THE LIQUID-LIQUID EXTRACTION
OF METAL PERCHLORATES

By

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OF METAL PERCHLORATES

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INTRODUCTION

The work done in the preparation of this paper stems from a more general study in the field of liquid-liquid extraction of metal salts, carried on at Oklahoma A. and M. College under the auspices of the Atomic Energy Commission. Numerous papers have been published in recent years dealing with the theory and application of liquid-liquid extraction in regard to problems of engineering interest. The most pertinent of these is the work of Garwin and Hixson (6), after whose work this investigation was patterned. Although the solvent systems (2-octanol and water) and the method of equilibration are the same as employed by Dr. Garwin, the two studies differ in that Dr. Garwin was interested in the chemical engineering aspects of the problem while in the present investigation, the problem is approached from a theoretical standpoint.

The work under investigation in this phase of the general study of liquid-liquid extraction of salts deals with the two systems, $Co(ClO_4)_2$-$CoCl_2$ and $Ni(ClO_4)_2$-$Ca(ClO_4)_2$. It is an extension of a rather comprehensive study done on promoted cobalt perchlorate extraction which was recently completed (12). Some of the factors to be studied were: the nature of any complex formation in either phase of the system after equilibration; the effect on the extractability of one component of a variation in the concentration of a second component; the magnitude of the hydration numbers of the salts in the non-aqueous phase; and the variation of other properties of the system in the equilibrium state.

The extractability of a salt from water by a non-aqueous solvent depends on any factor that will alter the activity of the salt in either phase. If the solutions being studied were ideal, we could easily express distribution coefficient k_d in terms of the molal ratio of the salt distributed between the aqueous and non-aqueous phase.

$$k_d = \frac{m_{MA}\text{ (non-aqueous phase)}}{m_{MA}\text{ (aqueous phase)}}$$

The reader will immediately recognize this as a statement of Nernst Distribution Law. It is, however, very limited in application. In order that k_d remain constant, the activity coefficient of the extracted species must remain constant in both phases over the concentration range being considered. There are a number of factors which in concentrated solutions make this unlikely. Some of the more important of these concentration dependent factors are: the energy of solvation of ions in each phase; the extent of the cation-anion interactions; and, the magnitude of the stability constant of any complex formation in either or both phases. These factors should be related theoretically, but seldom are experimentally, to the charge, radii, electronic configuration, and polarizability of the ions as well as to the dielectric constants, dipole moments, and internal structures of the solvents.

One reason for the apparent lack of correlation between experimental and theoretical approaches to the problem is the difficulty of obtaining enough data which can be applied to a particular system. It is, however, often possible to combine the data from several similar systems and apply it to a single system so as to obtain a semi-quantitative comparison between experimental and theoretical distribution coefficients. This technique was used in the present study to obtain an estimate of the aqueous- and the 2-octanol-phase activity coefficients of the extracted species and the average hydration numbers for the extracted salts.

In an effort to give the reader an appreciation of the theoretical factors which influence the extractability of a single salt or salt pair, a number of these factors first will be discussed in some detail.

Effect of Complex Formation on Extractability

A direct correlation has been observed in some systems between the ease of complex formation and the relative extractability of the complexing species. An excellent example of this phenomenon is the extraction of $CoCl_2$ from systems having high chloride concentrations, (6). It was noted that appreciable extraction did not occur until the solutions showed a noticeably blue color as compared to the typical pink color of unpromoted aqueous $CoCl_2$. This blue color has been attributed to the presence of the $CoCl_2$ and $CoCl_3^-$ species (6).

A simple explanation for this phenomenon is readily available. If a solution is considered in which the species present consist of one or more completely dissociated compounds, the resulting ions will have a high degree of affinity for highly polar solvents. Therefore, the solubility of these ionic types in water will be high, and it follows that their ease of extractability by a less highly polar solvent would be low. On the other hand, if an agent, of such a nature as to effect the formation of a molecular aggregate of the extractable entity is added to the aqueous phase, the resulting complex may be considered to be less compatible with water and, therefore, more readily extracted into organic solvents. This is apparently due to the replacement of electrovalent type bonding by coordinate covalent bond types usually associated with complexes.

Effect of the Variation of the Dielectric Constant of the Solvent on Extractability

It has been shown that the development of an expression for the distribution constant of a hypothetical compound MX_n on purely theoretical electrostatic grounds will contain a term that involves the electrical work of discharging an ion in a medium of one dielectric constant and recharging in a second medium of a dissimilar dielectric constant (2). It is also known that increasing the noninteracting salt concentration in the aqueous phase will result in a lowering of the dielectric constant in the salt solution. Therefore, since the work of charging and discharging varies inversely with the dielectric constant, increasing the salt concentration of the solution prior to equilibration with the extracting solvent will have the effect of changing the partition coefficient in favor of the non-aqueous phase. Owing to the difficulty of obtaining data for the dielectric constant of concentrated aqueous salt solutions, no rigorous attempt has been made to evaluate this term. The advent of microwave techniques may, however, enable the gathering of sufficient data to test the validity of this expression in the future.

Effect of Common Ions

It was pointed out earlier that the addition of a second compound to a solution of the solute to be extracted exhibits a marked effect on the magnitude of its distribution coefficient. A portion of this phenomenon can be attributed to a mass action effect in cases where the additional solute has an ion in common with the extracted salt.

However, in many cases, the increase in extractability of the salt far exceeds the amount which would be predicted on the basis of mass action alone. A unified theory of solvent extraction must also explain the demoting effect caused by certain other added electrolytes.

Effect of the Ionic Size of the Extracted Species

It seems reasonable to assume that by comparing the relative solubility of salts in a solvent of low base strength a correlation can be drawn between these solubility measurements and the degree of extraction to be expected. It becomes apparent from a study of this type that salts composed of small highly-charged cations and large anions of low charge generally can be expected to extract to a higher degree. This assumption has been justified in many of the cases tested.

HISTORICAL

For a comprehensive review of the literature on solvent extraction, the reader is referred to the recently completed work in this field by Laran (12).

A few recent investigations have dealt directly with systems of a similar nature to those under consideration in this thesis. Although numerous mention is made to these publications throughout the body of this thesis, it seems advisable to consider them here in more detail because of their direct bearing on the present investigation.

In 1949, Garwin and Hixson (6) published data on the extraction and separation of cobalt and nickel chlorides from their aqueous solutions containing hydrochloric acid with 2-octanol. It was noted that negligibly small amounts of either cobalt or nickel could be extracted at concentrations approaching 2 molal from a binary mixture. The addition of high concentrations of chloride ions caused the formation of stable chloro-complexes of cobalt which permitted the cobalt to be extracted from the aqueous phase to a higher degree than would be predicted from mass action considerations alone. Because nickel salts do not yield readily to complex formation, the distribution coefficient of the nickel salt was not similarly increased by the chloride ions and thereby an adequate separation of the two salts could be accomplished. Garwin utilized these findings for the pilot-plant scale separation of $CoCl_2$ from $NiCl_2$ in the presence of such promoting agents as HCl and $CaCl_2$ by a spray tower (10).

Yates and Moore (20) have further investigated the extraction of cobalt and nickel chlorides by 2-octanol in the presence of different valence-type extraction-promoting chlorides. Beaver et al. (1) have studied the chloro-complexing in the system $CoCl_2$-LiCl-H_2O-octanol. The purpose of these investigations has been to determine some of the factors influencing liquid-liquid extraction and to obtain some information about the nature of the extracting species. Activity data for the ternary mixtures $CoCl_2$-HCl-H_2O and $NiCl_2$-HCl-H_2O have also been made available by Moore, Gootman, and Yates (14) over the concentration range in which the octanol extraction of these salts has been studied.

In systems containing perchlorates of cobalt (II) and nickel (II), it has been demonstrated that the magnitude of the distribution coefficient is dependent primarily on mass action (12). Because of the large size of the perchlorate ion, it would be expected that extensive complex formation would not occur in either phase and thereby would not be instrumental in enhancing the degree of extraction. It was found, however, that the distribution coefficients of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ were several orders of magnitude greater than those of the corresponding chloride salts at equivalent concentrations prior to extraction. This enhanced extractability is to be attributed in part to the formation of a water sheath about both metal and perchlorate ions in the octanol-rich phase. This is supported by the high hydration numbers reported for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ (19) in 2-octanol. The hydrate water may be regarded as increasing the effective size of the ions and decreasing the work of ion transfer from water to octanol.

REAGENTS

Calcium Perchlorate

Calcium perchlorate was prepared by metathesis from reagent grade calcium carbonate obtained from Baker and Adams and 60% perchloric acid, reagent grade, purchased from Mallinckrodt. The carbonate was added to the hot acid until the solution became strongly turbid, indicating an excess of the carbonate. The excess carbonate was filtered off, and the filtrate was tested for acidity and the presence of chlorides. The filtrate was found to be neutral and chloride-free.

The solution was evaporated to dryness, and the resulting crystals were heated at 120° until the anhydrous salt was obtained (18). Anhydrous calcium perchlorate was stored in a vacuum dessicator over Dehydrite.

Cobalt and Nickel Perchlorate

Cobalt and nickel perchlorates were also prepared by the action of 60% perchloric acid on C. P. cobalt and nickel carbonates. Because of the instability of the anhydrous heavy-metal perchlorates, no attempt was made to evaporate the salts to dryness. The stock solution was analyzed, and the desired concentration was obtained by dilution.

Karl Fisher Reagent

This reagent was prepared by a method recommended by Mitchell and Smith (13).

2-Octanol

The 2-octanol used was obtained from the Matheson, Coleman, and Bell Chemical Company. It was anhydrous and reagent grade.

Tetraphenylarsonium Chloride

Twenty-seven grams of this reagent were prepared by an improved method given by Pope and Turner (15). The method can be best described in a condensed form by the following set of equations:

A. $3C_6H_5Cl + AsCl_3 + 6Na \longrightarrow (C_6H_5)_3As + 6NaCl$

B. $(C_6H_5)As + H_2O_2 \longrightarrow (C_6H_5)_3AsO + H_2O$

C. $(C_6H_5)AsO + C_6H_5MgBr \longrightarrow (C_6H_5)_4AsOMgBr$

D. $(C_6H_5)_4AsOMgBr + 3HCl \longrightarrow (C_6H_5)_4AsCl{\cdot}HCl + MgClBr + H_2O$

The melting point was found to be 198° for the crude product and 204° after recrystallization from concentrated hydrochloric acid. Literature value is 204° to 208°.

Supporting Electrolyte

The use of this reagent will be described later under octanol phase, chloride analysis. It was prepared by saturating a 0.5 N. solution of potassium chloride solution with silver chloride. Fifteen liters of potassium chloride solution were stored in a large bottle and allowed to come to equilibrium with solid silver chloride for a period of two weeks prior to its use. The reservoir was fitted with a siphon and encased in a light-tight container.

Miscellaneous Chemicals

All other reagents used during the course of this investigation were the best grade obtainable and were used without further purification.

EXPERIMENTAL

Preparation of Stock Mixtures

The concentration range over which the system $CoCl_2$-$Co(ClO_4)_2$ could be studied was limited by two factors:

(1) The upper limit was governed by the fact that solutions of this particular salt pair undergo extensive precipitation of an unidentified salt if the total cobalt concentration was greater than 4 molal in the water phase.

(2) The unpromoted cobalt chloride would not extract sufficiently to be detected by available analytical techniques if its concentration in the water phase before equilibration was below 2 molal.

It was decided, therefore, to make up a set of solutions containing 2 molal cobalt chloride and containing cobalt perchlorate varying in concentration from 0.5 molal to 2 molal in approximately 0.25 molal steps. This was accomplished by preparing a stock solution containing 2 molal $CoCl_2$, 2 molal $Co(ClO_4)_2$, and diluting aliquot samples of this solution with a second solution of $CoCl_2$ at a concentration of 2 molal. Thus there was obtained a series of solutions with a constant $CoCl_2$ concentration and a $Co(ClO_4)_2$ concentration varying between the limits previously mentioned.

In order to permit a comparison between the two systems, $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ and $Co(ClO_4)_2$-$Ca(ClO_4)_2$, the $Ni(ClO_4)_2$ concentration was accurately adjusted to 0.243 molal. Calculated quantities of anhydrous $Ca(ClO_4)_2$ were added to aliquot samples of this stock solution to yield a series of solutions varying from 0 to 4.2 molal.

Equilibration of 2-Octanol and Water Phase

Fifty-milliliter portions of 2-octanol were added to equal volumes of the solutions to be extracted in 250-ml. Erlenmeyer flasks fitted with ground glass stoppers. Each stopper was fastened securely in place with adhesive tape in order to prevent the loss of any of the solution during the equilibration period. The flasks were clamped to a mechanical shaker and immersed in a constant temperature bath at 25° C. The shaker was adjusted so that adequate mixing occurred between the two phases. The solutions were shaken for a period of 24 hours. This was followed by an additional 24-hour period during which the samples were allowed to remain suspended in the constant temperature bath without agitation. Studies made by previous workers have shown that this treatment is sufficient to bring about equilibrium between the two phases (6).

After equilibrium had been reached, the two phases were separated by means of separatory funnels and transferred to ground glass stoppered Erlenmeyer flasks. The stoppers were sealed in place with paraffin in order to prevent evaporation and subsequent change in concentration of the solutions.

Analytical Techniques

Because much of the time devoted to this investigation was consumed in developing and employing various analytical methods that could be applied successfully to the types of solutions being studied, it seems advisable to describe in some detail the various problems encountered and the methods finally adopted.

In general, the aqueous phase analysis presented only minor problems. The solutions were at high concentrations and of insufficient complexity to prohibit the use of most standard analytical procedures.

In the system $CoCl_2$-$Co(ClO_4)_2$, the total cobalt in the water phases was determined by electrodeposition on a platinum cathode at 1 ampere. If the sample taken for analysis was sufficiently large to yield 0.1 g. cobalt, this method was found to give consistent precision of 0.1% or better between aliquot portions of the water phase. The chloride ion concentration was determined by potentiometric titration with $AgNO_3$ after it was found that the end point of a colorimetric titration was effectively hidden by the strongly colored cobalt ion.

Portions of the octanol phase were back-extracted three times with equal volumes of water and analyzed for the total cobalt and chloride ion concentration. The cobalt perchlorate was determined by differences. First attempts were to analyze for chlorides potentiometrically, using a silver nitrate solution made up in 75% acetone, and to carry on the titration near the freezing point of the solution in order to reduce the solubility product of the silver chloride. Even with these precautions and a very sensitive potentiometer, no inflection point in the E.M.F. was noted. Anodic polarography was considered, but was discarded when it was found that the wave was ill-defined and the results were of low precision.

The method finally adopted was one employed by Kolthoff and Kuroda (9). A silver-silver chloride electrode was placed into each of two half cells. These electrodes were connected through a galvanometer. One of the half cells contained a solution of high ionic strength made up of 0.5 N. KNO_3 saturated with AgCl. The other half cell contained the unknown in a solution made up to approximately equal ionic strength. The circuit was completed by means of a salt bridge, and the unknown was titrated to a null point on the galvanometer. The titrating agent was 0.002 N. $AgNO_3$ which had been previously adjusted in such a way as to be of equal ionic strength with the standard half cell and the unknown. This method was found to be satisfactory, and yielded a precision never less than 0.2%.

The total cobalt was determined without difficulty by means of the Model XXI recording polarograph. The cobalt wave was found to be well defined and the wave height was linearly dependent on concentration over the interval under consideration as shown in Figure 1. A precision of 2% was obtained by this technique. This is considered to be about the error normally associated with this analytical procedure.

In the system $Ni(ClO_4)_2$-$Ca(ClO_4)_2$, it was found that the electrodeposition technique used for cobalt in the aqueous phase was not applicable for an accurate and precise nickel determination. At low calcium concentrations, satisfactory results were obtained, but as the calcium concentration was increased, the precision dropped off so rapidly that at a calcium perchlorate concentration of 1.5 molal, the precision was reduced to 3% between weighed samples of the water phase. A gravimetric method involving dimethylglyoxime was also tried without success because of occlution of the promoting salt within the dimethylglyoxime precipitate. Owing to the interference of the calcium perchlorate in the most common gravimetric analytical methods, they were abandoned in favor of a spectrophotometric method. Before employing this method, it was necessary to determine whether or not the calcium ion had any effect on the optical density of the nickel perchlorate solution. It was necessary, therefore, to prepare

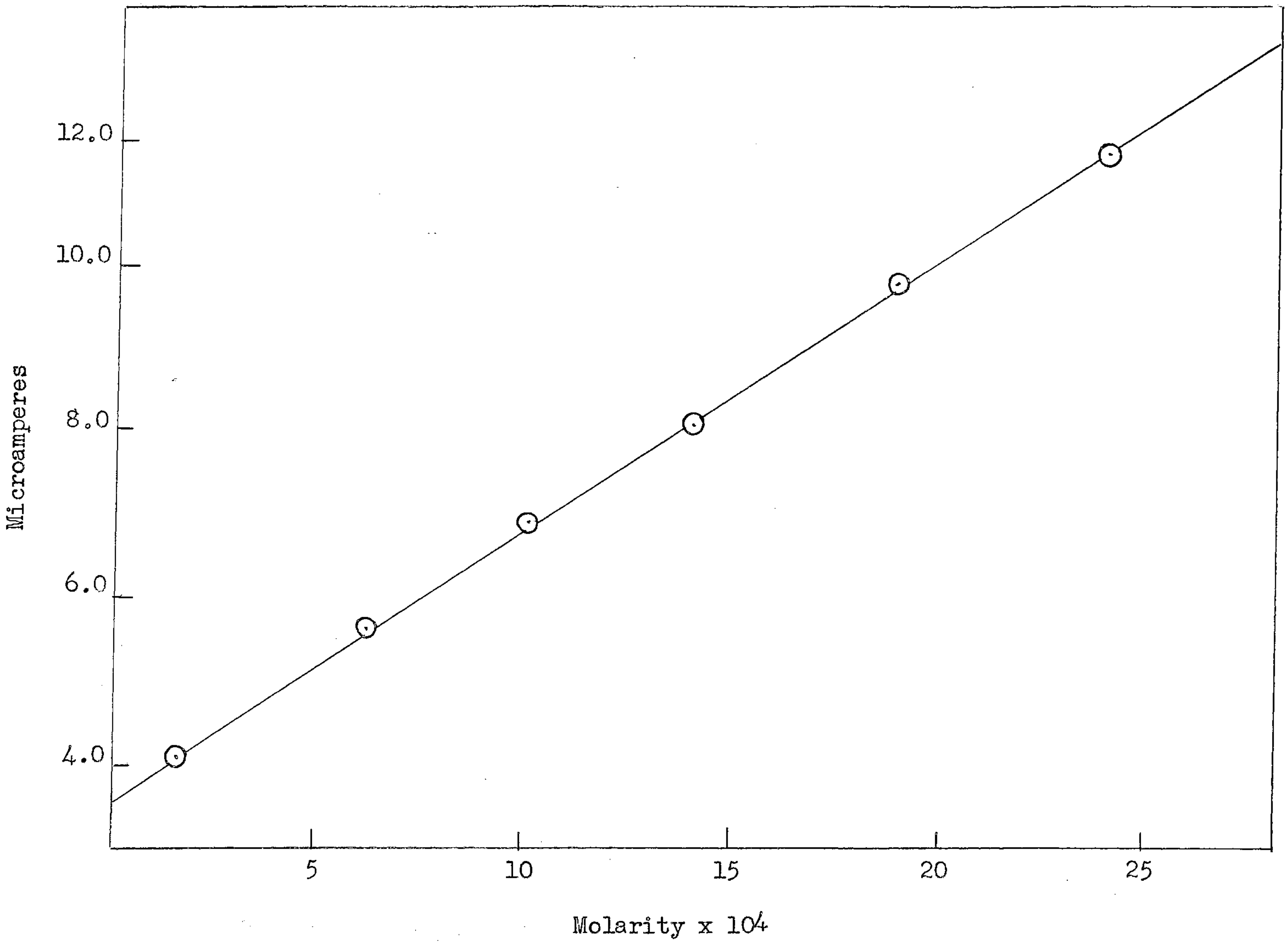

Figure 1: Polarographic Standard Curve

duplicate sets of nickel standards. One set of standards was prepared by diluting accurately a nickel perchlorate solution of a known concentration. The second set of standards was prepared by adding varying concentrations of anhydrous $Ca(ClO_4)_2$ to aliquots of the first set of standards. Optical densities (O.D.) of both sets of standards were measured at a wavelength of 720 millimicrons with a Beckman Model DU Spectrophotometer. The results of this study showed that $Ca(ClO_4)_2$ had no effect on the absorption maximum, Figure 2.

Measurements were made directly on the aqueous phase without dilution. The O.D. of the aqueous phase ranged between 0.311 and 0.514. Since measurements were made on the aqueous phase without performing any operation on the solution, it was possible to obtain highest precision between aliquot samples of the same solution. It is known, however, that the photometric method cannot yield better than 1 to 2% precision.

The calcium concentrations of the various samples were determined by precipitating the calcium as the oxalate and titrating the calcium oxalate with potassium permanganate. A precision of 0.5% was obtained.

The concentration of the two salts in the 2-octanol phase of the promoted nickel extraction was determined via spectrophotometric and gravimetric techniques after back extraction with water.

As in the case of the water phase, the nickel was determined on the DU Spectrophotometer. It was necessary, however, to employ a modification of the method of Classen and Bastings (4) to this determination because of exceptionally low nickel concentration found after extraction. Approximately 5 g. samples were weighed out and diluted

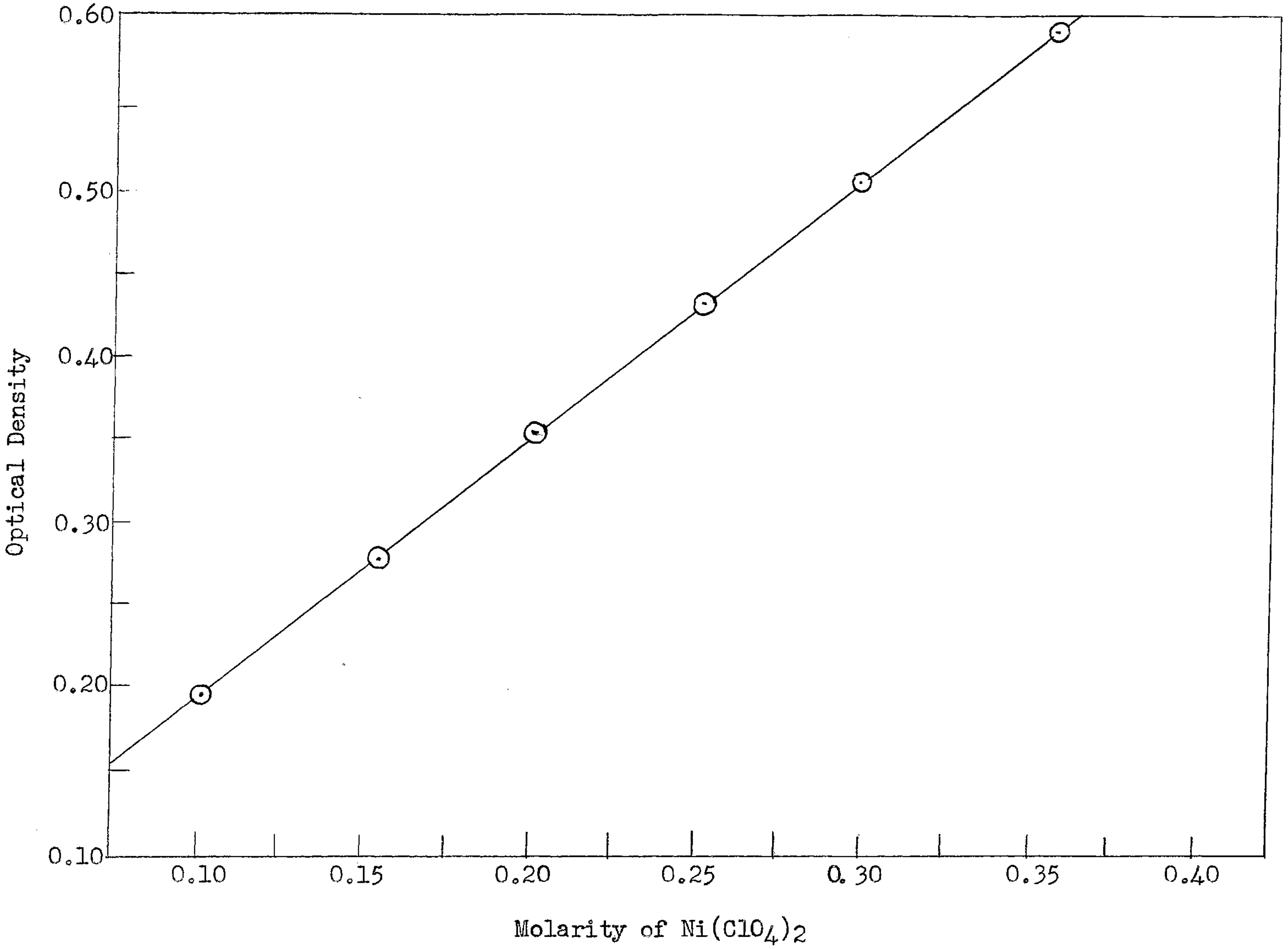

Figure 2: Standard Curve: Ni Determination, Water Phase

with 20 ml. of 95% ethanol saturated with NaOH. One ml. of 0.1% dimethylglyoxime was added and allowed to react for 30 minutes at 60°C. The solution was cooled to room temperature and diluted to 100 ml. with ethanol. The resulting solutions were allowed to stand for 24 hours in order to settle the fine precipitate that developed from the formation of $Ca(OH)_2$. Colors of the solutions ranged from a deep red, characteristic of nickel dimethylglyoxime, to a light yellow at low nickel concentrations. This yellow color also was evident when the sodium hydroxide concentration was below the concentration used in this determination. This was probably due to incomplete reaction between the nickel salt and the dimethylglyoxime. This supposition is borne out by the fact that standards prepared in the presence of low hydroxyl ion concentrations did not yield smooth curves when optical density was plotted against concentration. The standard curve used is shown in Figure 3. Duplicate samples agreed within 1.5%.

Total perchlorate concentration of this phase was determined by precipitation of the perchlorate as the tetraphenylarsonium salt. It was necessary to determine the proper medium for this precipitation as the reference to the original work done on this method (11) was unobtainable. The most satisfactory checks were obtained by performing the precipitation in a solution of 0.5 m NaCl at a temperature of 60° C. The resulting precipitate was coarse enough to be separated with a fritted filter crucible of medium porosity and had only a slight tendency to creep or cling to the sides of the container. Checks were obtainable within 0.2% if the sample weighed was approximately 100 mg. and slightly less for smaller samples. In the most dilute region, it was necessary to employ a single large sample

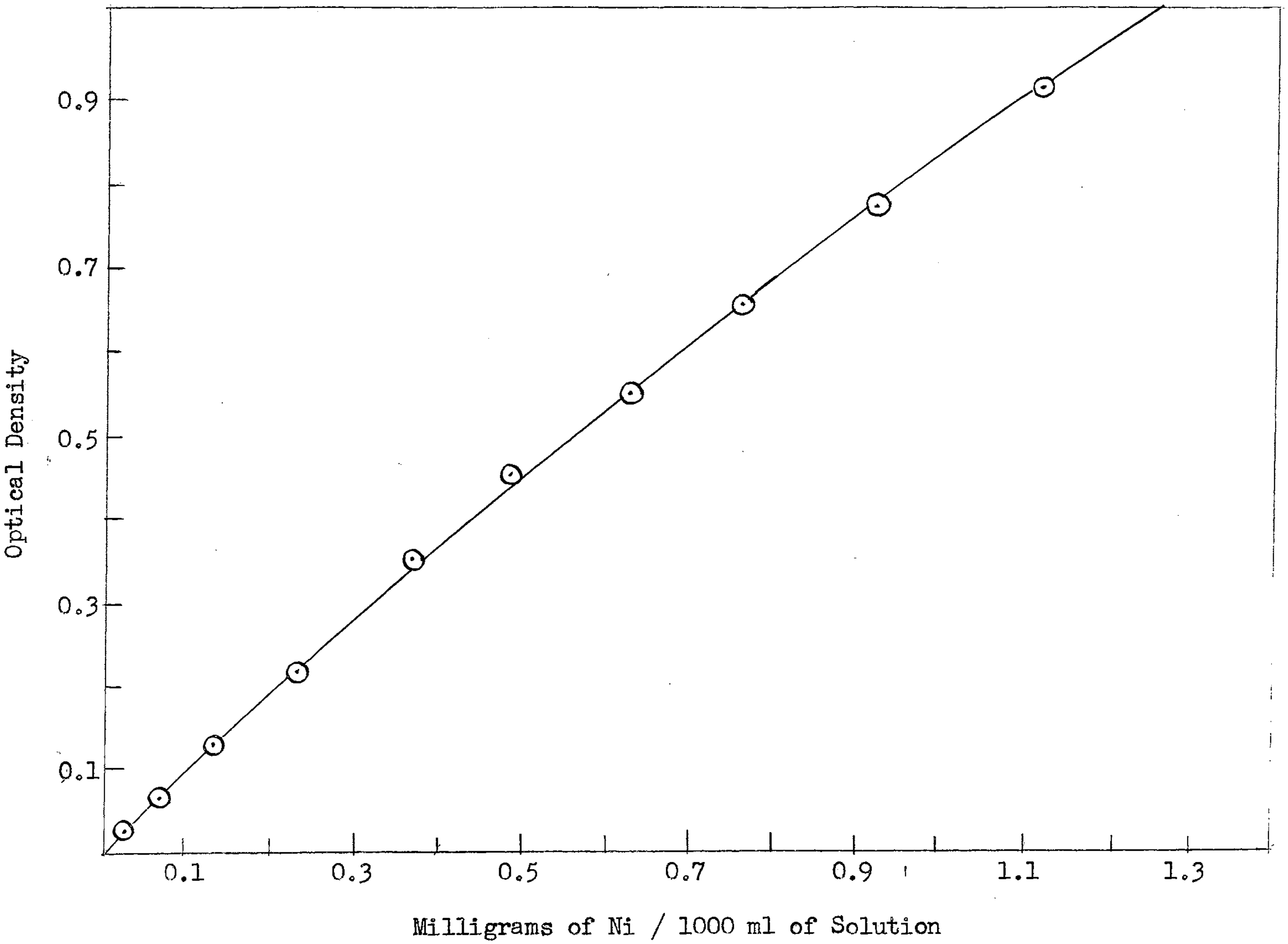

Figure 3: Standard Curve: Ni Determination, 2-Octanol Phase

of the back-extracted 2-octanol phase; therefore, the precision could not be determined.

Water concentrations of the 2-octanol phase of both systems were determined by means of a Karl Fisher titration employing a "dead-stop" end point technique.

Spectrophotometric Studies of CoCl Complex

In an attempt to determine the nature of the species present in the 2-octanol phase after extraction of the system $CoCl_2$-$Co(ClO_4)_2$, the spectra of the solutions were studied in a region between 400 and 750 millimicrons. The Beckman Model DU Spectrophotometer was employed for this study. Measurements were made at 5 millimicron intervals with the samples in 1-cm. matched Corex cells.

TABULATION AND PRESENTATION OF EXPERIMENTAL RESULTS

Determination of K_d, K_M, K_m Values

All concentrations are expressed in terms of moles of salt per 1000 g. of solvent. Since an appreciable amount of water dissolves in 2-octanol, the molalities listed in the tables and figures are calculated on the basis of 2-octanol plus water as opposed to moles per 1000 g. of pure 2-octanol. Tables 1 and 2.

As a measure of the extractability of each of the salts, a distribution coefficient (K_d) was calculated for each of the solutions. Tables 3 and 4. This coefficient is defined as the ratio of the molality of the salt in 2-octanol (as defined above) to the molality of the salt in water. The K_d expressed in this manner does not equate the chemical potential on each side of the phase boundary. It is important to note, therefore, that K_d cannot be expected to remain constant, but will vary as a function of the concentration of the compound being considered and as a function of the total concentration of the common ion in solution.

It is known that mass action plays an important role in determining the amount of salt which is extracted into the non-aqueous phase of the system; therefore, it seemed advisable to formulate a distribution coefficient which takes into account the effect of the added concentration of a common ion. A plot of this function against total equivalents in the aqueous phase can then be discussed in terms of the amount of its deviation from a constant value with increasing total concentration of the common ion. For these considerations,

TABLE 1

MOLAL CONCENTRATIONS IN THE SYSTEM $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ AFTER EXTRACTION

$Ni(ClO_4)_2$		$Ca(ClO_4)_2$	
Aqueous Phase Concentration	2-Octanol Phase Concentration x 10^4	Aqueous Phase Concentration	2-Octanol Phase Concentration x 10^2
0.327	0.575	----	-----
0.316	8.79	1.05	0.335
0.305	19.0	1.41	0.808
0.303	49.4	1.85	1.71
0.301	111.	2.25	3.80
0.263	313.	2.95	14.7
0.254	332.	3.08	18.2
0.233	812.	3.46	25.4

TABLE 2

MOLAL CONCENTRATION IN THE SYSTEM $CoCl_2$-$Co(ClO_4)_2$ AFTER EXTRACTION

$CoCl_2$		$Co(ClO_4)_2$	
Aqueous Phase Concentration	2-Octanol Phase Concentration	Aqueous Phase Concentration	2-Octanol Phase Concentration
2.00	------*	.650	-----*
2.01	0.0032	.873	0.037
2.01	0.0032	1.07	0.069
2.02	0.0129	1.29	0.127
2.03	0.0212	1.52	0.212
2.05	0.0323	1.81	0.338

*Concentration too small to be analyzed by existing techniques

TABLE 3

DATA FOR CALCULATING THE DISTRIBUTION FUNCTIONS FOR THE SYSTEM $Ni(ClO_4)_2$-$Ca(ClO_4)_2$

Aq. Phase Total Eq. ClO_4^-			$Ni(ClO_4)_2$			$Ca(ClO_4)_2$
	$K_d \times 10^2$	K_m	$\gamma \pm$(aq.)	$\gamma \pm$(oct.)	$K_M \times 10^{10}$	$K_d \times 10^2$
0.654	0.0176	5.42×10^{-12}	0.574	1.00	0.287	-----
2.72	0.278	2.65×10^{-8}	1.32	0.323	3.87	0.319
3.42	0.623	2.09×10^{-7}	2.95	0.221	0.879	0.573
4.30	1.63	1.70×10^{-6}	3.45	0.168	1.90	0.924
5.10	3.68	1.37×10^{-5}	5.25	0.115	1.43	1.69
6.42	11.9	3.66×10^{-4}	14.0	0.108	1.68	4.98
6.66	11.1	5.41×10^{-4}	16.3	0.112	1.55	5.91
7.38	14.8	2.87×10^{-3}	34.6	0.150	2.33	7.34

TABLE 4

DATA FOR CALCULATING THE DISTRIBUTION FUNCTIONS FOR THE SYSTEM $CoCl_2$-$Co(ClO_4)_2$

Total Number of Moles (Aq)	$CoCl_2$		$Co(ClO_4)_2$	
	$K_d \times 10^3$	$K_m \times 10^6$	$K_d \times 10^2$	$K_m \times 10^4$
2.65	----	----	----	----
2.88	1.60	.0326	5.69	0.487
3.08	3.58	.315	7.90	1.02
3.31	6.38	1.73	9.84	4.10
3.55	10.4	7.15	13.9	12.7
3.86	15.7	23.7	18.6	33.5

the mass action distribution coefficient (K_m) will be defined for a hypothetical 2:1 electrolyte (MA_2) as:

$$K_m = \frac{[M^{++}]\ [A^-]^2\ \text{2-oct.}}{[M^{++}]\ [A^-]^2\ \text{aq.}}$$

Tables 3 and 4 give the K_m values found for the salt whose concentration was held constant prior to extraction for each system.

In an effort to formulate a true distribution constant, it was necessary to know the activity of the salts being extracted in each of the two phases. If this knowledge is available for any system and the following expression for 2:1 electrolyte MA_2 is used:

$$K_M = \frac{(\gamma\pm)^3\ \text{2-oct.}\ \ [M^{++}]\ [A^-]^2\ \text{2-oct.}}{(\gamma\pm)^3\ \text{aq.}\ \ [M^{++}]\ [A^-]^2\ \text{aq.}}$$

$$= \frac{(\gamma\pm)^3\ \text{2-oct.}}{(\gamma\pm)^3\ \text{aq.}}\ K_m$$

the values of K_M obtained should be constant over the entire concentration range considered.

Since the system $CoCl_2$-$Co(ClO_4)_2$ has never been studied before, no data were available on the respective activity coefficients of the components in the mixtures. Any assumptions about the activity coefficients of the two components in the mixtures would have to be made from a knowledge of their respective activity coefficients in binary solutions, and in our present state of knowledge of electrolyte mixtures this cannot be done with any degree of certainty. Due to this lack of suitable data, no attempt was made to formulate a K_M value for the system $CoCl_2$-$Co(ClO_4)_2$.

In the case of the system which contains the perchlorate ion only, in order to obtain the necessary data for the determination of K_M values, it was necessary to make certain general assumptions concerning the mean ionic activity coefficients of 2:1 perchlorates.

The following two assumptions were made as a first approximation:

(1) The mean ionic activity coefficients of $Ni(ClO_4)_2$ and $Ca(ClO_4)_2$ are equivalent and in mixtures with each other the activity coefficients can be determined by considering the two salts as a single 2:1 electrolyte at a concentration equal to the sum of the individual concentrations of the two salts.

(2) Since neither $Mg(ClO_4)_2$ nor $Zn(ClO_4)_2$ exhibit any marked difference in activity coefficients, it is possible to employ data for the activity coefficient of a single salt of comparable cation size for the activity coefficients of $Ni(ClO_4)_2$ and $Ca(ClO_4)_2$.

The activity data were from Sandell (16). His values for the activity coefficient of $Zn(ClO_4)_2$ were selected as being representative of the average activity coefficient for the two salts in the mixed system.

The values for the activity coefficient of $Ni(ClO_4)_2$ in the 2-octanol phase were determined by a plot, made available by Laran (12), of concentration versus activity coefficient for $Ni(ClO_4)_2$ in 2-octanol. The values used in plotting this curve were obtained for the unpromoted extraction of $Ni(ClO_4)_2$ by combining the concentration data found after equilibration with the values obtained from Sandell for the activity coefficients of $Zn(ClO_4)_2$.

Estimation of Average Hydration Number

In order to obtain a better understanding of the nature of the species found in the 2-octanol rich phase after extraction, an attempt was made to determine the hydration numbers of the extracted salts in the non-aqueous phase. Since in both systems there existed two different compounds, it would be impossible to determine the hydration number of one component from the total hydrate water without a knowledge of the hydration number of the second component. It was necessary, therefore, to make certain assumptions in each of the two cases studied, and to discuss the results in the light of these assumptions.

Various methods have been described for the determination of the amount of water that can be defined as hydrate water. Of historical interest is the method proposed by Katzin and Sullivan (8). Their method was based on the assumption that all of the water found in the organic phase existed there in the form of hydrate water. By employing this assumption, they could determine the hydration number of the extracted salt by evaluating the slope of a line obtained by plotting moles of salt extracted against total moles of water in the organic phase. If their assumption was valid, the resulting curve should be linear. Generally, this was not found to be the case. The curve usually exhibited a minimum in the region of low salt concentration. Katzin and Sullivan attempted to explain this lack of linearity by the fact that the water activity in the aqueous phase was lowered before a sufficient amount of hydrated salt had been extracted to offset this effect. A study of the activity of water in regions of low salt concentration shows this to be true. When the salt concentration in the aqueous phase is low, the water activity is high and extraction of free water will occur to a considerable extent. As the salt concentration is increased, the water activity is reduced resulting in less and less water being extracted as free water. This phenomenon is balanced by the fact that more and more hydrated salt is being extracted with increasing salt concentration in the aqueous phase. The increase in hydrate water tends to bring about an upswing in the curve after the two above-mentioned factors reach a balance at the minimum of the curve. It follows from these considerations that the method is unsatisfactory for the determination of the salt hydration number. A wide range of hydration numbers could be determined for a single salt in an organic solvent depending on the position of the curve at which the hydration number is evaluated. It is also apparent that there is no evidence to support the assumption that the activity of the water is reduced so low at high salt concentrations that it ceased to be a factor to be considered in any hydration study.

The method used in the present study was a modification of the Katzin and Sullivan method proposed by Yates and Moore (20). The method is also similar to that suggested independently by Gardner, McKay, and Warren (5). Before attempting to evaluate the amount of water extracted as hydrate water, the amount of water extracted as free water must first be determined. A salt which will not extract to an appreciable extent even at high salt concentrations in the aqueous phase was selected to make this determination. Various concentrations of salt solutions were equilibrated with 2-octanol, until a point was reached where the salt begins to extract. Below this point, all the water extracted was considered to be free water. If the water activity in the aqueous phase is plotted against molality in the 2-octanol phase, a working curve is obtained from which it is possible to determine the amount of water extracted as free water from solutions of known water activity in the aqueous phase. This is shown in Figure 4.

The salt selected for this determination was LiCl. It was chosen because of its low extractability into 2-octanol and because the water activity at various salt concentrations was readily available (7). The shape of the curve obtained followed theoretical predictions. It was observed that in regions of high salt concentration, the slope of the curve approached a straight line. This is predicted by Henry's Law and affords a method by which the free water concentration in the 2-octanol phase can be determined beyond the point at which data can no longer be obtained from the LiCl plot due to extraction of the LiCl itself.

From the relation predicted by Henry's Law:

$$a'_w = kN'_w$$

(where a'_w is equal to the water activity in the organic phase, k is Henry's Law constant, and N'_w is the mole fraction of the free water in the organic phase) and the equation for the equality of chemical potentials of a component distributed between two phases in equilibrium with one another:

$$\frac{a'_w}{a_w} = K$$

we can obtain an expression which relates the mole fraction of the free water in the non-aqueous phase to the activity (a_w) of the water in the water phase:

$$N'_w = \frac{K}{k} a_w = \bar{\underline{K}}\, a_w$$

For the sake of uniformity, the symbolism used in the above derivation is in accord with that adopted by Laran (12).

The $\bar{\underline{K}}$ evaluated by this method was determined and used only in regions of low water activity. It is in these regions that Henry's Law can be expected to be applicable. This is predicted not only

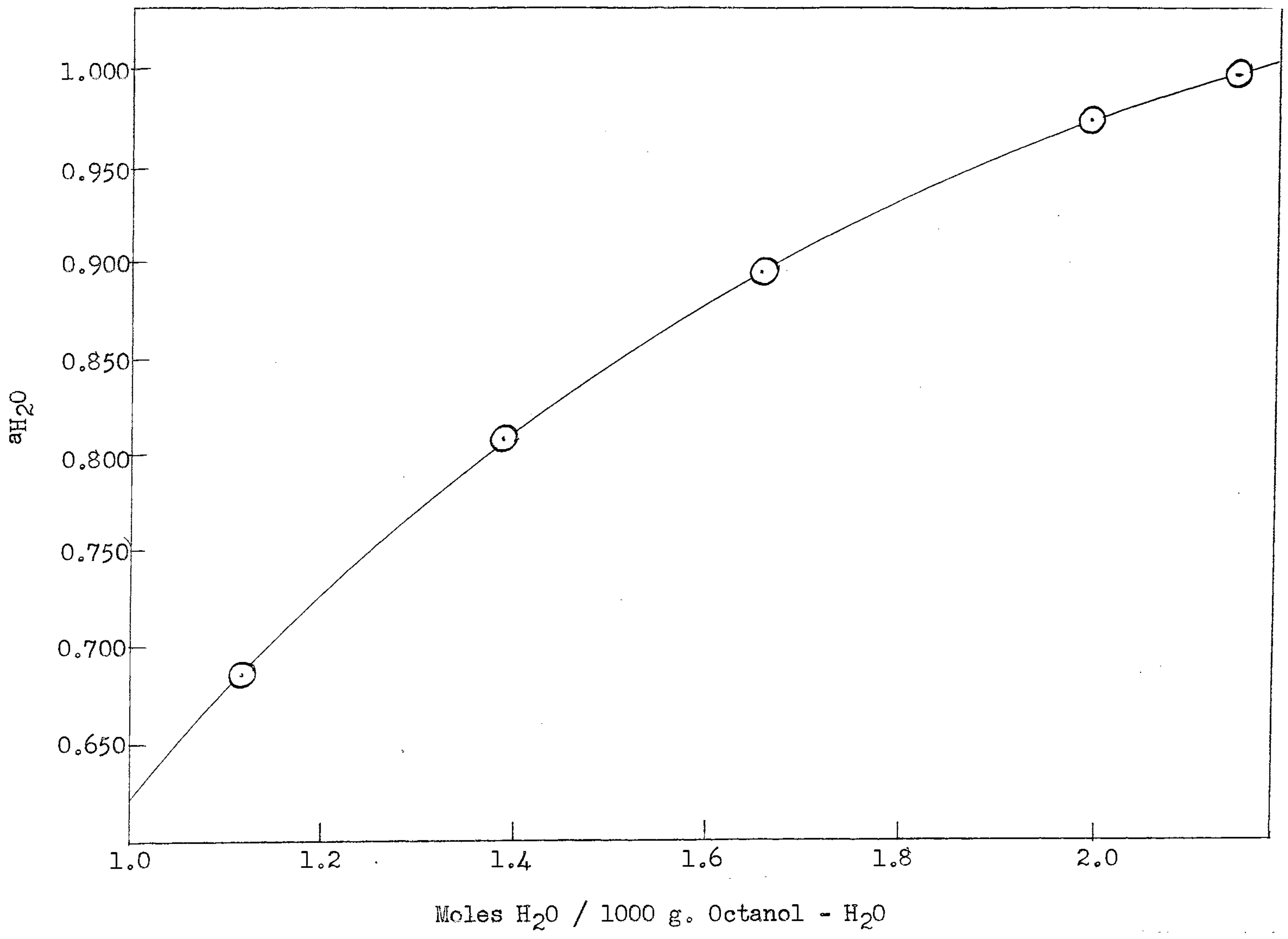

Figure 4: Amount of H_2O Extracted into 2-Octanol as a Function of Activity of H_2O in Aqueous Phase

from theory but from the approaching linearity of the LiCl curve in regions of high salt concentration.

The same assumptions used in determining a distribution constant for the $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ system was also necessary for the determination of the average hydration number for this system. Data for the activity of water at various concentrations of $Zn(ClO_4)_2$ (17) were employed as being representative of the mixed system. It was necessary to use a Henry's Law calculation for three of the points obtained at high salt concentrations. Table 5.

Since even approximate data for the activity of water are not available for the system $CoCl_2$-$Co(ClO_4)_2$, no direct attempt was made to evaluate the hydration numbers of the components. However, from a knowledge of the total water extracted, obtained by a Karl Fisher titration, and the knowledge of the hydration numbers found for the salts in binary octanol solutions, the free water can be estimated on the assumption of constant hydration numbers. Table 6.

Identification of Species Present in 2-Octanol from Absorption Spectra

As was mentioned in the introduction to this thesis, the formation of certain complexes by the interaction of a salt pair has a marked effect on the extractability of the salt in question. The formation of a relatively stable complex entity was suspected in the system containing both the chloride and perchlorate ion. Evidence for the existence of this complex was provided by a study of the spectrum of the mixed system and comparison with existing data on chloro-complexes of cobalt II in octanol (1).

No attempt was made to investigate the entire spectrum of the nickel and calcium system for the presence of any complex form. It

TABLE 5

HYDRATION NUMBER DATA FOR THE SYSTEM $Ni(ClO_4)_2$-$Ca(ClO_4)_2$

Water Phase a_{H_2O}	Total Water	Free Water	Hydrate Water
0.983	2.20	2.05	0.15
0.891	1.81	1.62	0.19
0.847	1.73	1.47	0.26
0.830	1.77	1.44	0.33
0.720	1.90	1.18	0.72
0.602*	2.81	0.894	1.92
0.580*	3.07	0.857	2.27
0.520*	3.82	0.763	3.06

All concentrations are listed as moles of water / 1000 g. of water + 2-octanol.
*Activity values determined from Henry's Law.

TABLE 6

HYDRATION NUMBER DATA FOR THE SYSTEM $CoCl_2$-$Co(ClO_4)_2$

Total Water	Hydrate Water	Free Water
1.73	0.44	1.28
2.04	0.84	1.20
2.63	1.55	1.08
3.37	2.58	0.79
4.34	4.28	0.06

All concentrations are listed as moles of water / 1000 g. of water + 2-octanol. Hydrate water was estimated by predicting a hydration number of 12.5 for $Co(ClO_4)_2$ and 2 for $CoCl_2$.

is reasonable to predict that, if such an investigation had been attempted, however, no evidence of a complex would have been found. This is based on the knowledge that the perchlorate ion is so large and nonpolarizable that the single negative charge that it possesses is effectively dissipated when it is spread over the entire anion. Both the large size of the ion (which prevents close ionic approach) and the low polarizability for the ion decrease the amount of distortion and covalent bonding resulting from the effect of the positive field of the cation.

DISCUSSION AND INTERPRETATION OF EXPERIMENTAL RESULTS

Degree of Promoting Action Exhibited by $Ca(ClO_4)_2$ on $Ni(ClO_4)_2$

It has been shown in previous investigations of unpromoted systems involving the perchlorate ion (12) that very slight differences in extractability are exhibited between systems containing unpromoted $Co(ClO_4)_2$ and $Ni(ClO_4)_2$. In the light of these findings, it is of interest to compare the results of the present study with the results from the $Ca(ClO_4)_2$ promoted extraction of $Co(ClO_4)_2$. Figure 5 shows the results of this comparison. It will be noted that the line obtained by plotting the concentration of the $Ni(ClO_4)_2$ in the aqueous phase against the concentration of the $Ni(ClO_4)_2$ in the 2-octanol phase is quite similar in both form and position to the line obtained by plotting the concentration of the $Co(ClO_4)_2$ in the aqueous phase against the $Co(ClO_4)_2$ in the 2-octanol phase. In both the promoted and the unpromoted systems the extractability of $Co(ClO_4)_2$ is greater than that of $Ni(ClO_4)_2$, however.

Undoubtedly, some of the difference can be attributed to experimental error, since it was necessary to correlate the results of four independent analyses in order to obtain each of the points shown in the figure. The accuracy of each determination is well within the limits determined by the analytical technique employed; however, the total error, when considered as the sum of all the errors encountered in each determination, probably is significant. When this is taken into account, it follows from Figure 5 that the effect of the promoting action of $Ca(ClO_4)_2$ on both $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ is very

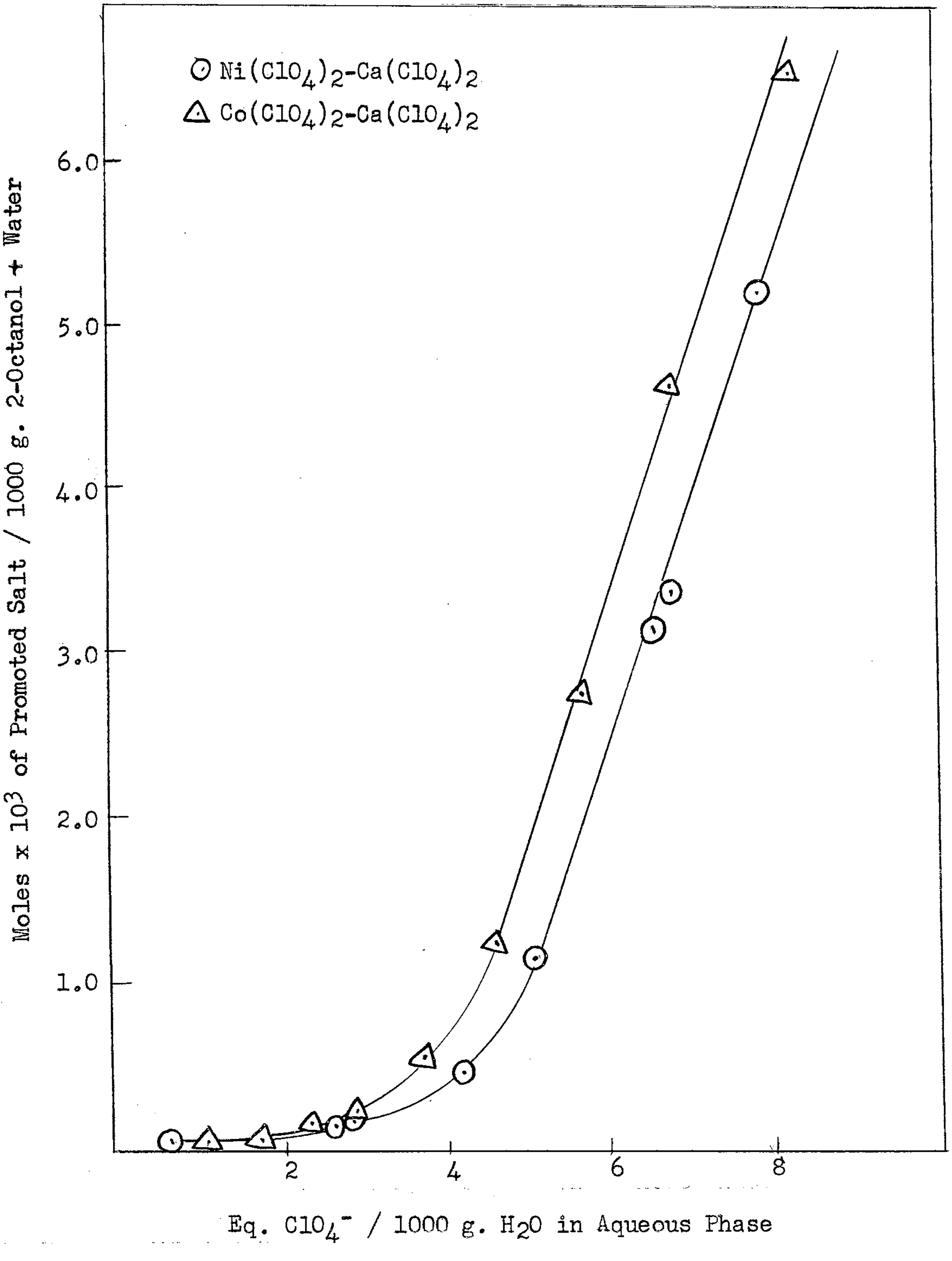

Figure 5: Comparison of Extractability of the $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ Systems

similar. The main factor influencing the promotion of $Ni(ClO_4)_2$ by $Ca(ClO_4)_2$ is undoubtedly a mass action effect brought about by the addition of the common perchlorate ion.

In addition to the common ion effect referred to above, there is some evidence of a specific ion effect caused by the presence of the Ca^{++} ion. This can be shown by comparing the K_m values for the system plotted against total perchlorate equivalences. This particular form of the distribution coefficient attempts to take into account the effect of mass action on the extracted species. It will be noted from a study of Figure 5 that the first point shown (denoted by a square) is well off the line determined by the other points. This point refers to the system containing $Ni(ClO_4)_2$ only. This lack of continuity between the promoted and unpromoted system, after correction has been made for the mass action effect, leads to the conclusion that the system is also effected by the addition of a foreign cation--in this instance, the calcium ion.

I draw these conclusions with some degree of hesitancy, however, for two reasons. A single value cannot be considered as conclusive evidence, and this study has not uncovered any additional information that would lend support to this theory. Furthermore, it has been shown by the previous investigation of the $Co(ClO_4)_2$ system that the anion is the principal factor governing the action of the promoting salt. This was proved by noting the effect of a number of different valence-type promoting perchlorates on the extractability of $Co(ClO_4)_2$. It was observed that this promoting effect was identical in all cases. In order that these findings do not conflict with the conclusions drawn from the plot of K_m versus total perchlorate concentration, it

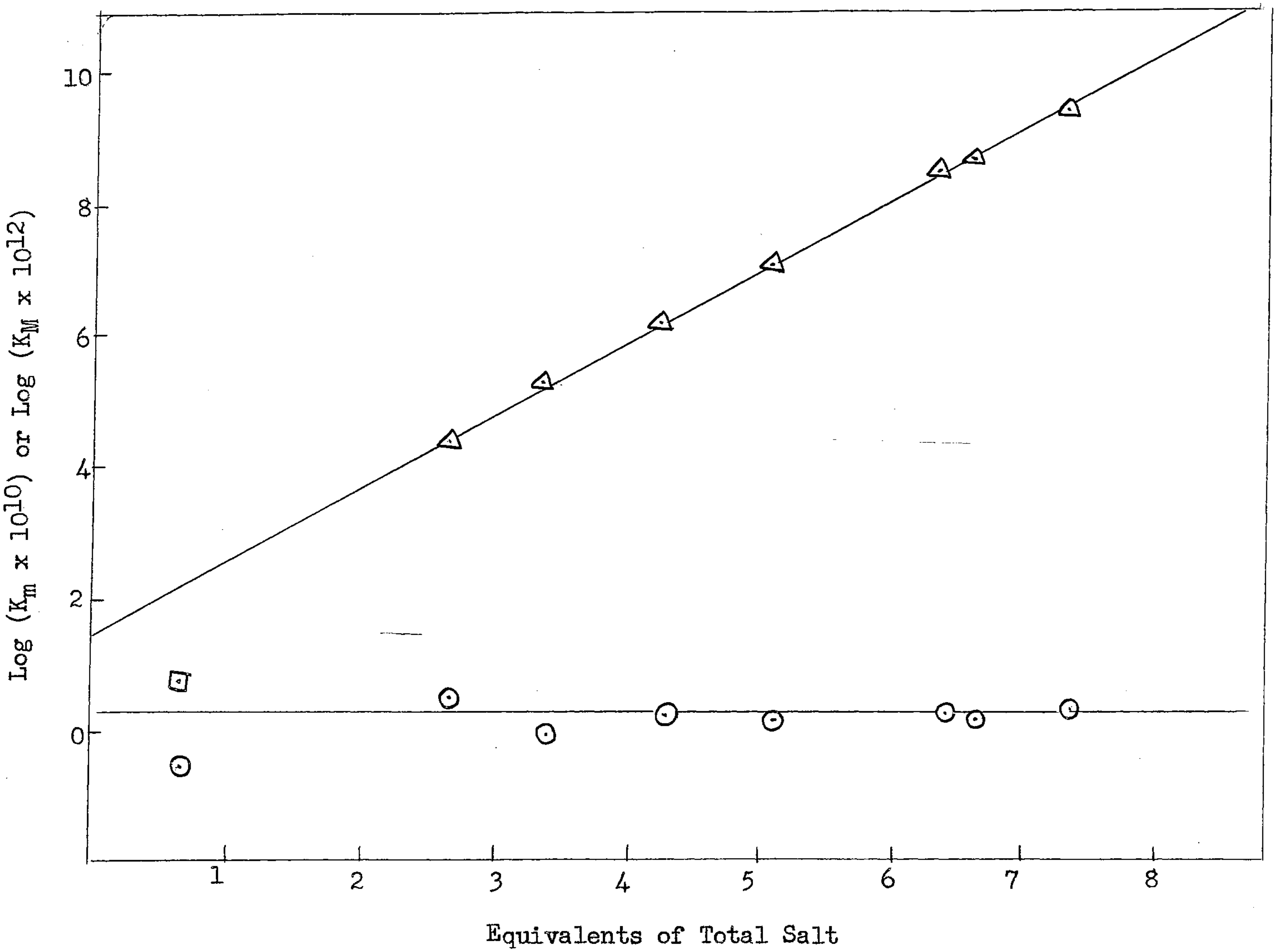

Figure 6: Comparison of K_M and K_m for $Ni(ClO_4)_2$ in $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ System

must be assumed that the specific action caused by the presence of a foreign cation is equivalent for all 2:1 electrolytes having a common anion with the extracted salt. This supposition may be unjustified, and must be made tentatively pending further investigation.

It is also seen from the same figure that the assumptions made about the relation between the activity coefficients of nickel and calcium perchlorate are valid. Although some randomness is found in the values for the thermodynamic equilibrium constant K_M for the mixed system, it is interesting to notice that no general trend exists in the values determined at each of the various salt concentrations. This is in marked contrast to the K_m values which vary several orders of magnitude with changing concentration of the promoting salt.

Average Hydration Number of Nickel and Calcium Perchlorate

By evaluating the slope of the line obtained from a plot of hydrate water versus moles of total salt, Figure 7, it was found that the average hydration number of the two salts was 12.5 in the region of low salt concentrations. This value is in close accord with the value previously obtained in the unpromoted nickel system which was reported to be 12.6 (19). It also lends support to the theory that perchlorates in general are extensively hydrated and it extends this theory to include mixed 2:1 perchlorate systems.

In regions of high salt concentration, the hydration number was found to be slightly lower. It is important to recall that the values obtained at these higher salt concentrations were evaluated by means of a Henry's Law expression. Therefore, it is not unlikely that some error may be introduced in the determination by the failure of the

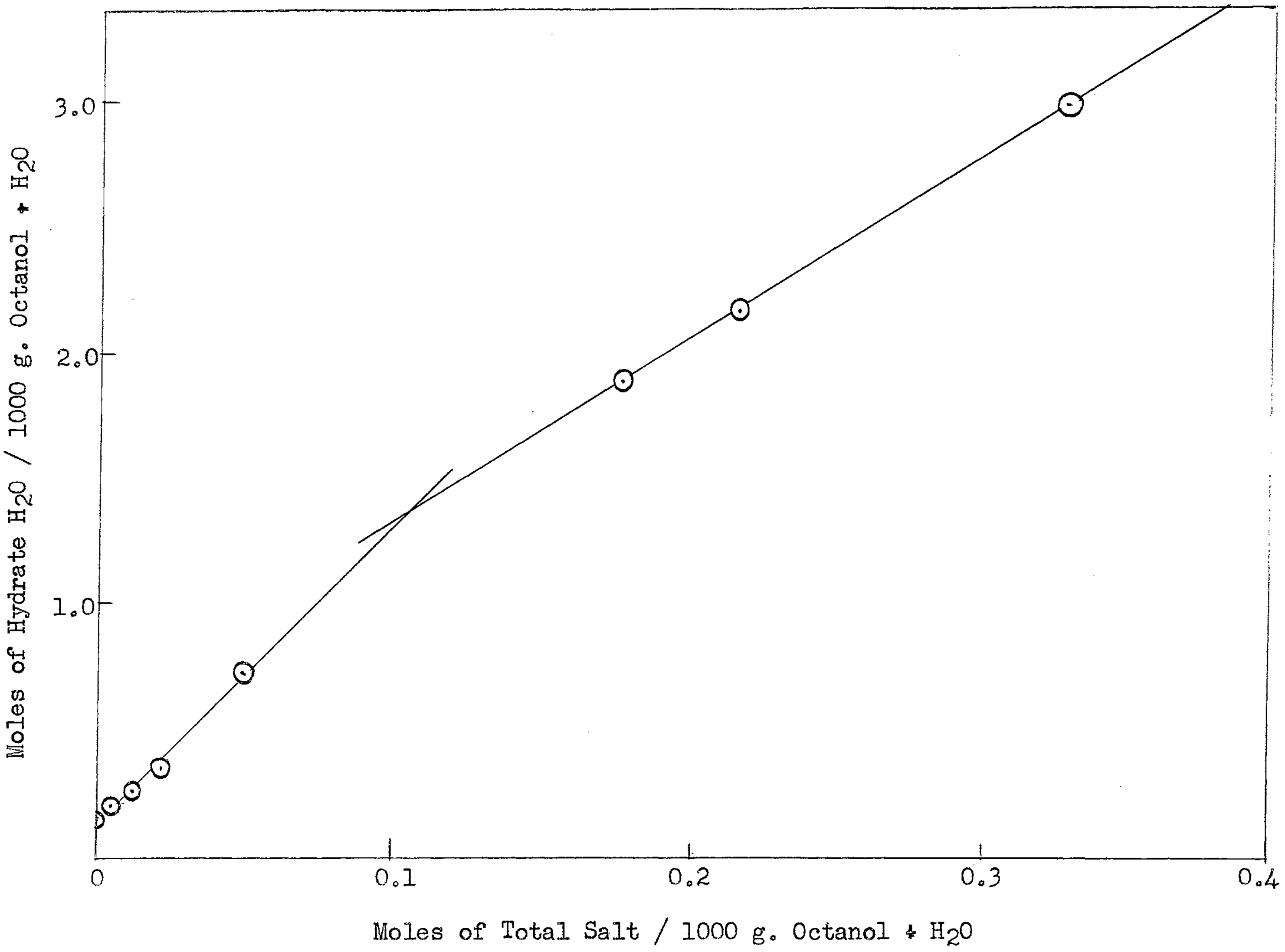

Figure 7: Determination of Average Hydration Number in $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ Mixtures

law to hold rigorously. It is also possible that the average hydration number actually decreases in the regions of highest salt concentration.

The exceedingly high degree to which the perchlorates are hydrated is undoubtedly related to their extensive and nonspecific extraction by 2-octanol.

Mutual Promotion Exhibited in $CoCl_2$-$Co(ClO_4)_2$ System

It was of interest to study the effect of $Co(ClO_4)_2$ which extracts to a considerable extent on $CoCl_2$ which does not extract at all below a concentration of 2 molal. The results of this extraction show that $Co(ClO_4)_2$ exhibits a very definite promoting action on the extractability of $CoCl_2$. A study of Table 2 indicates steadily increasing concentration of $CoCl_2$ in the 2-octanol phase as the molality of the promoting agent, $Co(ClO_4)_2$, is increased in the water phase. Table 4 shows that values determined for the simple stoichiometric distribution coefficient (K_d) also vary with increasing concentration of the promoting agent and, therefore, do not follow the Nernst Distribution Law.

It is easily shown that the octanol phase concentration of $CoCl_2$ increases more rapidly than would be expected from the increase in concentration of the cobalt ion based upon mass action considerations. This shows that a knowledge of the variation of the activity coefficient with concentration would be required to understand the observed variation in distribution coefficient. It has been found that, in general, the addition of a second noninteracting electrolyte to a solution causes an increase in the activity coefficient of the first component. This statement, however, may not be entirely applicable in this case, since there is definite evidence of complex formation taking place. The effect of this complex formation would be to lower the activity coefficient of the salts in the phase in which it occurs. How closely these two opposing factors tend to balance out is unknown.

Since the extractability of the cobalt ion in particular is one of the basic interests in this investigation, it is necessary to examine the extractability of the $Co(ClO_4)_2$ as well as the $CoCl_2$ in the mixed system. Figure 8 shows the effect of $CoCl_2$ at constant molality on the extractability of $Co(ClO_4)_2$ from the mixed system. As the figure indicates, the concentration of $Co(ClO_4)_2$ in the 2-octanol phase is higher in the mixed system than in the unpromoted system at comparable water-phase concentrations. Here again, it is difficult to ascribe this promotion to a particular factor or group of factors without additional information about the system.

Generalized Relationship Between Extractability of Promoting and Promoted Species

It was first observed for the system $CoCl_2$-$Co(ClO_4)_2$ that a linear relationship existed between the distribution coefficients of the two salts. It was later noted that this relationship also was valid for the $Ni(ClO_4)_2$-$Ca(ClO_4)_2$ system. Figures 9 and 10 demonstrate the linearity for these two systems. This simple relationship still awaits a theoretical explanation, however.

Spectrophotometric Study

Two interesting regions are noted in a plot of optical density versus wavelength for the 2-octanol phase of the $CoCl_2$-$Co(ClO_4)_2$ system, Figure 11. The main peak was located at 520 millimicrons. This peak is characteristic of the hydrated cobalt ion which seems to be

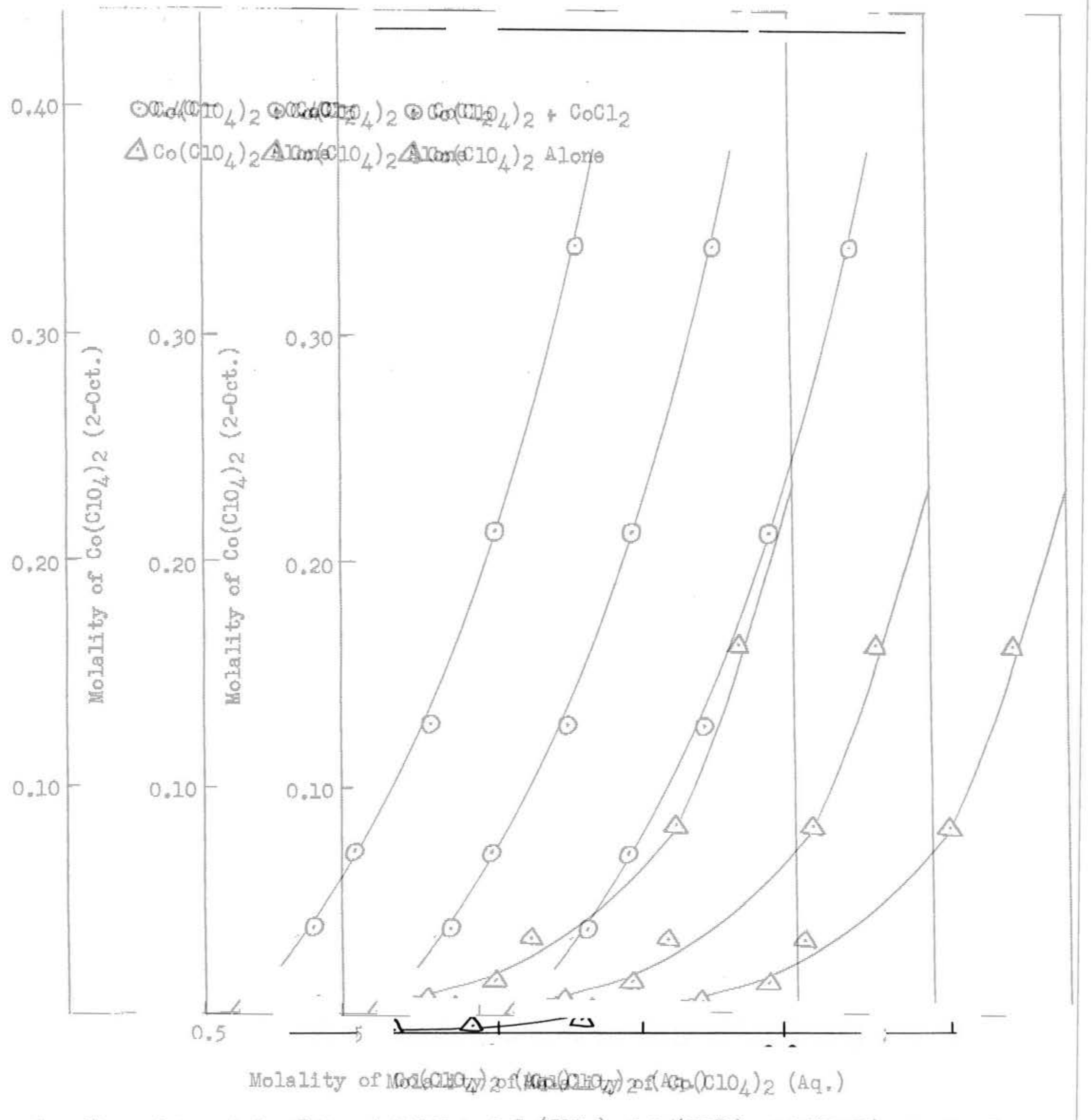

Figure 8: Comparison of the Extractability of $Co(ClO_4)_2$ in the Presence of 2 Molal $CoCl_2$ with Unpromoted $Co(ClO_4)_2$

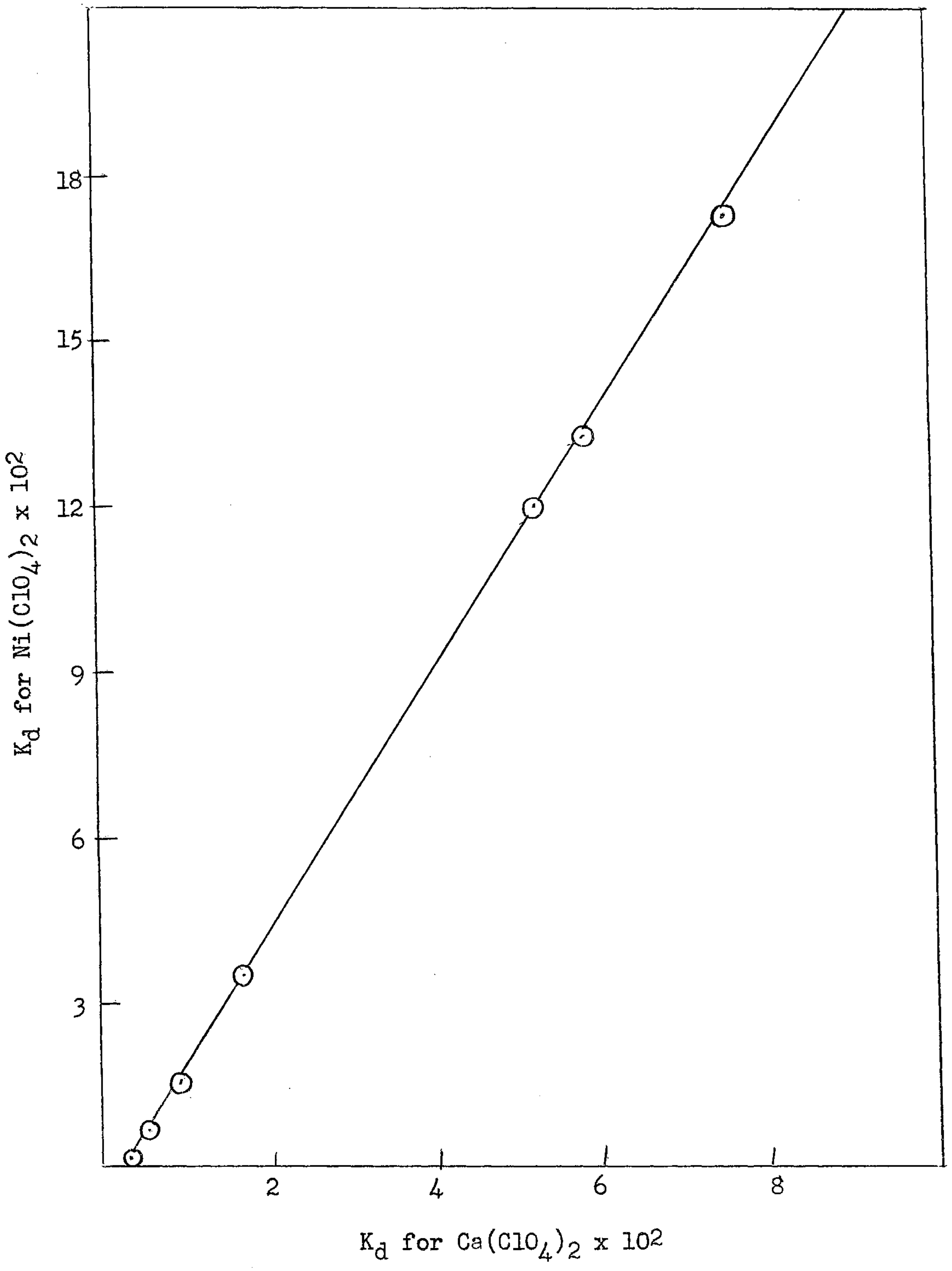

Figure 9: Interdependence of K_d for System $Ni(ClO_4)_2$-$Ca(ClO_4)_2$

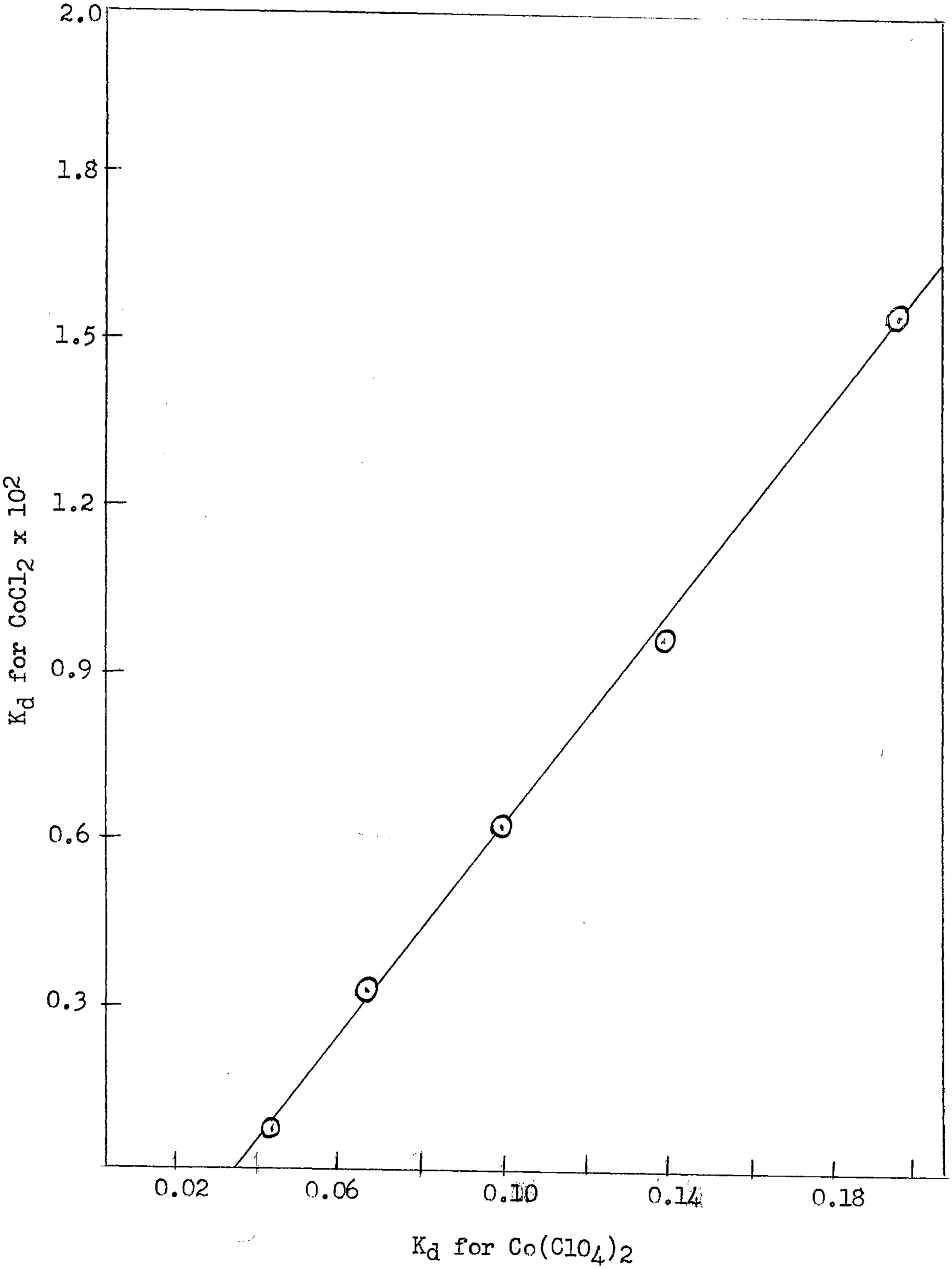

Figure 10: Interdependence of K_d for System $CoCl_2$-$Co(ClO_4)_2$

present in the non-aqueous phase to a large extent. A rather broad absorption band is also observed in the region from 580 to 720 millimicrons. It was in this region that Beaver, et al. (1) reported the presence of absorption which was attributed to several chloro-complexes of cobalt II including $CoCl^+$. The systems studied by Beaver were very similar to the ones under investigation here except for the concentration ranges involved. Since the ratio of chloride ion concentration to cobalt ion concentration is lower in the mixed system than in the unpromoted system, being always less than 1, it is suspected that the principal complex formed is $CoCl^+$. Because the regions of absorption were so broad, it was impossible to pick a maxima which could definitely be identified as being caused by $CoCl^+$, however.

Suggested Values for the Hydration Numbers of $CoCl_2$ and $Co(ClO_4)_2$

As was pointed out in the previous section, no method was available by which the hydration numbers of $CoCl_2$ and $Co(ClO_4)_2$ could be determined in the mixed solution. It was possible to assign tentative values for the hydration numbers of each of the two salts, and then to determine whether or not it was possible to have these numbers fit the available data. The values selected were 12.5 for $Co(ClO_4)_2$ and 2.0 for $CoCl_2$. This selection was made on the basis of what is already known about the hydration numbers of the two salts in unpromoted extractions.

Table 6 shows the molality of hydrate water determined on the basis of this assumption. These values were subtracted from the amount of total water in each solution as determined by a Karl Fisher analysis and the difference was denoted as free water. The amount of free water can then be qualitatively examined. Column 3 shows the

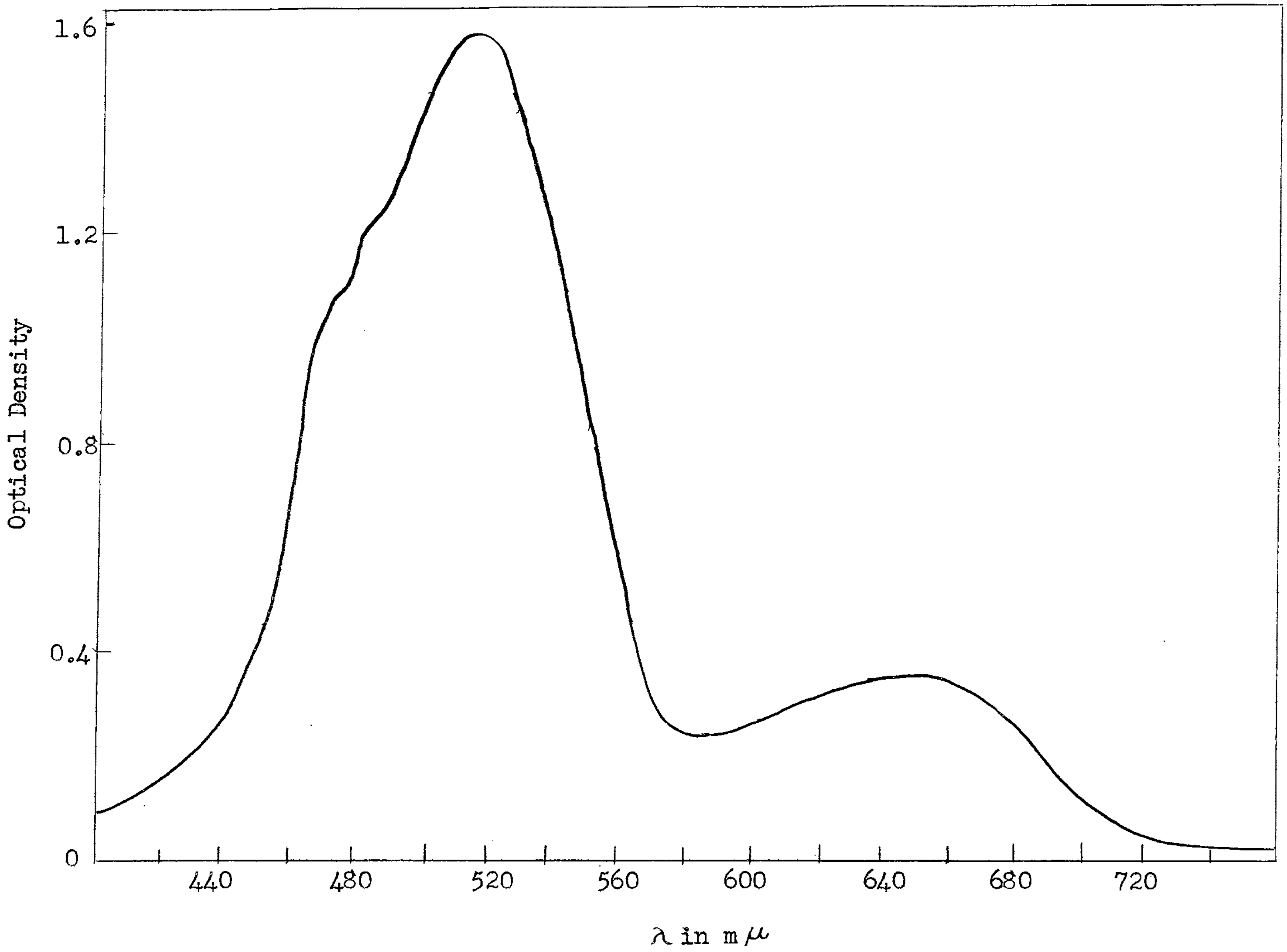

Figure 11: Spectrum of 2-Octanol Rich Phase of the System $CoCl_2$-$Co(ClO_4)_2$

variation in concentration of free water with increasing salt concentration. The concentration range seems to be quite reasonable. It is encouraging not to find any negative values for the free water molality at high salt concentrations which would have completely invalidated the assumptions made. It is also apparent that the calculated free water molalities decrease with increasing salt concentrations. This is in accord with the fact that at high salt concentrations the activity of the water in the aqueous phase is low and, therefore, the amount of water extracted would be low. The only conclusion that can be safely drawn is that the assigned values are not impossible in the light of the observed experimental results. It does not rule out many other possible combinations of hydration numbers which would fit the data equally well.

SUMMARY AND CONCLUSIONS

The promoting effect of calcium perchlorate on nickel perchlorate was found to compare favorably with the promoting effect of calcium perchlorate on cobalt perchlorate. The cause of this promotion was attributed principally to a mass action effect. The average hydration number was found for the mixed system, and it was shown that practically no change occurred in the apparent degree of hydration of the nickel perchlorate by the presence of $Ca(ClO_4)_2$. Simple stoichiometric (K_d) and mass-law type (K_m) distribution coefficients were determined on the basis of the concentration of the salts in solution. Making certain assumptions as to the equivalence of activity coefficients for all perchlorates, a thermodynamic activity constant (K_M) was evaluated and was found to be relatively constant over the concentration range studied.

Studies made on the $CoCl_2$-$Co(ClO_4)_2$ system showed the cobalt chloride to be extensively promoted by the presence of cobalt perchlorate. A spectrophotometric study of the 2-octanol phase of the $CoCl_2$-$Co(ClO_4)_2$ system exhibited two large areas of absorption. It was noted that one of these regions (580-720 $m\mu$) coincided with an absorption region reported to be due to the formation of chloro-complexes of cobalt II (1). Although it is suspected that the principal complex formed is the 1:1 complex, the curve lacked sufficient structure to identify this species. By an indirect method, it was shown that in the mixed system containing a common cobalt ion, the hydration numbers of the salt pair could be taken as those found in the 2-octanol phases of unpromoted extractions.

It was also found that in the mixed systems studied the distribution coefficient for one of the components was a linear function of the distribution coefficient of the other component.

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