	18.5	17.5
18	10.5	13.4	16.1	17.7	18.4	18.2	17.2
19	10.4	13.2	15.8	17.4	18.0	17.8	17.0
20	10.2	13.0	15.5	17.1	17.7	17.5	16.6
21	9.8	12.6	15.0	16.5	17.2	17.0	16.3
22	9.6	12.3	14.7	16.2	16.8	16.6	15.8
23	9.3	11.8	14.2	15.6	16.3	16.0	15.3
24	9.0	11.6	13.8	15.2	15.8	15.6	14.8

TABLE XI

EXTINCTION COEFFICIENT FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.0588 M

Wavelength

Sample No.	890	920	Water Molar	Molar Ratio
Anh.	19.5	17.8	0.082	1.39
1	19.6	17.7	0.082	1.39
2	19.5	17.7	0.163	2.79
3	19.4	17.7	0.245	4.18
4	19.2	17.4	0.326	5.58
5	18.9	17.3	0.407	6.97
6	18.7	17.2	0.507	8.72
7	18.6	16.9	0.608	10.4
8	18.4	16.6	0.708	12.2
9	18.2	16.5	0.808	13.9
10	17.9	16.3	0.907	15.7
11	17.7	16.1	1.01	17.4
12	17.4	15.9	1.11	19.2
13	17.2	15.8	1.20	20.9
14	17.0	15.6	1.31	22.7
15	16.8	15.4	1.40	24.4
16	16.7	15.2	1.59	27.9
17	16.3	14.9	1.78	31.4
18	15.9	14.6	1.98	34.9
19	15.7	14.3	2.16	38.4
20	15.4	14.1	2.36	41.8
21	15.0	13.8	2.73	48.8
22	14.7	13.2	3.10	55.8
23	14.2	13.0	3.46	62.7
24	13.7	12.5	3.89	69.7

TABLE XII

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

700 Millimicrons

	0.0588 M						0.118 M		
Sample No.	C_{H2O}	$\bar{E}_{700}$	C^*_{H2O}	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{700}$	Molar Ratio
Anh.		14.4						14.5	
1	0.082	13.9	0.150	0.047	0.0597	0.787	0.197	13.7	1.40
2	0.163	13.6	0.320				0.392	13.2	3.34
3	0.245	13.4	0.435	0.151	"	2.53	0.586	12.9	5.05
4	0.326	13.1	0.625	0.154	"	2.58	0.779	12.5	6.67
5	0.407	12.9	0.790	0.181	"	3.03	0.971	12.2	8.34
6	0.507	12.7					1.16	11.8	10.0
7	0.608	12.5	1.14	0.210	"	3.52	1.35	11.5	11.7
8	0.708	12.3					1.54	11.2	13.4
9	0.808	12.1	1.47	0.249	"	4.18	1.72	11.0	15.0
10	0.907	11.9	1.66	0.269	"	4.50	1.91	10.8	16.7
11	0.101	11.7					2.09	10.6	18.3
12	1.11	11.5	1.97	0.300	"	5.02	2.27	10.5	20.0
13	1.20	11.4					2.49	10.3	21.7
14	1.31	11.2					2.64	10.2	23.4
15	1.40	11.1	2.43	0.379	"	6.35	2.81	10.1	25.0
16	1.59	10.9					2.99	9.98	26.7
17	1.78	10.7	2.76	0.407	"	6.82	3.17	9.84	28.4
18	1.98	10.5					3.53	9.68	31.7
19	2.17	10.4	3.40	0.462	"	7.74	3.86	9.37	35.0
20	2.36	10.2					4.20	9.16	38.4

TABLE XII

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

700 Millimicrons

	0.0588 M						0.118 M		
Sample No.	C_{H_2O}	$\bar{E}_{700}$	$C^{*}_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{700}$	Molar Ratio
21	2.73	9.9					4.54	9.08	41.7
22	3.10	9.6					4.87	8.96	45.0
23	3.46	9.4					5.20	8,50	48.4
24	3.82	9.1					5.68	8.36	53.4

TABLE XIII

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

725 Millimicrons

	0.0588 M						0.118 M		
Sample No.	C_{H_2O}	$\bar{E}_{725}$	$\overset{*}{C}_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{725}$	Molar Ratio
Anh.		18.2						18.2	
1	0.082	17.7	0.135	0.062	0.0597	1.04	0.197	17.6	1.40
2	0.163	17.4	0.270	0.122	"	2.04	0.392	17.1	3.34
3	0.241	17.2	0.445	0.141	"	2.36	0.586	16.5	5.05
4	0.326	16.8	0.635	0.144	"	2.42	0.779	15.8	6.67
5	0.407	16.5	0.800	0.171	"	2.86	0.971	15.4	8.34
6	0.544	16.3					1.16	15.1	10.0
7	0.608	15.9	1.16	0.185	"	3.10	1.35	14.7	11.7
8	0.708	15.6					1.54	14.4	13.3
9	0.808	15.4	1.51	0.214	"	3.58	1.72	14.1	15.0
10	0.907	15.3					1.91	13.8	16.7
11	1.01	15.0	1.87	0.222	"	3.72	2.09	13.6	18.4
12	1.11	14.9	2.00	0.275	"	4.60	2.27	13.4	20.0
13	1.20	14.6					2.49	13.2	21.7
14	1.31	14.4					2.64	13.0	23.4
15	1.40	14.3	2.47	0.339	"	5.68	2.81	12.9	25.0
16	1.59	14.0					2.99	12.8	26.7
17	1.78	13.6	2.78	0.392	"	6.57	3.17	12.6	28.4
18	1.98	13.4	3.09	0.441		7.40	3.53	12.3	31.7
19	2.17	13.2	3.35	0.512		8.58	3.86	12.0	35.0
20	2.35	13.0					4.20	11.7	38.4

TABLE XIII

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

725 Millimicrons

	0.0588 M						0.118 M		
Sample No.	C_{H_2O}	$\bar{E}_{725}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{725}$	Molar Ratio
21	2.73	12.6					4.54	11.5	41.7
22	3.10	12.3					4.87	11.3	45.0
23	3.46	11.8					5.20	10.9	48.4
24	3.82	11.6					5.68	10.6	53.4

TABLE XIV

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

775 Millimicrons

Sample No.	0.0588 M						0.118 M		Molar Ratio
	C_{H_2O}	$\bar{E}_{775}$	$C^{*}_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{775}$	
Anh.		23.1						23.1	
1	0.082	22.8					0.197	22.6	1.40
2	0.163	22.4	0.285	0.107	0.0597	1.79	0.392	21.9	3.34
3	0.245	22.1	0.460	0.126	"	2.11	0.586	21.2	5.05
4	0.326	21.8	0.610	0.169	"	2.83	0.779	20.7	6.67
5	0.407	21.4	0.775	0.196	"	3.28	0.971	20.2	8.34
6	0.507	21.1					1.16	19.6	10.0
7	0.608	20.7					1.35	19.2	11.7
8	0.408	20.5	1.32	0.222	"	3.72	1.54	18.9	13.3
9	0.808	20.2					1.72	18.5	15.0
10	0.907	19.9	1.67	0.239	"	4.0	1.91	18.2	16.7
11	1.01	19.6	1.85	0.242	"	4.06	2.09	17.9	18.4
12	1.11	19.5					2.27	17.7	20.0
13	1.20	19.2	2.23	0.269	"	4.50	2.49	17.3	21.7
14	1.31	18.8					2.64	17.0	23.4
15	1.40	18.7	2.50	0.314	"	5.27	2.81	16.8	25.0
16	1.59	18.4					2.99	16.7	26.7
17	1.78	18.0	2.82	0.352	"	5.90	3.17	16.4	28.4
18	1.98	17.6					3.53	16.1	31.1
19	2.17	17.4	3.42	0.437	"	7.33	3.86	15.6	35.0
20	2.35	17.1	3.72	0.477	"	7.98	4.20	15.3	38.4

TABLE XIV

ADJUSTMENT CURVE DATA FOR THE COPPER PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

775 Millimicrons

	0.0588 M						0.118 M		
Sample No.	C_{H_2O}	$\bar{E}_{775}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	C_{H_2O}	$\bar{E}_{775}$	Molar Ratio
21	2.73	16.5					4.54	15.1	41.7
22	3.10	16.2					4.87	14.8	45.0
23	3.46	15.6					5.20	14.2	48.4
24	3.82	15.2					5.68	13.9	53.4

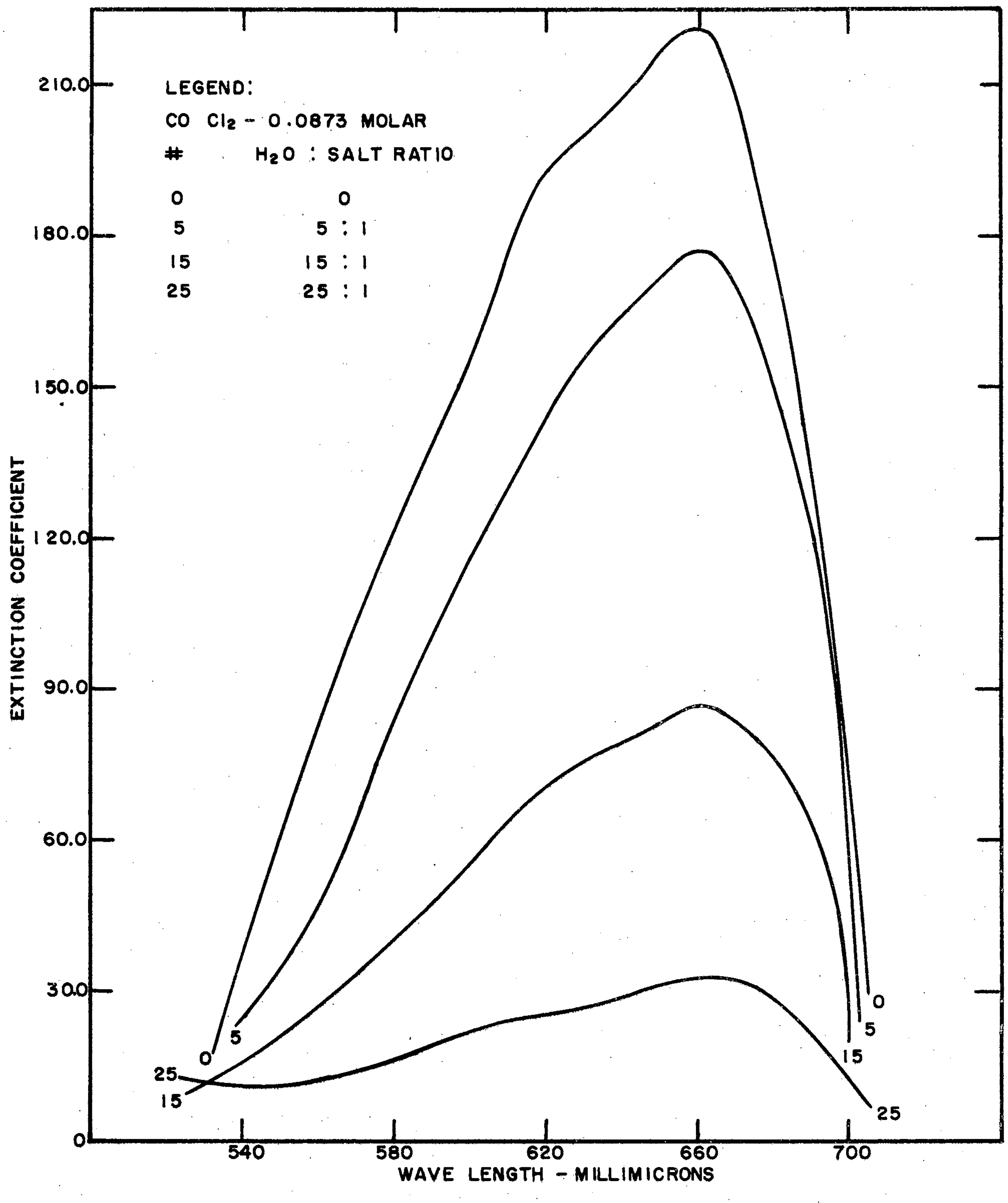

FIGURE 13

SPECTRA OF THE COBALT CHLORIDE-WATER BUTANOL SYSTEM

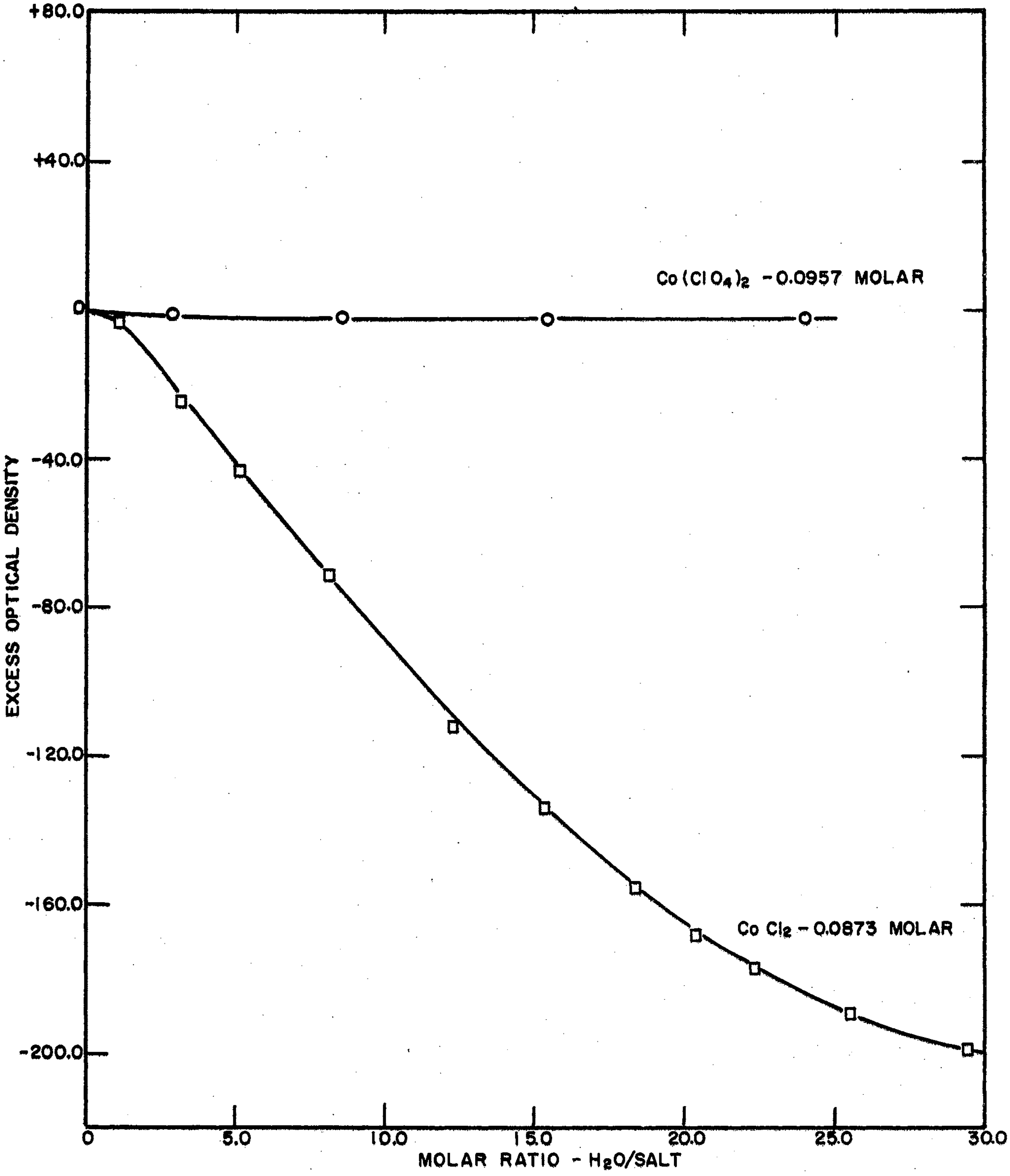

FIGURE 14

EXCESS OPTICAL DENSITY FOR THE COBALT CHLORIDE, COBALT PERCHLORATE-WATER-BUTANOL SYSTEMS

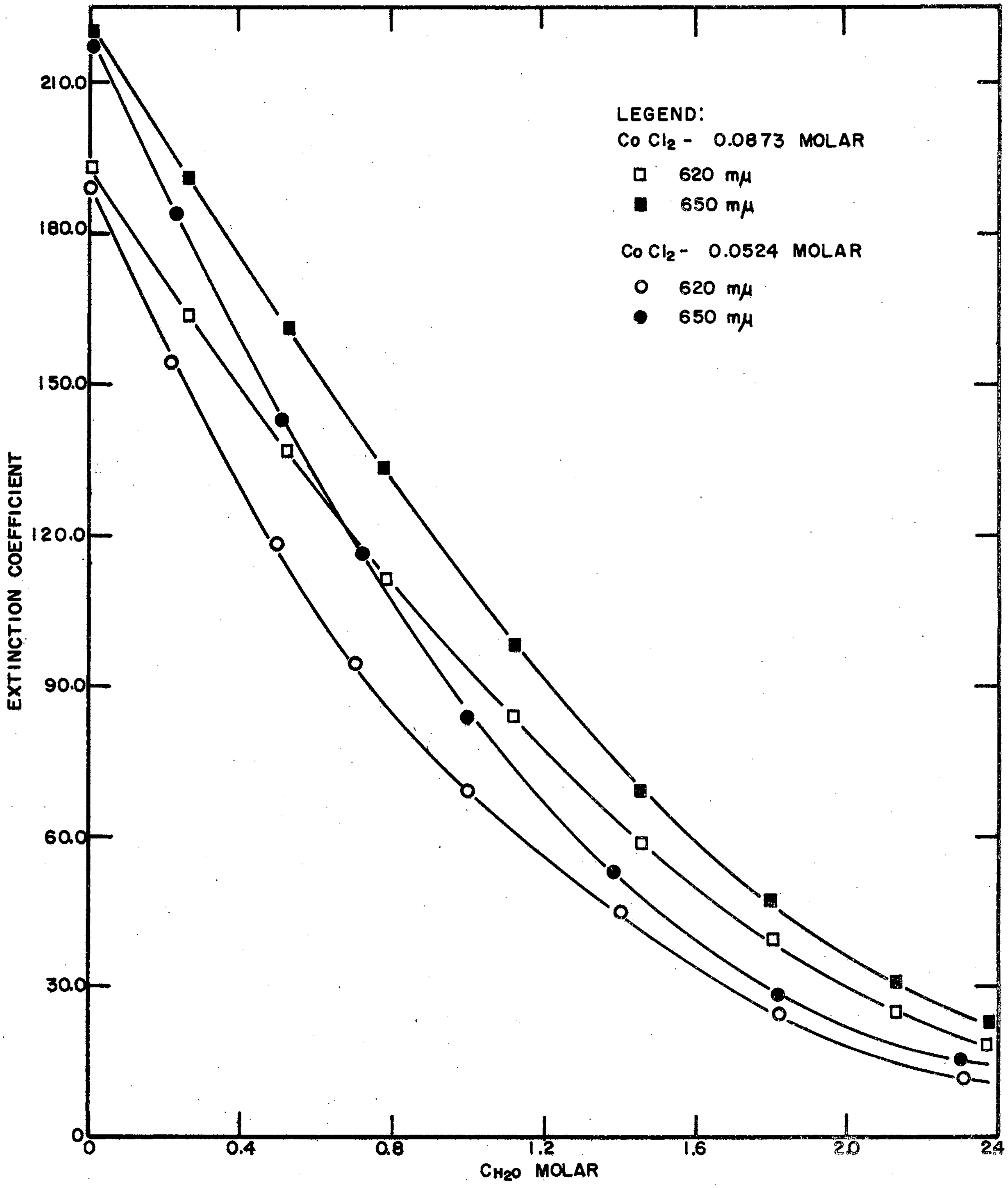

FIGURE 15

ADJUSTMENT CURVES FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

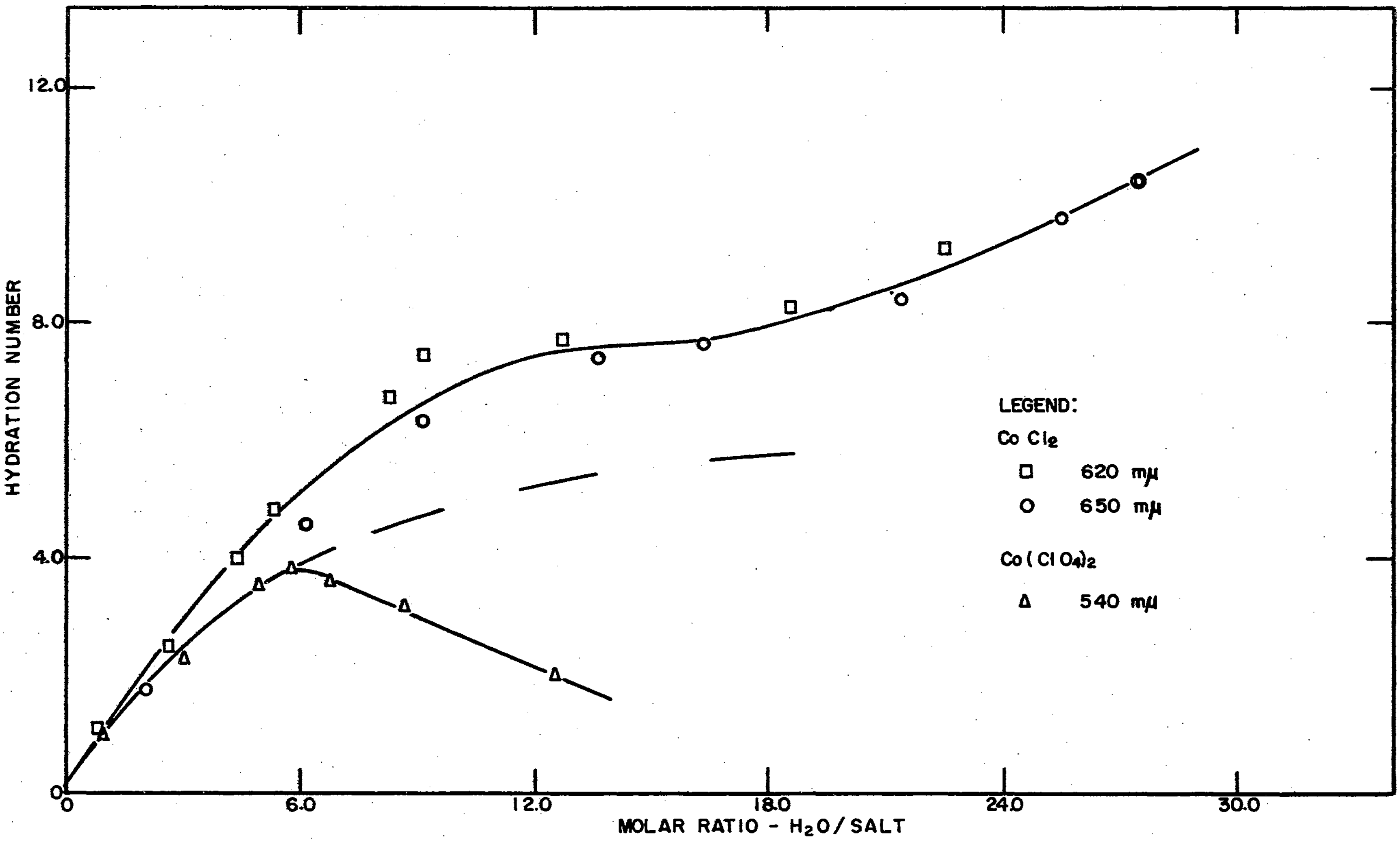

FIGURE 16

FORMATION CURVE FOR THE COBALT CHLORIDE, COBALT PERCHLORATE–WATER–BUTANOL SYSTEMS

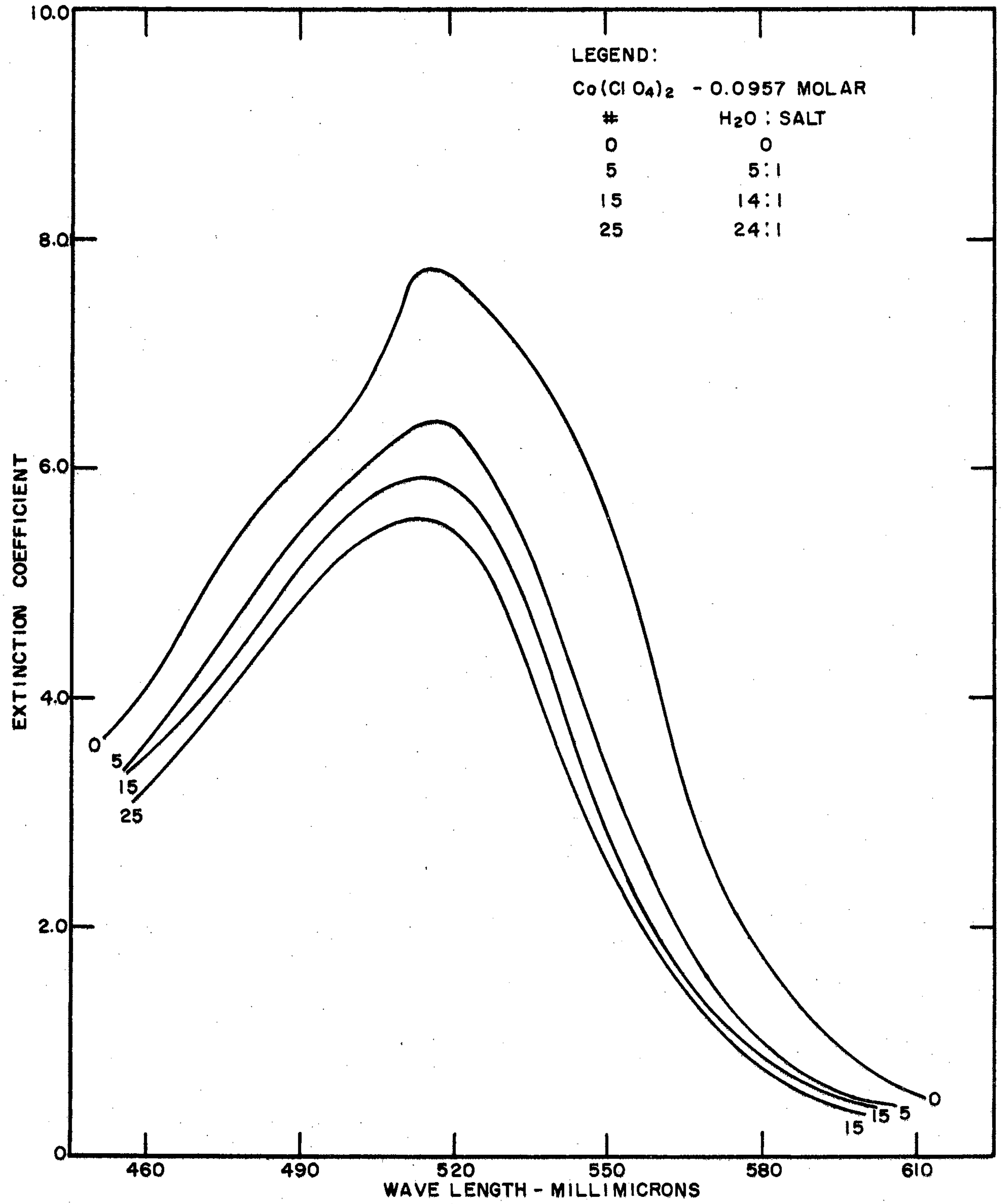

FIGURE 17

SPECTRA OF THE COBALT PERCHLORATE-WATER-BUTANOL SYSTEM

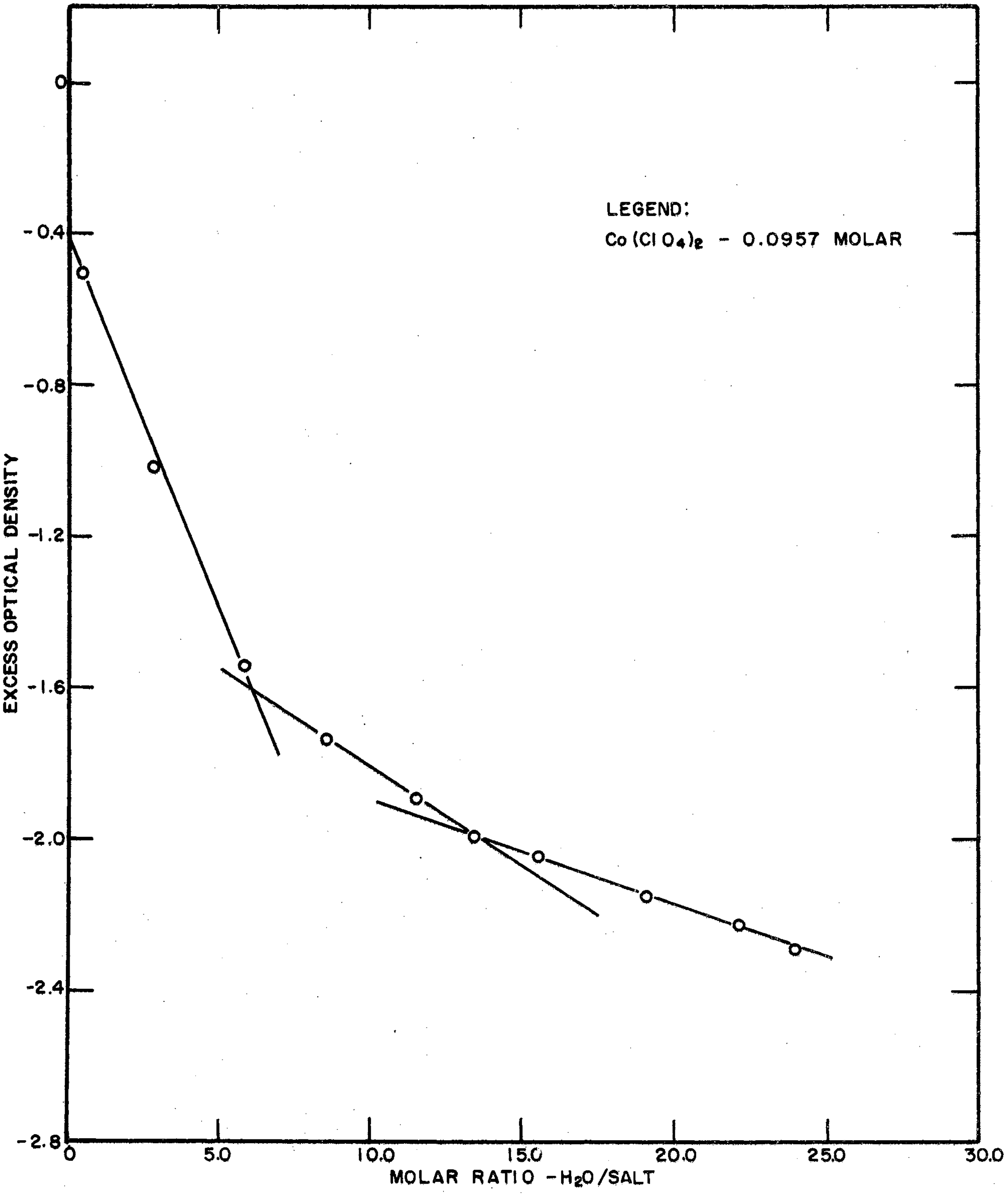

FIGURE 18

EXCESS OPTICAL DENSITY FOR THE COBALT PERCHLORATE—WATER—BUTANOL SYSTEM

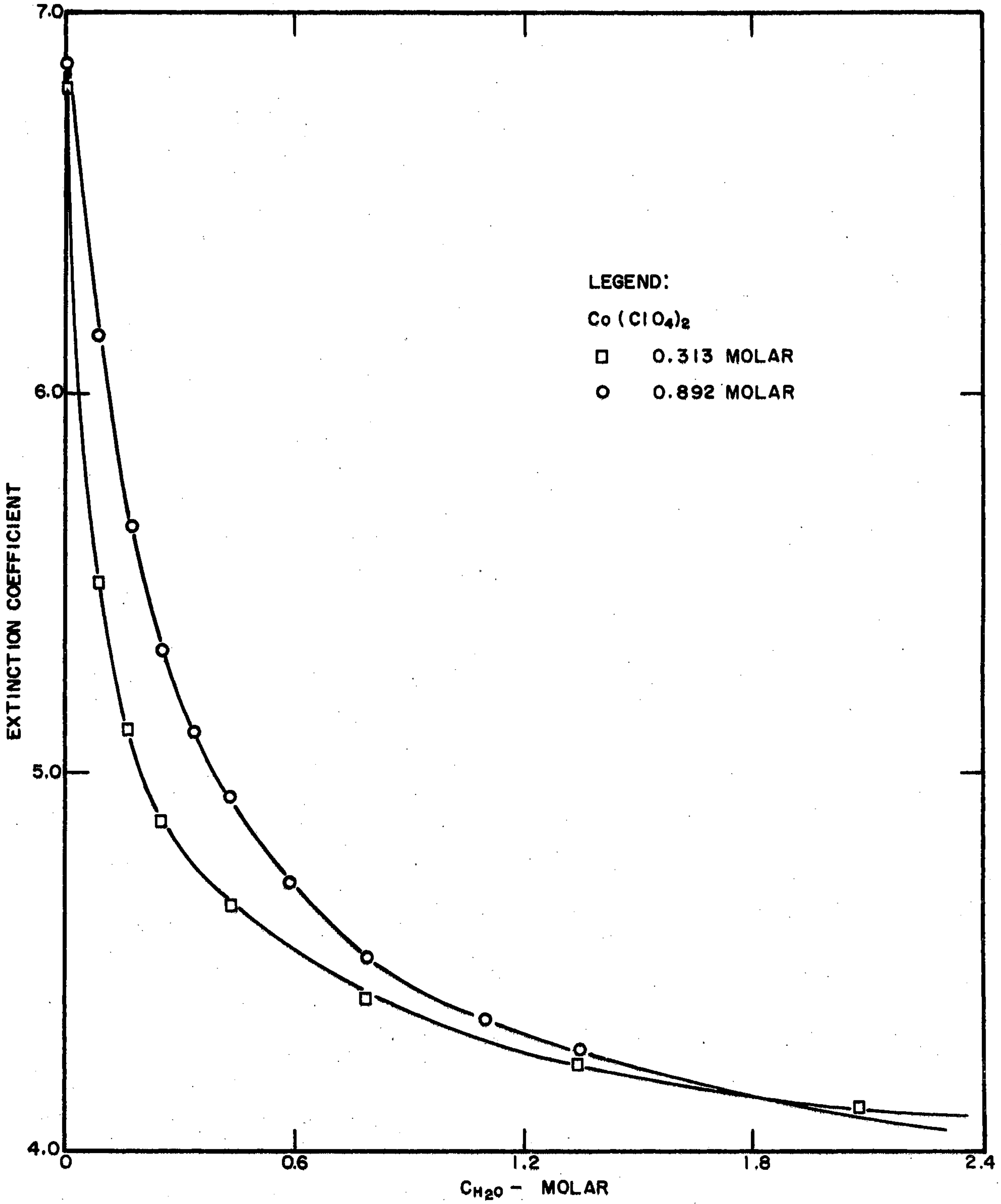

FIGURE 19

ADJUSTMENT CURVE FOR THE COBALT PERCHLORATE-WATER - BUTANOL SYSTEM

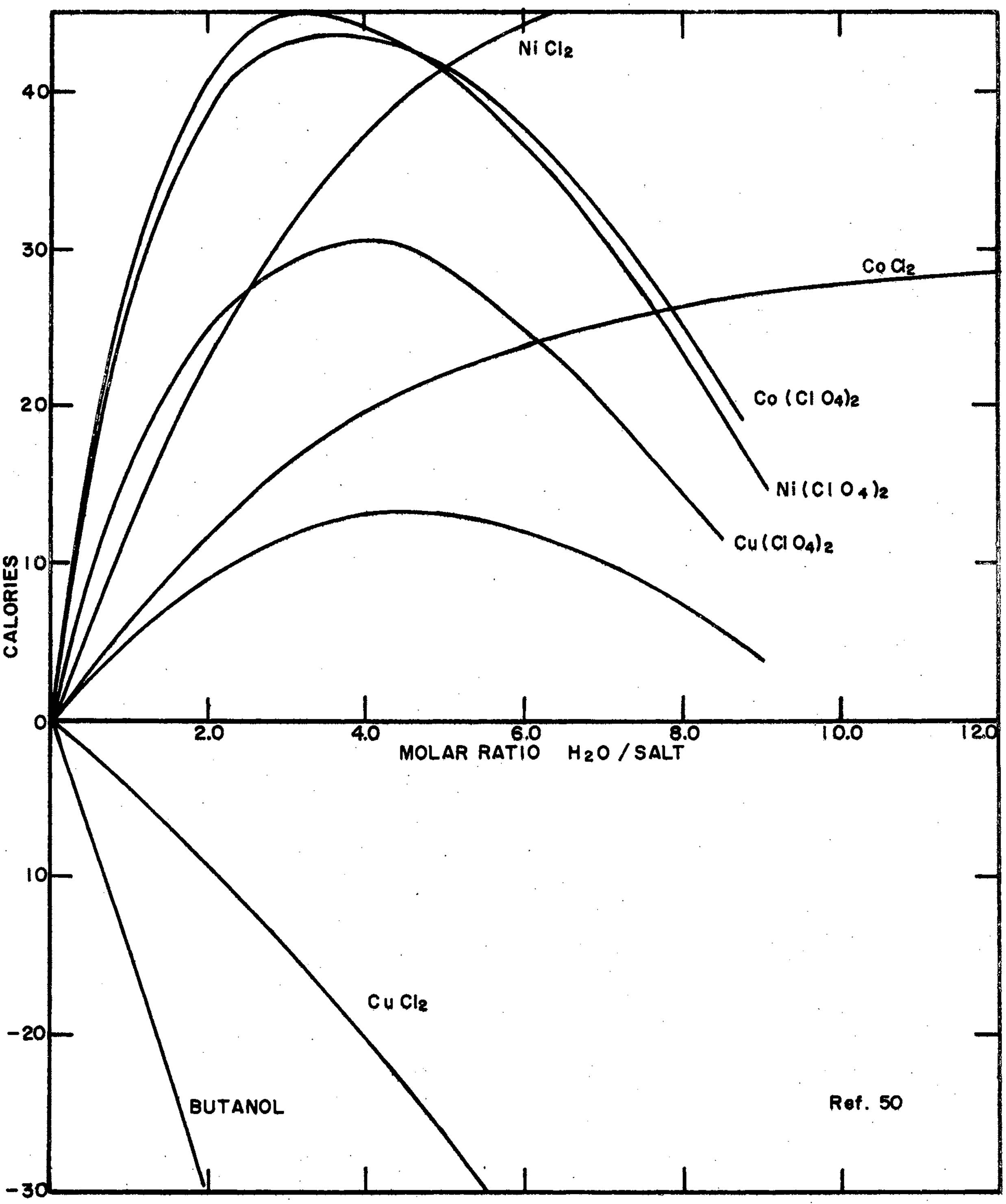

FIGURE 20

ENTHALPY OF MIXING H_2O WITH 0.1 m SOLUTIONS OF SALTS IN n-BUTANOL

TABLE XV

EXTINCTION COEFFICIENT FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.0873 M

Sample No.	Wavelength 540	560	580	600	600	640
Anh.	37.7	80.4	124.	154.	193.	207.
1	32.0	72.0	115.	147.	184.	202.
2	29.1	64.2	107.	141.	174.	193.
3	27.2	58.1	98.7	133.	163.	184.
4	24.3	51.8	89.5	123.	150.	172.
5	24.2	48.3	84.9	118.	144.	163.
6	22.2	44.7	78.8	112.	136.	157.
7	20.6	40.8	72.3	103.	125.	143.
8	19.7	39.2	69.3	98.8	121.	138.
9	18.8	35.2	64.0	90.8	111.	129.
10	17.9	32.6	59.4	85.6	104.	121.
11	17.2	29.5	52.5	74.2	91.0	104.
12	16.4	27.6	49.5	71.0	87.5	100.
13	16.1	27.0	47.5	67.5	83.2	94.5
14	16.0	27.2	45.3	63.8	77.6	88.5
15	15.8	26.1	41.4	57.5	69.5	79.6
16	15.7	24.1	38.3	53.0	64.4	73.4
17	15.4	22.7	35.0	48.9	58.8	67.2
18	15.2	20.6	31.6	43.8	52.6	60.8
19	14.5	18.2	28.3	39.6	48.1	55.3
20	13.6	16.5	24.7	34.6	41.6	48.2
21	13.4	16.7	24.4	33.3	39.3	44.8
22	12.9	15.1	21.8	29.6	35.4	40.8
23	12.4	13.9	19.4	26.4	31.4	36.2
24	11.9	13.1	18.0	24.8	29.6	34.0
25	11.1	12.0	16.0	21.2	25.6	29.2
26	11.1	11.9	15.4	20.1	23.6	27.0
27	11.1	11.1	13.6	17.6	20.8	23.5
28	10.6	10.1	12.1	15.5	18.4	20.5
29	10.6	9.96	11.9	15.1	17.6	19.8
30	9.7	9.20	10.4	13.1	15.1	17.1

TABLE XV

EXTINCTION COEFFICIENT FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C 0.0873 M

Sample No.	Wavelength 650	660	680	700	Water Molar	Molar Ratio
Anh.	218.	222.	176.	68.6		
1	216.	219.	174.	68.6	0.088	1.02
2	200.	209.	169.	68.6	0.177	2.04
3	190.	197.	163.	68.4	0.264	3.06
4	179.	185.	156.	67.5	0.352	4.08
5	171.	178.	151.	62.5	0.439	5.10
6	163.	170.	144.	58.6	0.526	6.12
7	149.	156.	135.	56.5	0.613	7.14
8	143.	150.	131.	54.8	0.700	8.16
9	134.	140.	123.	53.3	0.786	9.18
10	125.	132.	117.	50.5	0.872	10.2
11	109.	113.	99.8	40.1	0.957	11.2
12	105.	108.	95.1	37.0	1.04	12.2
13	98.5	102.	90.4	35.5	1.13	13.3
14	91.6	96.8	86.0	33.7	1.21	14.3
15	83.1	87.7	78.0	32.1	1.30	15.3
16	75.8	80.3	71.5	29.8	1.38	16.3
17	69.8	73.7	66.5	25.8	1.47	17.3
18	62.9	66.3	59.0	22.9	1.55	18.4
19	57.6	61.1	54.6	22.5	1.63	19.4
20	50.2	53.2	47.6	21.0	1.72	20.4
21	47.1	49.7	43.8	19.9	1.80	21.4
22	42.2	44.8	40.2	17.9	1.88	22.4
23	37.8	40.1	35.5	16.6	1.97	23.5
24	35.7	37.5	33.7	15.6	2.05	24.5
25	30.5	32.3	29.2	13.3	2.13	25.5
26	27.9	29.8	26.1	12.6	2.21	26.5
27	24.5	26.0	22.9		2.29	27.5
28	21.5	22.8	20.2	9.2	2.37	28.6
29	20.6	21.7	19.2	8.9	2.46	29.6
30	18.0	19.0	16.6	8.0	2.54	30.6

TABLE XVI

ADJUSTMENT CURVE DATA FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

650 Millimicrons

	0.0524 M						0.0873 M		
Sample No.	C_{H_2O}	$\bar{E}_{650}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	$\bar{E}_{650}$	C_{H_2O}	Molar Ratio
Anh.		219.					218.		
1	0.055	209.					216.	0.088	1.02
2	0.110	202.	0.115	0.062	0.0349	1.77	200.	0.177	2.04
3	0.166	193.	0.180	0.084	"	2.41	190.	0.264	3.06
4	0.221	183.					179.	0.352	4.03
5	0.275	178.	0.310	0.129	"	3.70	171.	0.439	5.10
6	0.330	166.	0.365	0.161	"	4.62	163.	0.526	6.12
7	0.385	160.					149.	0.613	7.14
8	0.439	152.	0.505	0.195	"	5.60	143.	0.700	8.16
9	0.498	143.	0.568	0.218	"	6.25	134.	0.786	9.13
10	0.552	135.	0.630	0.242	"	6.49	125.	0.872	10.2
11	0.602	126.					109.	0.957	11.2
12	0.656	117.					104.	1.04	12.2
13	0.710	114.	0.870	0.258	"	7.40	98.5	1.13	13.3
14	0.764	107.					91.6	1.21	14.3
15	0.818	102.	1.03	0.268	"	7.68	83.1	1.30	15.3
16	0.872	93.6	1.12	0.262	"	7.52	75.8	1.38	16.3
17	0.925	89.5	1.195	0.251	"	7.20	69.8	1.47	17.3
18	0.979	83.6					62.9	1.55	18.4
19	1.03	83.2	1.36	0.273	"	7.83	57.6	1.63	19.4
20	1.08	80.8					50.2	1.72	20.4
21	1.19	73.5	1.51	0.290	"	8.32	47.1	1.80	21.4

TABLE XVI

ADJUSTMENT CURVE DATA FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

650 Millimicrons

	0.0524 M						0.0873 M		
Sample No.	C_{H_2O}	$\bar{E}_{650}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	$\bar{E}_{650}$	C_{H_2O}	Molar Ratio
22	1.30	64.0	1.59	0.292	0.0349	8.38	42.2	1.88	22.4
23	1.40	54.4					37.8	1.97	23.5
24	1.51	45.8					35.7	2.05	24.5
25	1.61	41.1	1.79	0.339	"	9.75	30.5	2.13	25.5
26	1.72	34.4					27,9	2.21	26.5
27	1.82	29.1	1.92	0.365	"	10.4	24.5	2.29	27.5
28	1.92	23.8					21.5	2.37	28.6
29	2.03	21.7					20.6	2.46	29.6
30	2.13	19.1					18.0	2.54	30.6
31	2.33	15.1							

TABLE XVII

ADJUSTMENT CURVE DATA FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

620 Millimicrons

	0.0524 M							0.0873 M	
Sample No.	C_{H_2O}	$\bar{E}_{620}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	Molar Ratio	$\bar{E}_{620}$	C_{H_2O}
Anh.		191.						193.	
1	0.055	182.	0.047	0.041	0.0349	1.17	1.02	183.	0.088
2	0.110	174.	0.109	0.068	"	1.94	2.04	174.	0.177
3	0.166	165.	0.176	0.088	"	2.52	3.06	163.	0.264
4	0.221	156.					4.08	150.	0.352
5	0.275	145.	0.300	0.139	"	3.99	5.10	144.	0.439
6	0.330	134.	0.355	0.171	"	4.92	6.12	136.	0.526
7	0.385	134.					7.14	124.	0.613
8	0.439	127.					8.16	121.	0.700
9	0.498	118.	0.548	0.238	"	6.83	9.18	111.	0.786
10	0.552	110.	0.612	0.260	"	7.46	10.20	104.	0.872
11	0.602	105.					11.21	91.4	0.957
12	0.656	98.9					12.2	87.5	1.04
13	0.710	94.1	0.860	0.268	"	7.70	13.3	83.2	1.13
14	0.764	88.0					14.3	77.6	1.21
15	0.818	85.0					15.3	69.5	1.30
16	0.872	78.0					16.3	64.4	1.38
17	0.925	73.8					17.3	58.8	1.47
18	0.979	69.5					18.4	52.6	1.55
19	1.03	69.3	1.35	0.283	"	8.13	19.4	48.1	1.63
20	1.08	67.6					20.4	41.6	1.72
21	1.19	61.8	1.50	0.305	"	8.74	21.4	39.3	1.80
22	1.30	53.4	1.56	0.317	"	9.09	22.4	35.4	1.88

TABLE XVII

ADJUSTMENT CURVE DATA FOR THE COBALT CHLORIDE-WATER-BUTANOL SYSTEM

Temp. 25° C

620 Millimicrons

	0.0524 M						0.0873 M		
Sample No.	C_{H_2O}	$\bar{E}_{620}$	$C^*_{H_2O}$	ΔC_L	ΔC_M	$\bar{n}$	Molar Ratio	$\bar{E}_{620}$	C_{H_2O}
23	1.40	45.1	1.64	0.325	0.0349	9.32	23.5	31.4	1.97
24	1.51	37.6					24.5	29.6	2.05
25	1.61	34.1	1.77	0.359	"	10.3	25.5	25.5	2.13
26	1.72	28.4					26.5	23.5	2.21
27	1.82	24.0	1.93	0.355	"	10.2	27.5	20.8	2.29
28	1.92	20.0	2.01	0.364	"	10.4	28.6	18.3	2.37
29	2.03	18.1					29.6	17.5	2.46
30	2.13	16.1					30.6	15.1	2.54
31	2.33	12.9							

TABLE XVIII

EXTINCTION COEFFICIENT FOR THE COBALT PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

0.0957 M

Sample No.	Wavelength					
	460	480	500	515	520	540
Anh.	4.09	5.50	6.55	7.83	7.73	6.59
1	3.97	5.26	6.35		7.23	5.84
2	3.98	5.23	6.30	7.00	6.98	5.45
3	3.93	5.13	6.21	6.79	6.71	5.10
4	3.86	5.03	6.07	6.60	6.53	4.83
5	3.73	4.89	5.96	6.43	6.35	4.60
6	3.68	4.82	5.85	6.35	6.18	4.48
7	3.65	4.75	5.82		6.10	4.36
8	3.60	4.72	5.77	6.18	6.04	4.27
9	3.64	4.71	5.76		6.00	4.20
10	3.55	4.68	5.72		5.94	4.18
11	3.60	4.68	5.69		5.87	4.14
12	3.55	4.62	5.66		5.85	4.07
13	3.56	4.62	5.64		5.83	4.05
14	3.55	4.60	5.62		5.78	4.03
15	3.54	4.59	5.57		5.75	3.97
16	3.47	4.51	5.53		5.67	3.94
17	3.47	4.49	5.50		5.65	3.88
18	3.48	4.49	5.48		5.64	3.88
19	3.45	4.48	5.44		5.60	3.86
20	3.44	4.45	5.43		5.57	3.84
21	3.42	4.45	5.41		5.56	3.82
22	3.41	4.44	5.39		5.54	3.80
23	3.43	4.44	5.36		5.50	3.78
24	3.38	4.38	5.33		5.45	3.75
25	3.35	4.37	5.31		5.43	3.73

TABLE XVIII

EXTINCTION COEFFICIENT FOR THE COBALT PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C | 0.0957 M

Sample No.	Wavelength			Molar Ratio	Water Molar
	560	580	600		
Anh.	3.96	1.70	0.78		
1	3.27	1.40	0.679	0.962	0.092
2	2.98	1.32	0.731	1.92	0.184
3	2.71	1.18	0.700	3.85	0.367
4	2.52	1.10	0.658	4.81	0.461
5	2.26	0.961	0.574	5.77	0.548
6	2.13	0.910	0.543	6.73	0.638
7	2.10	0.878	0.538	7.69	0.728
8	2.06	0.846	0.533	8.65	0.818
9	1.99	0.856	0.543	9.62	0.908
10	1.96	0.825	0.522	10.6	0.997
11	1.93	0.815	0.522	11.5	1.08
12	1.91	0.815	0.522	12.5	1.17
13	1.91	0.805	0.522	13.5	1.26
14	1.90	0.794	0.522	14.4	1.35
15	1.87	0.784	0.512	15.4	1.47
16	1.82	0.768	0.501	16.3	1.53
17	1.80	0.773	0.496	17.3	1.61
18	1.80	0.783	0.522	18.3	1.70
19	1.80	0.773	0.496	19.2	1.75
20	1.79	0.768	0.501	20.2	1.87
21	1.76	0.773	0.501	21.1	1.96
22	1.77	0.773	0.501	22.1	2.04
23	1.75	0.768	0.501	23.1	2.13
24	1.74	0.742	0.501	24.0	2.21
25	1.71	0.731	0.491		

TABLE XIX

ADJUSTMENT CURVE DATA FOR THE COBALT PERCHLORATE-WATER-BUTANOL SYSTEM

Temp. 25° C

540 Millimicrons

	0.0313 M							0.0892 M		
Sample No.	C_{H2O}	$\bar{E}_{540}$	C^{*}_{H2O}	ΔC_M	ΔC_L	$\bar{n}$	C_{H2O}	$\bar{E}_{540}$	Molar Ratio
1	0.086	5.49	0.029	0.0579	0.057	0.985	0.086	6.14	0.97
2	0.172	5.11	0.070	"	0.102	1.76	0.172	5.64	1.94
3	0.258	4.87	0.120	"	0.138	2.38	0.258	5.32	2.91
4	0.343	4.75	0.172	"	0.171	2.95	0.343	5.10	3.88
5	0.429	4.65	0.226	"	0.203	3.51	0.429	4.94	4.85
6	0.583	4.55	0.295	"	0.220	3.80	0.515	4.81	5.82
7	0.782	4.41	0.380	"	0.203	3.50	0.583	4.70	6.78
8	1.01	4.33	0.505	"	0.178	3.07	0.683	4.59	7.75
9	1.35	4.23	0.630	"	0.152	2.63	0.782	4.51	8.72
10	1.67	4.18	0.790	"	0.145	2.51	0.935	4.43	10.6
11	2.08	4.12	0.988	"	0.113	1.95	1.10	4.34	12.6
12							1.35	4.26	15.5

SUMMARY AND CONCLUSIONS

The colors of solutions of the perchlorates of nickel (II), copper (II) and cobalt (II) in 1-butanol are similar to those of aqueous solutions of the same salts. Addition of water to the anhydrous butanol solutions results in a progressive decrease in the extinction coefficient and a small shift in the absorption bands toward shorter wavelengths. Since the spectra of the anhydrous solutions are typically those for octahedral coordination, the observed small shifts toward higher energies are to be associated with increase in ligand field strength.

The formation of aquo complexes presumably occurs through the displacement of butanol molecules by more basic water molecules within the coordination shell of the transition metal ion. At water-to-butanol mole ratios equal to or less than the coordination number one may expect that the principal change occurring in the solution upon the addition of water is the hydration reaction, but at higher water concentrations changes in the properties of the medium may be expected also. Since in the case of the perchlorates the anion is probably separated from the cation by a solvent sheath even in non-dissociated aggregates, ionization favored by increase in the dielectric constant would not be expected to affect the absorption spectrum greatly. Consequently, a progressive shift in the spectrum upon the addition of water without band splitting is to be expected in view of the similarity of the butanol and water molecules, and the average ligand field approximation holds.

The method of corresponding solutions can be shown to be applicable to a system of solvates regardless of the degree of dissociation provided all kinetically stable species are in equilibrium and follow Beer's law of light absorption. The average ligand number $\underline{\bar{n}}$ can be found from the corresponding solutions, but it is a function of the ionization constants for the system as well as the formation constants for the aquo complexes.

The average ligand number for each of the three perchlorates studied shows rather different behavior with respect to change in the water/salt ratio. The hydration of nickel perchlorate was found to increase rapidly with a slope of approximately unity (increase in the hydration number of one per unit increase in the water/salt ratio). Instead of approaching a limiting value, however, the average hydration number increases to values in excess of 15 moles of water per nickel perchlorate. Such high hydration numbers must mean that shells of solvation beyond the first become filled with water. This is in good agreement with the hydration numbers reported for solutions of nickel perchlorate in 2-octanol.

For copper perchlorate the average hydration number appears to approach a limiting value of 4 waters per copper perchlorate at mole ratios as high as 20. At still higher mole ratios, however, the hydration number apparently increases above 4, but because of the very large experimental error in its determination at high ratios there is considerable uncertainty in the values. In the case of the cobalt salt again the average hydration number increases until there are about 4 waters per cobalt perchlorate, but then the values decrease again. A value of 4 would be expected for an octahedral complex with two positions occupied by anions; this also agrees with the fact that the heat of reaction of all three perchlorates reaches a maximum at a water/salt ratio of 4 (see Figure 20). However, the similarity in the observed hydration of cobalt and nickel perchlorates determined by extraction with 2-octanol and by spectrophotometry in 2-octanol contradicts the results obtained from corresponding solutions in butanol.

In the case of the chlorides of nickel, copper and cobalt the method of corresponding solutions would be expected to give widely different results. The nickel chloride spectrum, while that of an octahedral complex, is strongly shifted toward longer wavelengths. This probably means that chlorides are primarily bound to the metal. Displacement of four molecules of butanol and two chlorides by water should result in a limiting average hydration number of 6. Such is found to be the case. This agrees with the results from calorimetry also.

The cobalt chloride spectrum is that of a tetrahedral complex in which chlorides are almost certainly directly coordinated to the cobalt; however, the completely aquated complex is octahedral with an entirely different spectrum. The bands used in the corresponding solution analysis were those of the 4-coordinate complex since the intensity of the absorption bands in the visible which are characteristic of the 6-coordinate complexes are very weak. Again, as in the case of nickel chloride, a limiting hydration number was indicated, but at higher mole ratios of water to salt there was an apparent increase in the average hydration number above the limiting value of 8 found at ratios below about 18:1. Support for this is also found from measurement of the heat of reaction of water with cobalt chloride in butanol.

The method of corresponding solutions could not be used to study the average hydration number of copper chloride solutions in butanol. Calorimetric measurements have also indicated that aquo complexes of copper chloride are not readily formed in butanol.

For systems of similar ligands, J. Bjerrum has defined an average formation constant which is simply related to the average ligand number $\bar{n}$ when $\bar{n} = N/2$, where N is the maximum coordination number. Bjerrum's treatment essentially is based upon the assumption that successive formation constants are determined by the availability of coordination sites, and the average ligand number as a function of ligand concentration is theoretically a S-shaped curve. The Bjerrum treatment was applied to the data where it seemed applicable; i.e., when the formation function appeared to have approximately the theoretical shape. Constants so obtained are probably of limited significance, however, because of the uncertainty of the degree of ionization in the solution. Values found are as follows:

Nickel chloride-water-butanol system

$K_{av} = 1.84$ liter/mole

$(\frac{N}{2} = 3)$

Copper perchlorate-water-butanol system

$K_{av} = 4.04$ liter/mole

$(\frac{N}{2} = 2)$

$K_{av} = 0.605$ liter/mole

$(\frac{N}{2} = 4)$

Cobalt chloride-water-butanol system

$K_{av} = 9.55$ liter/mole

$(\frac{N}{2} = 4)$

The study in general has supported the conclusions regarding hydration and aquo complex formation of some of the transition metal salts in butanol based upon calorimetry, and it is concluded that the method of corresponding solutions can be used successfully to compliment other methods of studying solvation in nonaqueous solutions.

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APPENDIX A

To show that corresponding solutions have the same concentration of free ligand, one notes that for a system composed of a fully dissociated metal salt and a single ligand the formation function is given by

$$\bar{n} = \frac{\sum_{0}^{n} n\,(MA_n)}{C_M} = \frac{\sum_{0}^{n} n\beta_n\,(M)(A)^n}{C_M} \qquad (1)$$

By the definition of corresponding solutions, however, two solutions which are corresponding have the same fractions of total metal in the nth complex. Thus

$$\frac{(MA_n)_1}{C_{M_1}} = \frac{(MA_n)_2}{C_{M_2}} \qquad (2)$$

From equations (1) and (2) it follows that $\bar{n}_1 = \bar{n}_2$ and that $(A)_1 = (A)_2$.

For the case of 2:1 metal perchlorates dissolved in butanol with water as the added ligand, one cannot assume complete dissociation; however, since the spectra of the aqueous and butanol solutions are almost identical, it seems reasonable to assume that in any ion associate the perchlorate ion will be separated from the metal by at least one solvent molecule and not be a part of the coordination sphere of the metal. The formation constants for reactions in which water substitutes for butanol within the coordination sphere will then be approximately independent of the degree of ion association. One can write, therefore,

$$\beta_n = \frac{(M)\ (A)^n}{(MA_n)} = \frac{(MX)\ (A)^n}{(MA_nX)} = \frac{(MX_2)\ (A)^n}{(MA_nX_2)} \qquad (3)$$

where $A = H_2O$, $X = ClO_4^-$

$$\bar{n} = \sum_0^n \frac{n}{C_M}\left[(MA_n) + (MA_nX) + (MA_nX_2)\right] = \qquad (4)$$

$$\sum_0^n \frac{n\beta_n}{C_M}\left[(M) + (MX) + (MX_2)\right]\ (A)^n$$

and

$$\frac{\left[(MA_n) + (MA_nX) + (MA_nX_2)\right]_1}{C_{M_1}} = \qquad (5)$$

$$\frac{\left[(MA_n) + (MA_nX) + (MA_nX_2)\right]_2}{C_{M_2}}$$

From (4) and (5) it is seen that just as in the case of the fully dissociated case $\bar{n}_1 = \bar{n}_2$ and $(A)_1 = (A)_2$ or the concentration of free ligand is the same for corresponding solutions.

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Thesis: A SPECTROPHOTOMETRIC STUDY OF THE AQUO COMPLEXES OF COBALT (II), COPPER (II), NICKEL (II) CHLORIDES AND PERCHLORATES IN I-BUTANOL

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