THE EFFECT OF LARGE ANIONS

ON THE EXTRACTION OF COBALT

INTO 2-OCTANOL

By

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Buckhannon, West Virginia

1952

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ACKNOWLEDGEMENT

The author extends his sincere thanks to Dr. Thomas E. Moore in part payment for his patient guidance and help tendered during the course of this investigation.

Also the author is grateful for the help and advice given by the graduate students.

The research foundation is thanked for the financial aid given in the form of an Atomic Energy Research Fellowship.

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INTRODUCTION

Yates and Moore (47) have discussed the effect of a large anion with a low charge on the extraction of inorganic salts. They point out that for the same cation, salts of large anions and low charge are the most soluble in non-aqueous solvents, which may be supported by the higher solubility in organic solvents of chlorates, perchlorates, nitrates, chlorides, bromides, thiocyanates, and iodides when compared to that of the corresponding fluorides, hydroxides, sulfates, phosphates, carbonates, and cyanides. Additional indication of the favorableness of the large anion in extraction comes from considering on the basis of electrostatics alone the free energy of transfer from one solvent to another of salts of differing anion size.

They also point out that for anions compared to cations, both theoretical and experimental evidence indicates that solvation is less important in increasing ionic size in solution. In the first place an anion of a given electronic configuration is always larger than a cation of the same configuration, and the charge is distributed in the outer shell rather than localized at the center of the atom. Thus the negative field of the anion is more diffuse and much less intense than the positive field of a comparable cation. The second reason is that in most solvents the positive portion of the dipole is less localized than the negative portion of the dipole. Thus both the positive portion and the negative portion of the anion-dipole fields of attraction necessary for solvation are more diffuse than the corresponding cation-dipole fields. For this reason, it is likely that anionic

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radii are very close to being the same in solution as in the crystal, and the radii of even small or highly charged anions may be considered constant in the transfer process. This results in a larger unfavorable free energy of transfer for the small anions than if the effective radius had been increased by solvation, and the free energy of trans- fer of anions of large crystallographic radii is correspondingly less than for anions of small radii.

The enhanced extraction of salts with a large anion has been in- dicated by examination of the various extractions reported in the literature. In these laboratories it has been found that the perchlor- ates of nickel and cobalt compared to the chlorides have followed the expected trend (22). It became desirable to know how the bromides and iodides would effect the extraction of cobalt into 2-octanol. This thesis is based on those experiments.

HISTORICAL

Most of the literature on the solvent extraction of salts up to June, 1953, has been reviewed by Laran (22). Since that time there have been other reviews presented on the various aspects of solvent extraction.

Scheibel (31) has reviewed the recent advances as applied to laboratory studies in the field of simple liquid extraction and in fractional liquid extraction. The industrial applications of solvent extraction have been reviewed by Treybal (40, 41). Also a review of theory, techniques, plant equipment, and practical applications to industry has been presented by Woodwark (44).

A paper by Metzch (26) presents a discussion of requirements for solvents, use of solubilizers, and solubility theories. One table presents data for about 400 partially miscible pairs of anhydrous organic solvents, and a second table lists literature data for 360 systems used for the separation of organic and inorganic mixtures.

Work on the measurement of mass transfer rate for a variety of solutes passing from one to another of two immiscible liquids is reported by Gordon and Sherwood (11) along with a review of the theory, description of apparatus, and tabulation and graphing of results. Seltzer (33) has also studied mass transfer in the system water-acetic acid-methylisobutyl ketone using a spray type liquid-liquid extraction column with the ketone dispersed into the water. Wormser (45) has presented a mathematical approach to the theory and application of sol-

vent extraction to analysis.

Extraction of Iron

Carvers (4) has described an apparatus for studying mass trans-
fer in liquid-liquid extraction under conditions of concentration equi-
librium using tracer techniques. Values of overall transfer coefficients
and of overall height of a transfer unit have been obtained for trans-
fer of ferric chloride from acidic aqueous phase to isopropyl ether.
Ishiabashi and Yamamato (19) have found that five extractions are nec-
essary to extract ferric chloride and aluminum chloride from six normal
hydrochloric acid, with sulfate and phosphate ions having no effect.
Yamamato (46) has found that a 5:1 mixture and ammonium hydroxide or
a mixture of ether and butyl acetate (4:1) are suitable for the extrac-
tion of ferric chloride from a hydrochloric acid solution.

Extraction of Niobium

A method for the extraction of niobium into diisopropyl ketone
from hydrochloric acid solutions in the absense of hydrogen fluoride,
and a new reliable radiochemical separation procedure for niobium
based on these findings has been developed by Hicks and Gilbert (14).
Stevenson and Hicks (36) have found that the fluoride complexes of tan-
talum and niobium can both be extracted by diisopropyl ketone, but
that of tantalum so much more readily that a separation can be made.
Werning et al. (43) have produced products of tantalum and niobium of
greater than 99% purity by use of methyl isobutyl ketone in a perforated
plate pulse column. Tantalum is extracted preferentially by the ke-
tone from a hydrofluoric acid solution. Addition of hydrochloric acid
to the aqueous raffinate and re-extraction with fresh ketone selective-

ly extracts the niobium from the remaining impurities.

Studies by Ellenburg, Leddicote, and Moore (6) using inactive niobium and tantalum as well as radioactive tracers of these elements, indicate the separation of niobium from tantalum by the liquid-liquid extraction of hydrochloric acid solutions of these elements with long-chain aliphatic and aromatic amines in organic solvents is quantitative. Further studies showed that niobium and tantalum sulfate and oxalate complexes extract with the solvated amines, but in the case of tribenzylamine in methylene chloride the niobium sulfate complex may be quantitatively separated from the tantalum sulfate complex if the ratio of organic to aqueous solution is maintained at 15 to 1.

In examining the extraction characteristics of a variety of solvent systems for the purpose of finding a method of separating zirconium and niobium from all other fission product elements, Scadden and Ballow (30) have found mixed butyl phosphoric acids in di-n-butyl ether to be effective. They also found conditions for separating the yttrium from the lanthanum group rare earths.

Moore (27) has found that the niobium carrier in oxalic acid markedly inhibits the extraction of protoactinium while sulfuric acid enhances the extractability into diisobutylcarbinol of protoactinium from dilute hydrochloric acid or hydrofluoric acid. Niobium is extracted into diisobutylcarbinol from a dilute hydrofluoric-sulfuric acid solution, and protoactinium remains in the aqueous phase.

Extraction as Metal-organic compounds

Steinbach (34) has reported that chromium(III), cobalt(III),

iron(III), beryllium, copper, aluminum, galium, indium, vanadium, zir-
conium, and zinc were extracted by acetylacetone to an extent depend-
ent upon the pH of the aqueous phase. Within this group it was found
possible to separate copper quantitatively from zinc by adjusting the
pH to 2. Also iron impurities can be removed from aluminum, gallium,
and indium from aqueous solutions with acetylacetone (35).

Benzene, toluene, xylene, and chloroform were found to be suit-
able for the extraction of 4 to 40 γ of aluminum and 2 to 20 γ of
copper as the 8-quinolinol complex by Sudo (38), but amyl acetate,
amyl alcohol, and benzyl acetate do not give complete extractions.
Dryssen and Dahlberg (5) have discussed the solvent partition of the
oxinate and cupferron of lanthanum(III), samarium(III), hafnium(IV),
thorium(IV), and uranium(VI) between an aqueous phase and chloroform
or hexanone.

The extraction of zinc as the dithiozonate complex in chloroform
and carbon tetrachloride has been studied over a wide range of reagent
concentrations and aqueous buffers of different pH and ionic strength
(16).

Sundaram and Banerjee (39) report that beryllium was extracted in
the presence of butyric acid, and of the solvents tried viz. ether,
benzene, chloroform, amyl acetate, ethyl acetate, and carbon tetra-
chloride, chloroform was the best, with ethyl acetate the second best.
Four extractions with chloroform will extract 99% of the beryllium.
Banerjee, Sundaram, and Sharma (1) have also studied the extraction of
beryllium from a solution of iron and aluminum.

Extraction of the Rare Earths

Peppard, Gray, and Markes (28) have made a comparison of the sol-

vent extraction behavior of the lanthanide and actinide series for the purpose of pointing out certain similarities between the two series in the trivalent state. It was shown, for example, that log K is a linear function of atomic number for both. Fischer et al. (8) have described the basis of the process, the apparatus used, and some examples of separation of rare earths by distribution between two solvents and report that the separation factor of an individual step has the same order of magnitude as in the crystal fractionation process; however, solvent extraction is preferable because of smaller time and work expended. Bochinski, Smutz, and Spedding (3) have found that the rare earths may be separated from each other by extracting rare earth nitrate solutions with undiluted tributyl phosphate without using nitric acid or salting out agents. The separation factors are almost independent of the composition of the rare earth nitrate mixture and at equilibrium the ratio of total rare earth solutes in tributyl phosphate to total rare earths in the aqueous phase is a function of the amount of rare earths present.

Extraction of Other Elements

The extraction of cobalt from nickel in aqueous ammonium thiocyanate solutions by methyl isobutyl ketone using a pulse column has been studied by Griffin, Jasny, and Tupper (12). Triblat (42) has investigated the extraction of perrhenic acid by butyl or isoamyl alcohol, the extracton of molybdenum(VI) by isoamyl alcohol, the extraction of isoamyl, benzyl, and octyl alcohols, of acetic, perchloric, nitric, hydrochloric, sulfuric acids, and several alkali perrhenates, and the extraction of $(C_6H_4)_4PCl$ by chloroform. Martin (23) has

studied the distribution of ruthenium tetroxide between carbon tetra-
chloride and aqueous alkali and neutral salt solutions. Huffman et
al. (15) have determined the distribution ratios and equilibrium
constants for the extraction of zirconium and hafnium from four molar
perchloric acid with various combinations of fluorinated β-diketones
and organic solvents. Hagiwara (13) has studied the distribution of
thorium between butyl acetate and water under various conditions.
Extraction of metal thiocyanate complexes with tri-n-butyl phosphate
has been studied by Melnick (25). Sege and Woodfield (32) used a
three inch diameter pulse column to study the extraction of uranyl
nitrate with tributyl phosphate. The extraction of uranyl nitrate
from ether by water at 25°C was studied by Jodra, Luina, and Oroz (20).

Extraction of the Halides

Irving and Rossotti (17) have found that in extracting the III B
(gallium, indium, thallium) halides from solutions varying in concen-
tration of the corresponding halogen acid into diethyl ether, the per-
centage of extraction increases with increasing acid normality. The
extactions pass through a maximum, and the acid normality at which
this occurs is lowest for the iodides with bromide and chloride next
in that order. Irving, Rossotti, and Drysdale (18) have found at the
respective optimum conditions for the extraction of indium from its
corresponding halogen acid solution that the amount extracted is great-
er for the iodides, a little less for bromides, and much less for the
chlorides.

McBryde and Yoe (24) have investigated the extraction of gold
from hydrobromic and hydrochloric acid solutions by isopropyl ether,

diethyl ether, ethyl acetate, and methyl isobutyl ketone. From a comparison of the results reported the bromides extract to a greater extent than the chlorides. The difference is most pronounced in isopropyl ether. Again a higher normality of hydrochloric than hydrobromic acid was needed.

Reagents

Cobalt and nickel iodides were prepared from C.P. metal carbonates and reagent hydroiodic acid. The acid was added until there was an excess, then the resulting solution was evaporated to dryness, taken up with water, filtered, and again evaporated to dryness. The resulting anhydrous salt was then dissolved in enough water to take up all the salt, filtered, and used to prepare the various solutions to be used.

Cobalt bromide was prepared in a manner analogous to the iodide. Where anhydrous salt was used, the salt was prepared by evaporating a solution of cobalt bromide to dryness.

Analysis: calculated   cobalt: 26.94   bromide: 73.06

         found   cobalt: 26.93   bromide: 72.61

The aluminum bromide solution was prepared by adding water drop-wise to the anhydrous salt, cooling with ice, collecting in water any hydrogen bromide released, and adding the resulting hydrobromic acid solution to the partially hydrolyzed aluminum bromide solution. The apparatus used is shown in Figure 1.

The 2-octanol used throughout was the best grade of anhydrous reagent from the Matheson Company.

Figure 1.
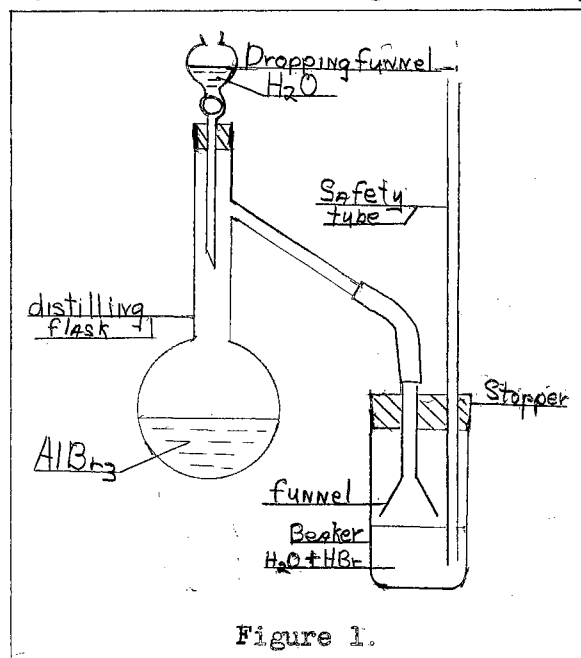
All other chemicals used were of C.P. grade.

Preparation of Solutions

Solutions of varying concentations of cobalt iodide and cobalt bromide were made by diluting the original stock with distilled water. Since a suitable range of concentrations included both dilute and concentrated solutions, the necessary dilutions were by measuring the solution and water with a graduated pipet to the nearest tenth of a milliliter.

Stock solutions of cobalt bromide-lithium bromide, cobalt bromide-calcium bromide, and cobalt bromide-aluminum bromide were prepared to be two molal in cobalt bromide. The cobalt bromide-lithium bromide and cobalt bromide-aluminum bromide solutions were prepared by adding calculated weighed amounts of anhydrous cobalt bromide to the stock solution of lithium or aluminum bromide. The cobalt bromide-calcium bromide solution was prepared by weighing calculated amounts of stock cobalt bromide and calcium bromide solutions and mixing them. The resulting solutions were then analyzed to check the concnetrations. A two-molal stock solution of cobalt bromide was prepared for diluting the respective solutions to give a range of concentrations of promoting salt from low to high with a constant cobalt bromide concentration of two molal. The dilutions were again made by measuring the stock solutions with a graduated pipet to the nearest tenth of a milliliter.

Extraction Procedure

The stock solutions, water, or diluting solution, and 2-octanol were pipeted into 125-ml. ground-glass stoppered Erlenmeyer flasks. The flasks were attached to a mechanical shaker in such a manner as

to have the flasks partially immersed in a 30°C. water bath with about two-thirds of the flask below the surface of the water. The flasks were shaken overnight and then allowed to stand without further shaking in the bath for twelve to twenty-four hours. The phases were then separated by means of a separatory funnel and stored in airtight containers until analyzed.

Analytical Procedures,

The methods for analysis are outlined in Table 1. The general procedure was to analyze the unpromoted extractions by cation determination in the 2-octanol phase and by anion determination in the aqueous phase and to analyze the promoted extractions for cobalt and the total anion concentration in both phases. The only methods which need to be considered in more detail here are the analysis of cobalt in the presence of aluminum and calcium, and the analysis of dilute bromide solutions.

The method used for the analysis of cobalt in concentrations of 0.01 molal and over was that described by Evans (7). This method consisted of making the cobalt solution slightly basic by the rapid addition of 20 ml. of a saturated borax solution, adding 10 ml. of a 4% potassium iodide solution, and then delivering enough standard potassium cyanide solution from a buret with stirring until the precipitate dissolved, plus a 5 ml. excess. Next 10 ml. of a 10% sodium carbonate solution was added and air bubbled through the solution for 6 minutes to convert all the cobalt to the $Co(CN)_5^{--}$ complex. After the addition of 10 ml. of 1:1 ammonium hydroxide and 25 ml. of 20% ammonium chloride solution, the excess cyanide is titrated with standard silver nitrate

to a turbid end point.

A modification was made so that the method could be used to analyze for cobalt without the precipitation of aluminum hydroxide or calcium carbonate masking the turbidity end point. The modification was the use of a solution of sodium hydroxide in place of the sodium carbonate solution. The substitution was made because the aluminum would be converted to sodium aluminate, and the calcium hydroxide is soluble in ammonium chloride solutions. In low concentrations of aluminum the sodium carbonate solution may be used.

The dilute bromide concentrations were determined by titrating with 0.002N alcoholic silver nitrate or 0.02N aqueous silver nitrate, with alcohol added to the solution to be titrated. Alcohol was used to enhance the end point which was determined potentiometrically using a saturated calomel reference electrode and a silver wire indicator electrode. A precision of ±1% was obtained.

Table 1

Summary of Analytical Methods

System	Aqueous Phase	2-octanol
$CoBr_2$-H_2O-2-octanol	Br: $AgNO_3$-dichlorofluoroscein	Co: Polarograph (21)
$CoBr_2$-LiBr-H_2O-2-octanol	Co: KCN-$AgNO_3$ titration (7)	Co: Polarograph and KCN and $AgNO_3$ (21 & 7)
	Li: Total bromide-$AgNO_3$ titration.	Li: Total bromide-potentiometrically.
$CoBr_2$-$CaBr_2$-H_2O-2-octanol	Co: KCN-$AgNO_3$ titration (7)	Co: Polarograph (21)
	Ca: Total bromide-$AgNO_3$ titration.	Ca: Total bromide-potentiometrically
$CoBr_2$-$AlBr_3$-H_2O-2-octanol	Co: KCN-$AgNO_3$ titration (7)	Co: Polarograph and KCN-$AgNO_3$ titration (21&7)
	Al: Total bromide-$AgNO_3$ titration	Al: Total bromide $AgNO_3$ titration
CoI_2-H_2O-2-octanol	I: $AgNO_3$ titration	NONE

RESULTS AND TREATMENT OF DATA

The discussion and interpretation of the data will be considered in relation to the individual series of extractions.

The Cobalt and Nickel Iodides

The original plan was to study both the iodides and the bromides, but the iodides were found to react with 2-octanol. The nickel iodide solutions upon standing were found to yield free iodine and apparently nickel hydroxide. Anhydrous cobalt iodide also was found to attack 2-octanol, but it was thought that the extraction from the aqueous solution would reduce the chances of such a reaction. Such was not the case. The products formed were free iodine and probably cobalt hydroxide indicating that the 2-octanol was being attacked and that hydrolysis had taken place. No further work was done with the iodides.

The Unpromoted Extraction of Cobalt Bromide

The remaining investigations were centered around the extraction of cobalt bromide by 2-octanol. The amount of extraction is dependent upon the aqueous phase concentration, which has been varied over a range from about 0.8 molal to 5.0 molal. From the equilibrium concentrations of the octanol-2 phase and the aqueous phase (Table 2), the distribution ratios have been calculated. The distribution ratio (D) is defined as the ratio of 2-octanol phase concentration to the aqueous phase concentration. A plot of the distribution ratios vs. the number of equivalents of bromide in the aqueous phase (Figure 2) shows that the distribution

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ratio is not a constant value as required by the Nernst equation, but from more concentrated aqueous solutions a higher degree of extraction occurs.

The activity coefficients of cobalt bromide in the 2-octanol phase were first calculated by the equation

$$K_a = \frac{(a\pm)^3 \text{oct.}}{(a\pm)^3 \text{aq.}} = \frac{(\gamma\pm)^3 \text{oct.}}{(\gamma\pm)^3 \text{aq.}} \frac{[Co^{++}][Br^-]^2 \text{oct.}}{[Co^{++}][Br^-]^2 \text{aq.}}$$

Assuming that $\gamma\pm$ equals unity for the most dilute 2-octanol phase and using literature values for $\gamma\pm_{aq.}$ (29), K_a was evaluated. Using the value obtained for K_a and the literature values for $\gamma\pm_{aq.}$ the remaining $\gamma\pm_{oct.}$ values were calculated from the experimental data (Table 2). When plotted against the concentration in the 2-octanol phase, a curve as in Figure 4 is obtained. Except for the point at the lowest concentration the curve resembles that obtained for cobalt perchlorate and nickel perchlorate (22). Owing to the low dielectric constant of 2-octanol it seemed most likely that cobalt bromide would be almost completely associated and that a more significant expression for K_a would be

$$K_a' = \frac{\gamma \text{oct.} [CoBr_2] \text{oct.}}{(\gamma\pm)^3 \text{aq.} [Co^{++}][Br^-]^2 \text{aq.}}$$

In evaluating K_a' this time $\gamma_{oct.}$ was assumed to equal unity for the most dilute solution, and the remaining $\gamma_{oct.}$ values were calculated using the evaluated K_a'. Plotting this time the newly obtained values of $\gamma_{oct.}$ vs. the concentration of 2-octanol phase (Figure 5), one obtains an essentially straight line for all points except the most concentrated. The same treatment of the data of Garwin and

Hixson (9) using literature values for $\gamma^{\pm}_{aq.}$ of cobalt chloride (37) yielded similar results (Figures 6 and 7, and Table 3). Since the plot of $\gamma_{oct.}$ vs. the concentration in the 2-octanol phase results in a straight line, the values of $\gamma_{oct.}$ may be expressed as a linear function of the 2-octanol phase concentration.
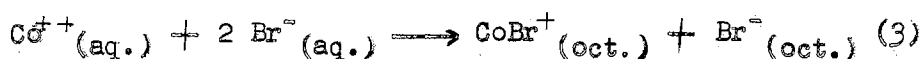
Thus, if

$$\gamma = km_{oct.} \tag{1}$$

then

$$K_a = \frac{km^2_{oct.}}{a_{aq.}} . \tag{2}$$

For the hypothetical reaction

$$Co^{++}_{(aq.)} + 2\ Br^{-}_{(aq.)} \longrightarrow CoBr^{+}_{(oct.)} + Br^{-}_{(oct.)} \tag{3}$$

an equilibrium distribution constant may be written having the same form as equation 2. While this reaction is not necessarily excluded, the agreement of the experimental results with the form of the equilibrium constant for reaction 3 is not proof of the occurrence of that reaction, especially in view of the low dielectric constant of 2-octanol. Furthermore, it has been assumed that the phases were completely immiscible, but this assumption is not entirely valid. It might also be pointed out that Beaver et al. (2) found evidence for a stable $CoCl^{+}$ species in anhydrous 2-octanol mixtures of cobalt chloride and cobalt perchlorate, and in dilute aqueous 2-octanol solutions of cobalt chloride, evidence was obtained for a $CoCl(H_2O)_2^{+}$ species.

Comparison of the distribution coefficients of cobalt perchlorate, cobalt bromide, and cobalt chloride between 2-octanol and water show that the values decrease in the order $Co(ClO_4)_2 > CoBr_2 > CoCl_2$. Those of cobalt bromide are greater than those of cobalt chloride as

expected on the grounds of the effect of anion size on the free energy

of transfer of the ions of a salt from one medium to another.

Table 2

Data on the CoBr$_2$ Unpromoted Extraction

m(aq.)	m x 10^3 (oct.)	D x 10^3	Br⁻eq.	$\gamma\pm$ (aq.)	$\gamma\pm$ (oct.)	γ (oct.)
0.867	0.5	0.6	1.734	0.634	1.00	1.0
1.354	0.6	0.4	2.708	0.883	1.81	8.5
1.812	1.4	0.8	3.624	1.27	1.50	26.1
2.310	3.4	1.5	4.620	1.94	1.20	79.6
3.702	41.5	11.2	7.404	6.12	0.50	814.
4.182	85.3	20.4	8.364	8.95	0.40	1841.
5.000	289.	57.8	10.00	15.36	0.24	4706.

Table 3

Activity Coefficients Calculated from the Data
of Garwin and Hixson (9).

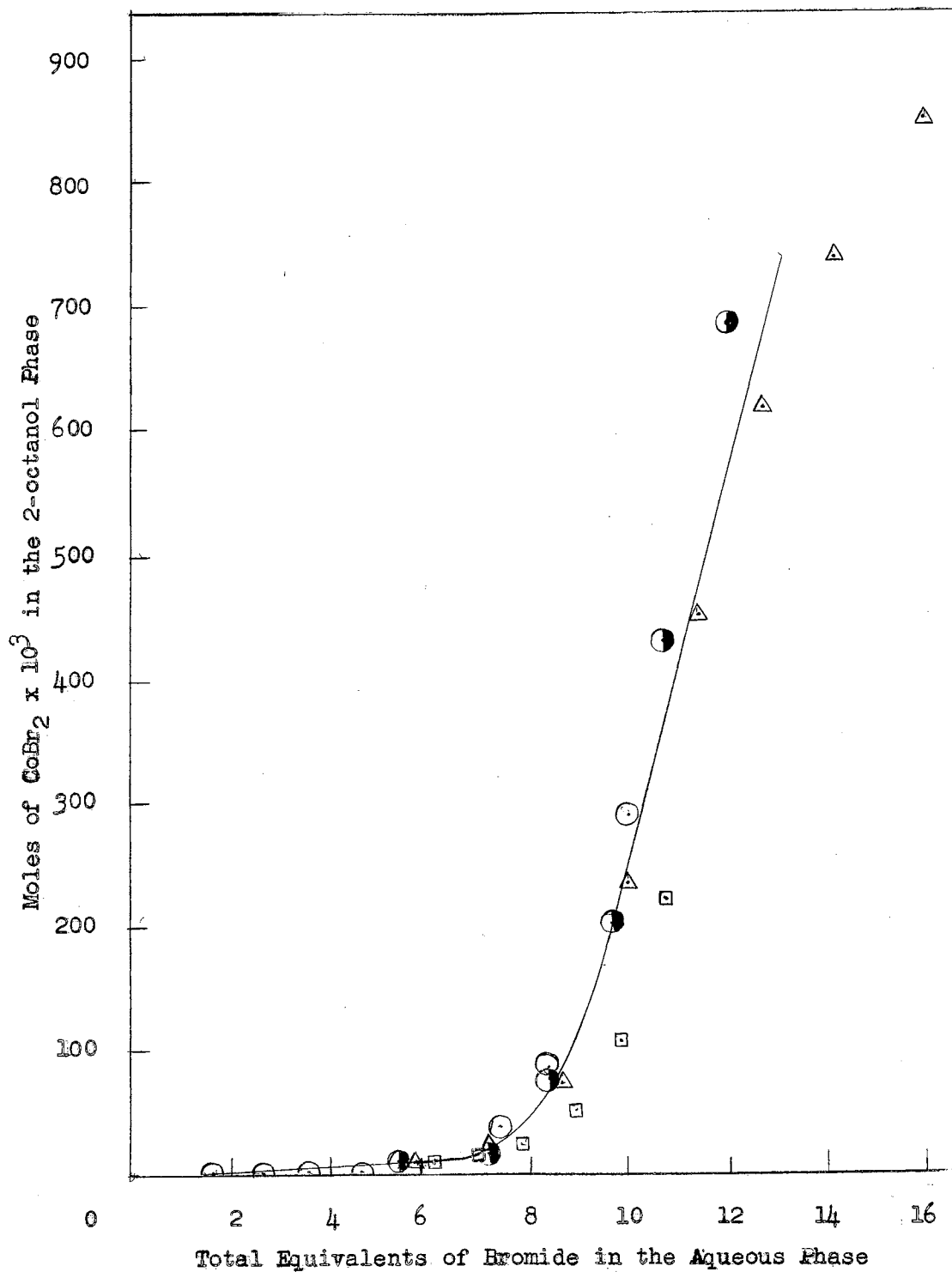| m(aq.)	m x 10^3 (oct.)	$\gamma\pm$ (aq.)	$\gamma\pm$ (oct.)	γ (oct.)
2.93	7.52	1.39	1.000	1.00
3.41	16.0	1.74	0.683	1.45
3.63	30.9	2.09	0.476	1.84
4.26	51.8	2.55	0.387	2.74

Figure 2.--Moles of cobalt bromide in the 2-octanol phase vs. total

equivalents of bromide in the aqueous phase. ⊙, unpromoted $CoBr_2$;

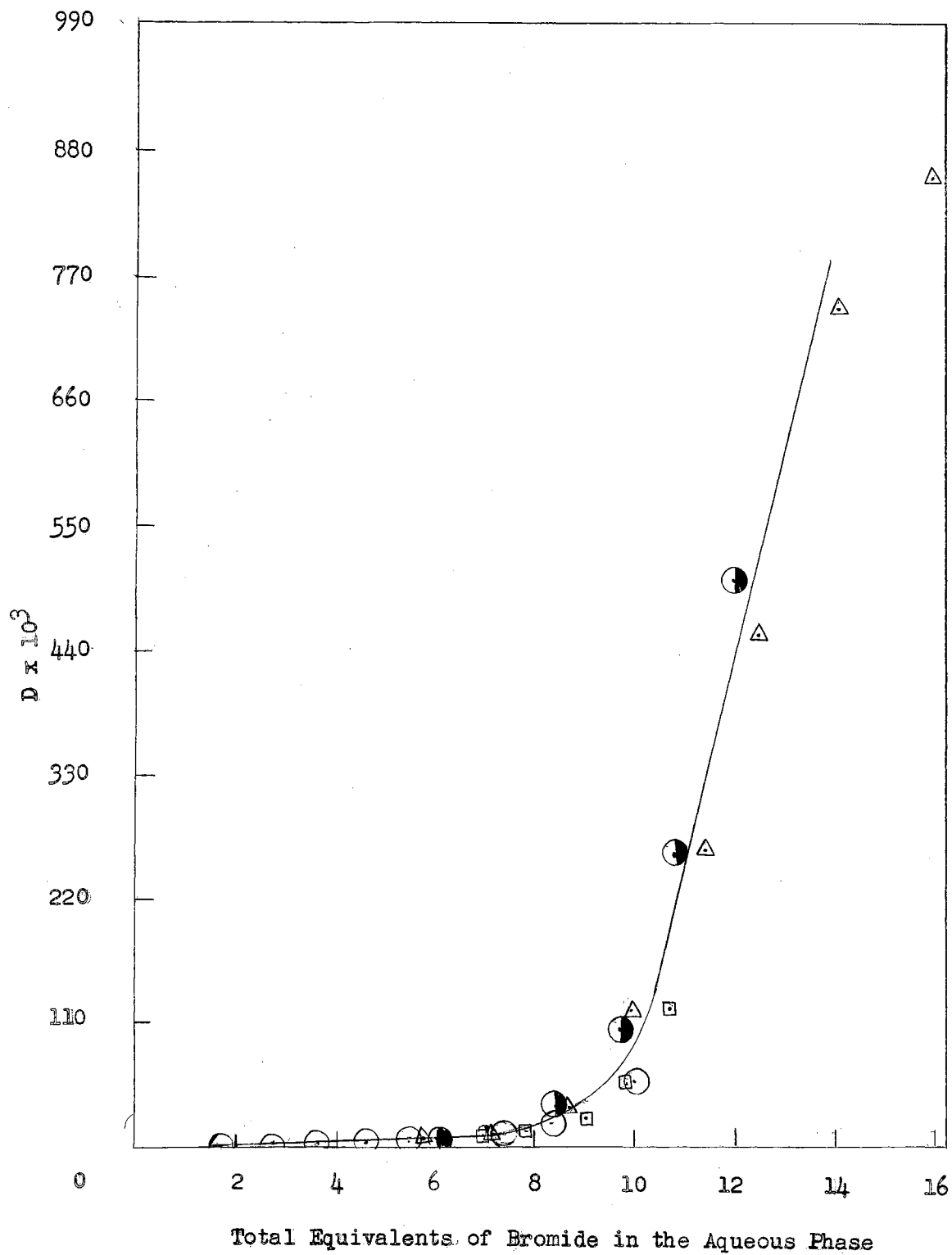△, LiBr promoted $CoBr_2$; ▣, $CaBr_2$ promoted $CoBr_2$; ◐, $AlBr_3$ promoted $CoBr_2$.

Figure 3.--D x 10^3 vs. total equivalents of bromide in the aqueous phase.
⊙, unpromoted $CoBr_2$; △, LiBr promoted $CoBr_2$; ▣, $CaBr_2$ promoted $CoBr_2$; ◑, $AlBr_3$ promoted $CoBr_2$.
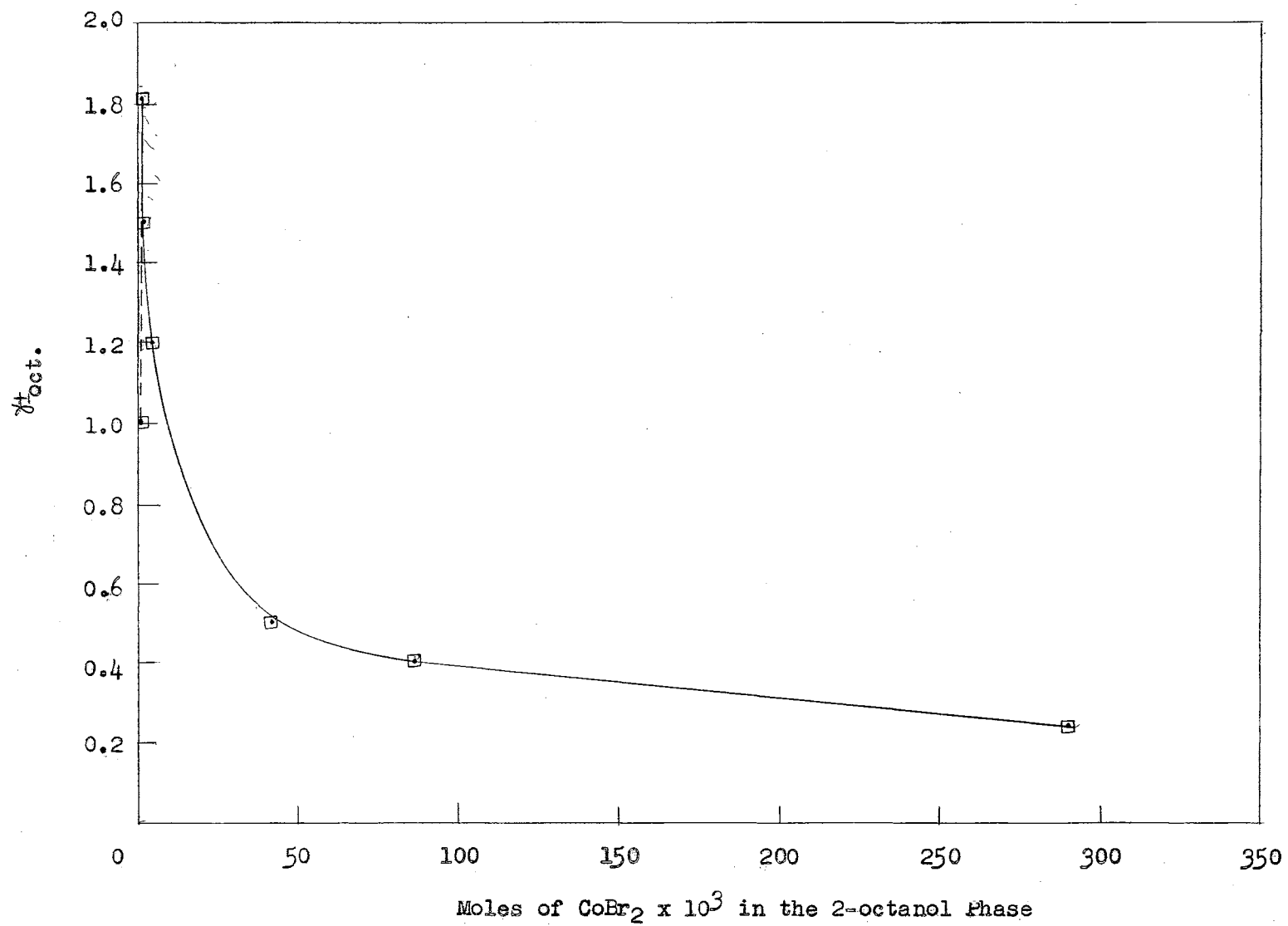
Figure 4.--$\gamma^{\pm}_{oct.}$ vs. the moles of cobalt bromide in the 2-octanol phase.

Figure 5.--$\gamma_{oct.}$ vs. the moles of $CoBr_2$ in the 2-octanol phase. The ⊙ are the expanded plot of region **A**. The scale for this plot is enclosed in parentheses.

Moles of $CoCl_2$ x 10^3 in the 2-octanol Phase

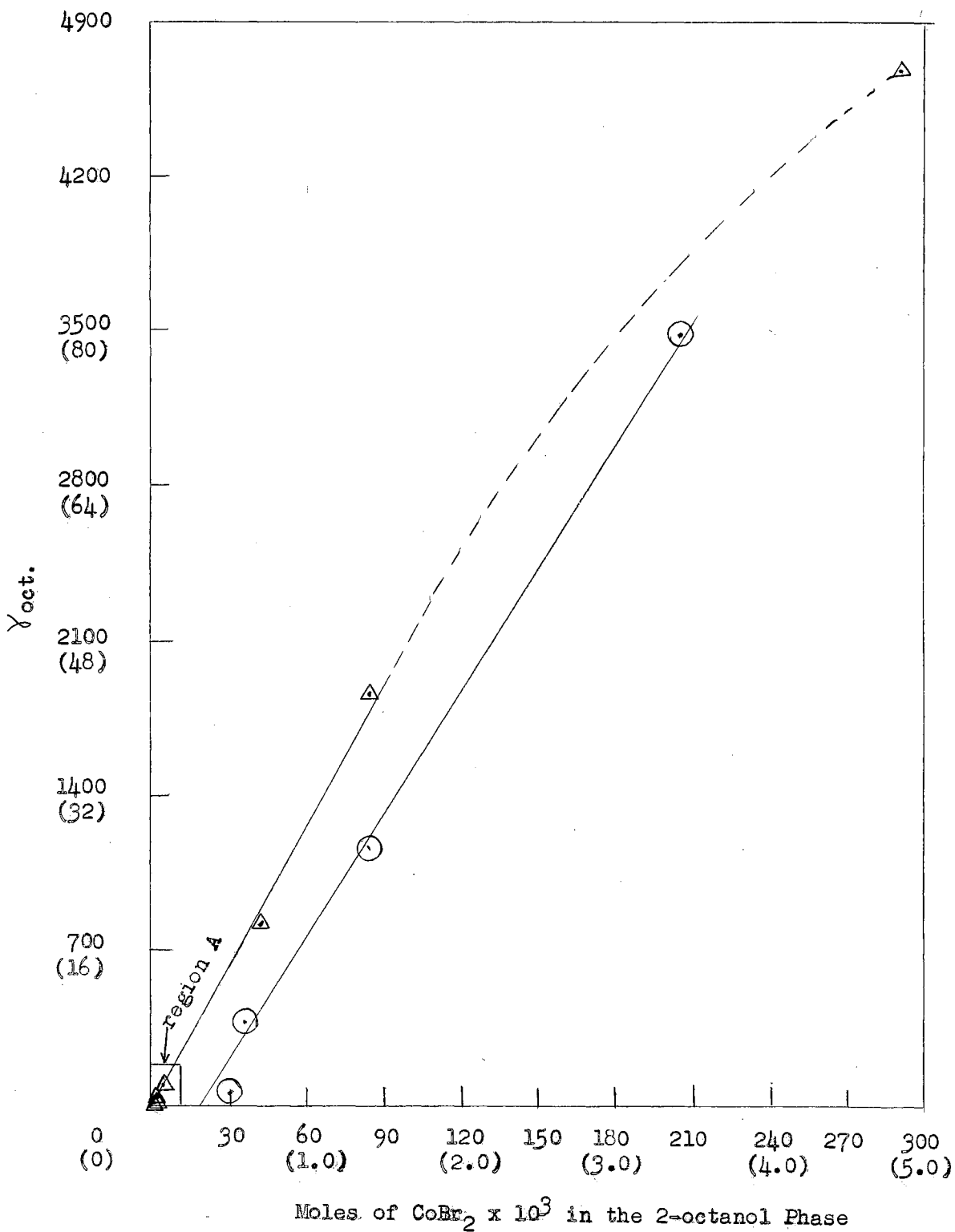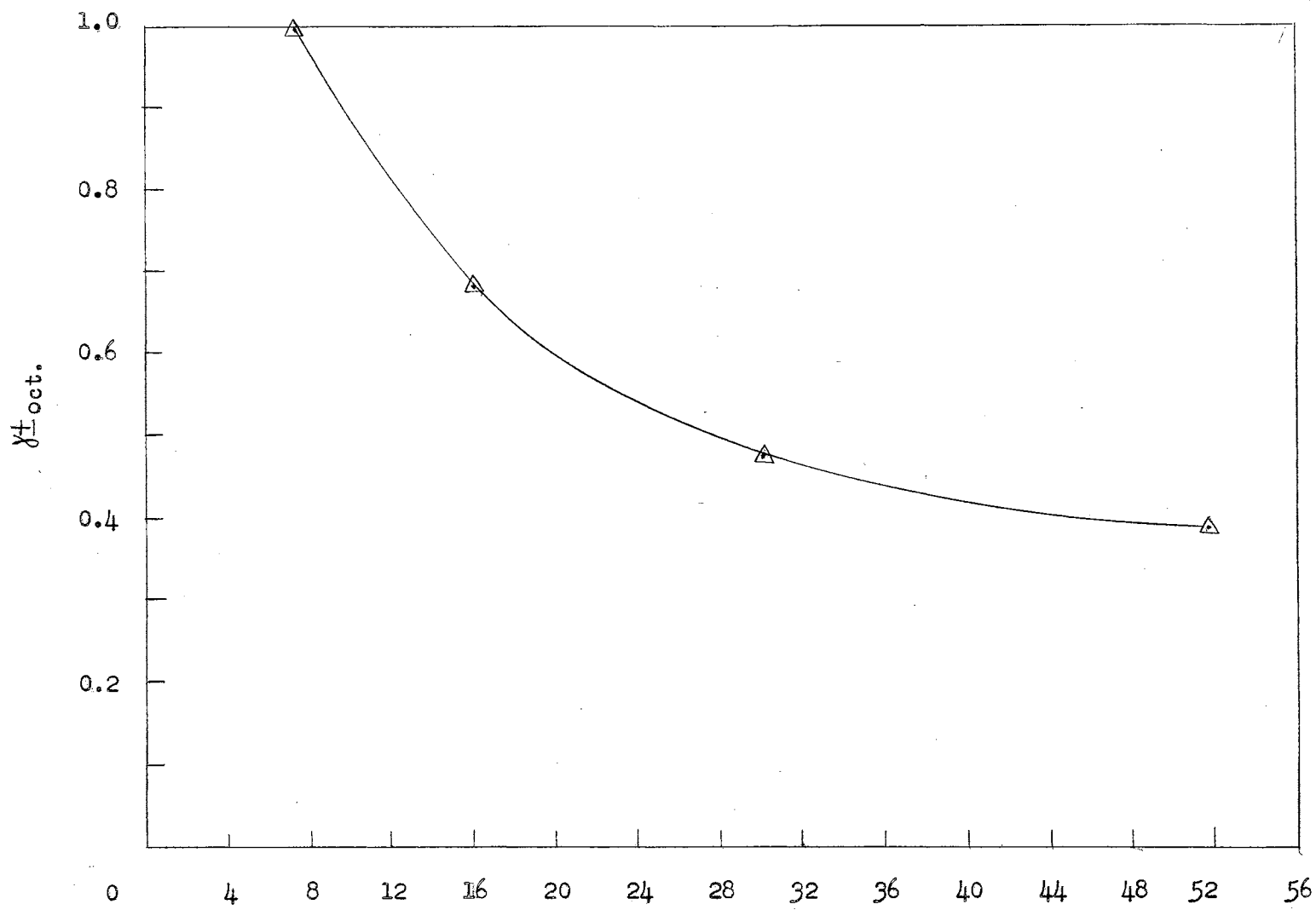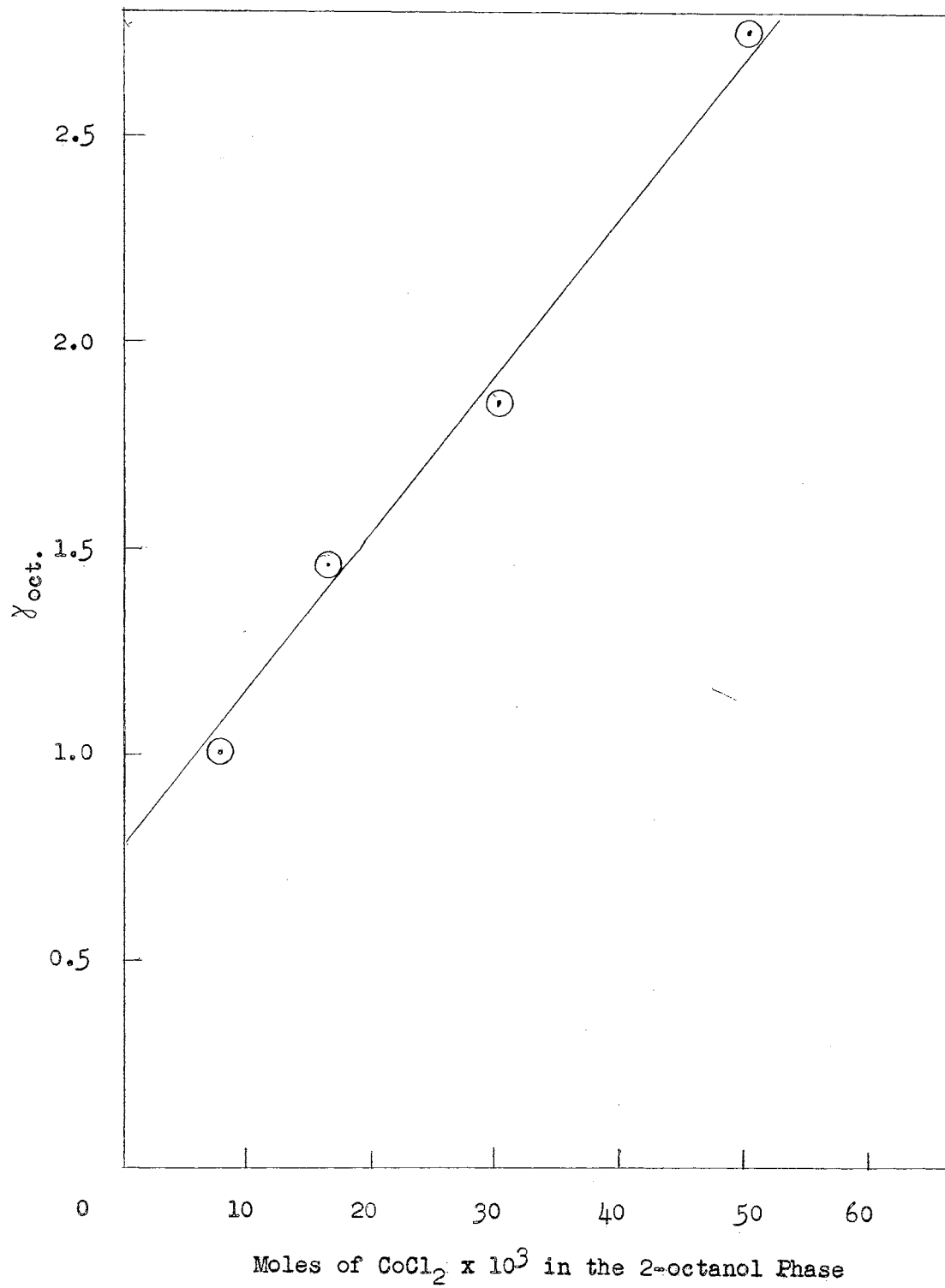Figure 6.--$\gamma\pm_{oct.}$ vs. the moles of cobalt chloride in the 2-octanol phase.

Figure 7.--$\gamma_{oct.}$ vs. the moles of cobalt chloride in the 2-octanol phase.

The Cobalt Bromide-Lithium Bromide-Promoted Extraction

These extractions were carried out with gradually increasing lithium bromide concentrations (2-17 molal), while the cobalt bromide concentration was held approximately constant (2 molal). The results of this series of extractions are tabulated in Table 4. From the plot of these results (Figures 2 and 3) showing the moles of cobalt bromide per 1000 grams of 2-octanol phase vs. the total equivalents of bromide per 1000 grams of the aqueous phase, it is clear that the amount of extraction is strongly dependent upon the total aqueous phase bromide concentration. The 2-octanol phase, however, after back extraction with water to remove the extracted salt, appeared yellow which showed that the 2-octanol had been attacked. This probably explains why some of the points do not fall exactly on the same curve as the others. There is less deviation at lower concentrations as might be expected since there is less discoloration.

The Cobalt Bromide-Calcium Bromide-Promoted Extraction

The extractions considered here cover a range of concentrations of calcium bromide varying from 0 to 3.5 molal with the cobalt bromide aqueous solution concentration initially for each extraction kept at 2 molal. The equilibrium concentrations and the distribution ratios are listed in Table 5, and the plots of these data are shown in Figures 2 and 3. No explanation can be offered at this time for the sudden drop in the 2-octanol phase concentration or the distribution ratios for the third and fourth extractions below the curve for the lithium bromide or aluminum bromide-promoted extractions. If the promoting action is primarily a mass action effect, the points should fall

on a common line. Garwin and Hixson (10) noted that hydrochloric acid and calcium chloride were not equally efficient in promoting the 2-octanol extraction of cobalt chloride, however. There were no indications of a reaction with the 2-octanol phase.

The Cobalt Bromide-Aluminum Bromide-Promoted Extraction

These extraction experiments were to investigate the effect of the charge type of the promotive salt cation on the amount of cobalt bromide extracted. As shown by plot (Figures 2 and 3) of the data in Table 6, there is some scatter of the aluminum data. This slight scatter can be explained in the same way as the lithium promotion deviations; i.e., the 2-octanol was visibly attacked by one of the salts. Yet in both reactions there were no observable precipitates. A possible reaction might be

$$MBr_n + H_2O \longrightarrow MOHBr_{n-1} + HBr$$
$$ROH + HBr \longrightarrow RBr + H_2O$$
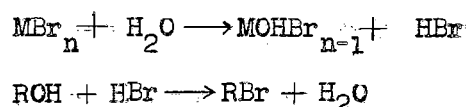
Taking into consideration the reaction with the 2-octanol, aluminum bromide promotes as well as any of the other bromides on the basis of number of bromide equivalents available rather than the number of moles of promoting salt.

It appears from this research that extraction promotion by lithium bromide, calcium bromide, or aluminum bromide is chiefly due to mass action in increasing the cobalt bromide aqueous phase activity by increasing the bromide concentration. It is unfortunate that almost nothing is known regarding the activity coefficients in electrolyte mixtures so that a fuller interpretation of the data presented in this thesis could be made.

Table 4

Data on CoBr$_2$-LiBr Extraction

CoBr$_2$				LiBr				Total Aqueous
m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	Equivalents Br$^-$
2.160	8.1	3.8	4.320	1.443	10.0	6.9	1.443	5.763
2.160	24.6	11.4	4.320	2.953	42.2	14.3	2.953	7.273
2.071	77.0	37.2	4.142	4.546	141.0	31.0	4.546	8.688
1.941	235.4	121.3	3.882	6.095	375.7	61.6	6.095	9.98
1.705	452.3	265.3	3.410	7.996	756.3	94.6	7.996	11.41
1.459	620.	425.	2.918	9.65	1119.	115.9	9.65	12.57
1.252	741.	592.	2.504	11.69	1547.	132.3	11.69	14.19
1.068	855.	801.	2.136	13.87	1975.	142.4	13.87	16.00
0.945	909.	962.	1.890	14.95	2008.	134.4	14.95	16.84

Table 5

Data on CoBr$_2$-CaBr$_2$ Extraction

CoBr$_2$				CaBr$_2$				Total Aqueous
m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	Equivalents Br$^-$
2.057	9.4	4.6	4.114	0.977	5.1	5.2	1.954	6.068
2.037	14.6	7.2	4.079	1.447	9.1	6.3	2.894	6.968
2.008	25.3	12.6	4.016	1.930	17.0	8.8	3.860	7.876
1.977	51.2	25.9	3.954	2.481	11.5	4.6	4.962	8.916
1.911	108.6	56.8	3.822	3.008	25.1	8.3	6.016	9.838
1.793	223.	124.	3.586	3.579	61.3	17.1	7.158	10.74

Table 6

Data on CoBr$_2$-AlBr$_3$ Extraction

CoBr$_2$				AlBr$_3$				Total Aqueous
m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	m(aq.)	m(oct.) x 10^3	D x 10^3	Br$^-$ Aq. Eq.	Equivalents Br$^-$
1.977	8.5	4.3	3.954	0.490	3.7	7.6	1.470	5.424
1.980	17.6	8.9	3.960	1.032	25.1	24.3	3.096	7.056
1.972	76.1	38.6	3.944	1.486	130.0	87.5	4.458	8.402
1.922	203.7	106.	3.844	1.945	347.	179.	5.835	9.679
1.656	432.	261.	3.312	2.461	560.	227.	7.383	10.70
1.362	681.	500.	2.724	3.092	756.	245.	9.276	12.00

SUMMARY AND CONCLUSIONS

The result of these experiments are that:

1. Unpromoted cobalt bromide extracts to a greater extent into 2-octanol than cobalt chloride in agreement with some of the theoretical aspects of the effect of large anions on solvent extraction.

2. The lithium bromide, calcium bromide and aluminum bromide promoted extraction appear to be largely the result of a mass action mechanism. At comparable concentrations the degree of extraction in the promoted systems is $CoCl_2 < CoBr_2 < Co(ClO_4)_2$.

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