THE MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN THE PRESENCE OF COBALT CHLORIDE AND NICKEL CHLORIDE

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INTRODUCTION

INTRODUCTION

In 1949, Garwin and Hixson[1] published equilibrium data on the system consisting of aqueous cobaltous and nickelous chloride solutions and capryl alcohol in the presence of hydrochloric acid or calcium chloride. They found that in simple aqueous solutions the separation factor was poor, and the distribution coefficient of the more easily extracted salt ($CoCl_2$) was low. However, in the presence of either high concentrations of hydrochloric acid or calcium chloride high values of both the separation factor and the distribution coefficient were found. Their data further showed an increased extraction of hydrochloric acid into octanol with increased salt concentration. In view of the drawbacks attending the existing chemical methods for accomplishing this separation, these results indicated that liquid-liquid extraction might be economically feasible for this metal pair. The classical Mond carbonyl, the neutral hypochlorite, the electrochemical, and other methods have been critically reviewed by Fink and Rohrman[2] and this paper may be referred to for further details.

Since the underlying principles of salt-promoted solvent extraction are not understood very well, this research was undertaken with the objective of obtaining data on the aqueous phase mean activity coefficient of hydrochloric acid in the presence of cobalt chloride or nickel chloride which then could be used in the interpretation of the extraction equilibrium involving these electrolytes. In addition to the above mentioned objective it was felt that a thorough study of the effect of these two related salts upon the activity

of hydrochloric acid over a wide concentration range, covering in part concentrated solutions, might contribute to a better understanding of concentrated solutions.

BACKGROUND TO THE PROBLEM

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General Survey.

Probably the most intensively studied system from the point of view of solvent extraction has been the ferric chloride-hydrochloric acid-ether system,[3] although the uranyl nitrate-metal nitrate-ether system[4] has received considerable attention. An extensive survey of the solvent extraction field has recently been made by Irving.[5] In many cases, the extraction of inorganic ions may be said to depend upon a "masking of ionic character." This "conferrence of organic character," according to Irving, may be brought about through the formation of chelate rings or by the addition of an appropriate ion of opposite charge. Since extraction coefficients in systems of the first type depend to such a large extent on the instability constants of the complex ions formed, the results obtainable from a study of such a system would probably be of a limited nature. The latter type offers intriguing possibilities because of the complexity of these systems and the probable wider applicability. In Figure 1 the percentages of various metal chlorides extracted by ether from hydrochloric acid are reproduced from the work of Irving;[5] the corresponding percentages of cobaltous chloride in capryl alcohol from the data of Garwin and Hixson[1] are included. In Figure 2, the data of Garwin and Hixson have been expanded to include the nickel data.

In their study of the five-component system cobaltous chloride-nickelous chloride-added electrolyte-water-capryl alcohol, Garwin and Hixson[1] observed two correlations: first, extraction of cobalt can be effected only from the

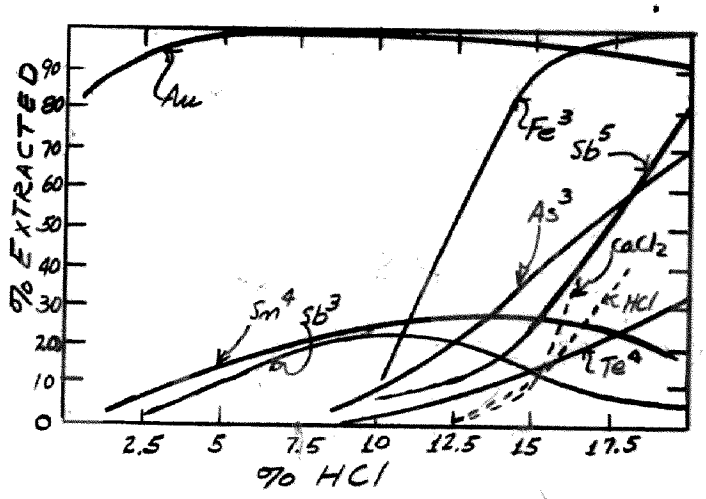


Fig. 1

dark blue aqueous solutions and best by solvents in which the anhydrous salt is soluble. Upon addition of a second electrolyte such as hydrochloric acid or calcium chloride, the extraction is greatly enhanced. Second, electrolytes having high activity coefficients in concentrated aqueous solution produce a marked color change from red to blue. They suggest that the first correlation would tend to support a dehydration hypothesis for the extraction mechanism, but would offer no explanation for the adverse action of such electrolytes as cadmium chloride or sodium sulfate on the extraction. The second correlation they state further might be interpreted as indicating an intensification of some property of cobalt, such as the activity coefficient in aqueous phase, thus favoring a greater transfer of cobalt into the organic phase. An examination of the literature showed that a considerable amount of work had been done relative to the nature of the color changes occurring in cobalt chloride solutions. The following discussion reviews this work.

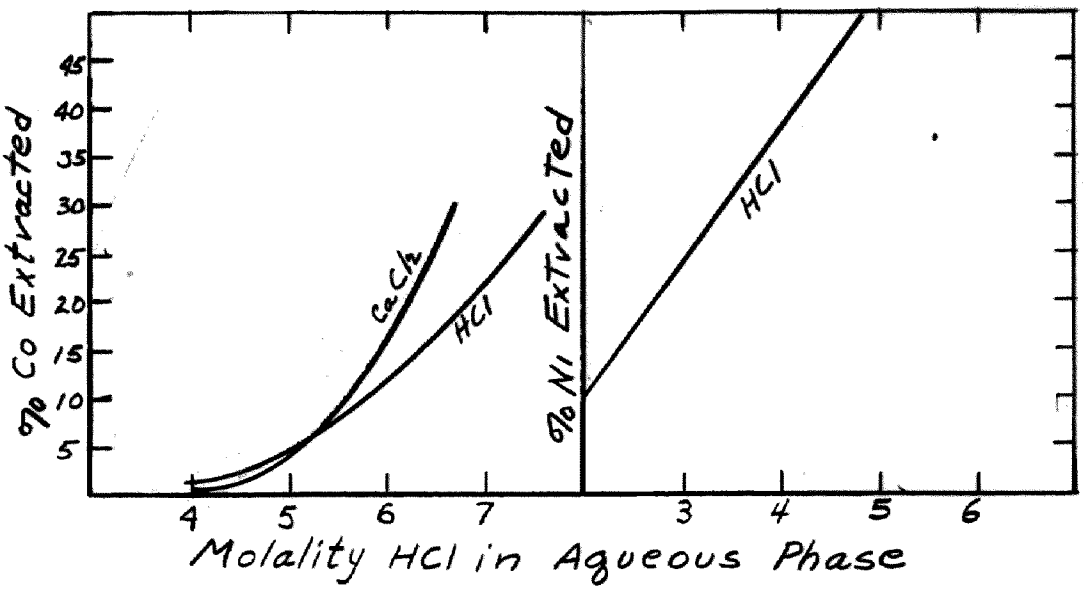


Fig. 2

Color Change Phenomena

In order to explain the color changes exhibited by cobaltous chloride solutions, four different hypotheses have been proposed: namely, the molecular compound, the ionic, the complex-ion, and the hydration.[6] H. C. Jones[7] made an early extensive and critical study of the subject. This work is valuable in presenting alternative points of view held at that time (1906), and although some of the hypotheses are no longer acceptable, the hydration theory and the complex ion theory are now regarded as offering the best explanations for this phenomenon. Mention will be made first of all of these theories as discussed by Jones but additional consideration will be given to those in support of which more recent data are available.

I. The Molecular Compound Theory

The molecular compound theory, proposed by Engel,[6,7] supposes that the blue color is due to the formation of double chloride salts in solution. He obtained, for example, a blue salt having the composition $CoCl_2 \cdot LiCl \cdot 3H_2O$

and reasoned that upon heating a solution of cobaltous chloride, the salt partially hydrolyzes, liberating hydrochloric acid which combines with unchanged cobaltous chloride to form the blue chlorohydrate analogous to $CoCl_2 \cdot LiCl \cdot 3H_2O$. Jones pointed out that this theory seemed untenable for a number of reasons. In the first place, several workers had already shown that even in concentrated solutions the double salts were broken down into simple salts[8] which in turn should throw a large number of ions into solution. Second, this theory was not in accord with the temperature effect. With a comparatively slight rise in temperature the increase in hydrolysis was not sufficient to liberate enough hydrochloric acid to account for the color change on the basis of formation of a double chloride. Third it was doubtful whether the blue color exhibited by cobalt in certain organic solvents, such as acetone, could be due to the presence of double salts.

II. The Ionic Theory

The original ionic theory proposed by Ostwald[6,7] states that, in general, the red color of cobalt solutions is due to the cobalt ion and the blue color to the anhydrous salt. Thus in agreement with theory, addition of chloride ions drives back the dissociation of the cobaltous chloride, but the theory does not account for the color change produced by warming a concentrated aqueous solution of cobaltous chloride. Jones and West[9] have shown that the slight change in dissociation from 25° to 80° would be incapable of accounting for the color changes. Further, the amount of hydrochloric acid liberated by by hydrolysis would be far too small to drive back the dissociation.

III. The Complex-ion Theory

Another early hypothesis, involving the formation of complex ions, is that of F. G. Donnan and H. Bassett.[6,7] This theory supposes the following reactions

to occur in solution:

$$CoCl_2 \text{ (blue)} \rightleftharpoons Co^{++} \text{ (red)} + 2Cl^-$$

$$CoCl_2 + Cl^- \rightleftharpoons CoCl_3^- \text{ or}$$

$$CoCl_2 + 2Cl^- \rightleftharpoons CoCl_4^=$$

Both the unionized salt and the complex ion are supposed to be blue in solution.

Jones[7] objected to this hypothesis since the presence of the same absorption bands in both aqueous solution and ethanol solution argues for the existence of the same type of ions in each solvent (which he considered unlikely).

IV. The Hydration Theory

According to Jones[7] it does not seem possible to escape the conclusion that hydrates exist in solution because of the nature of the absorption spectra. He reasons that if the color of the cobalt chloride solution is associated with the existence of some particular resonator whose mass can be increased by the addition of water, the effect will be to dampen the vibrations and thus cause the band to become narrower. Conversely, as the extent of hydration decreases, the regions of absorption would widen out and extend over a greater range of wave lengths. This would also correspond to a curve whose transmission minimum or absorption maximum would be correspondingly lower or higher. Exactly how the resonator is related electronically to the system, Jones believes, is not of fundamental importance to the existence or non-existence of hydrates. He thus cites several systems such as $CoCl_2 - H_2O$, $CoCl_2 - CaCl_2 - H_2O$, $CoCl_2 - AlCl_3 - H_2O$ etc., to illustrate the effect of a second salt on the absorption spectrum of cobalt chloride. These systems are interpreted by Jones in the sense that the relative amount of water at the disposal of each cobalt becomes less as the concentration of the second salt

or "dehydrating agent" increases. It is also to be expected that it would be more difficult to remove the last molecules of water from a given hydrated compound than the first. The fact that the increments of absorption decrease as the concentration increases means that the colored system resists the transfer of its associated water molecules to the "dehydrating agent" more and more, as the actual number of its associated water molecules becomes less and less.

The above theory also seems to explain the color changes that take place with changes in temperature. For example, when a red solution of cobalt is sufficiently warmed it becomes blue, which in terms of the theory, means that the system becomes less hydrated. When a deep blue solution of cobaltous chloride, made by using some one of the effective "dehydrating agents," is cooled sufficiently it becomes red.

V. Recent Work

Quite recently, Robinson and Brown[10] made an extensive study of the constitution of cobalt chloride in aqueous solutions. From the results of a series of isopiestic vapor pressure and spectrophotometric measurements, they point out that it is unnecessary to postulate the complex-anion hypothesis of Donnan and Bassett[6,7] in order to account for the color changes of cobalt chloride solutions. The rose color they believe is due to a heavily hydrated ion such as $\left[Co\cdot 6H_2O\right]^{++}$, which can undergo dehydration with a change in color. The reaction suggested for dehydration and association with chloride ions is:

$$\left[Co\cdot 6H_2O\right]^{++} + 2Cl^- \rightleftharpoons \left[CoCl_2\cdot 4H_2O\right] + 2H_2O.$$

A plot given in their paper of the molal vapor pressure lowering against the molality for calcium chloride, cobalt chloride, and zinc chloride shows that, even though the calcium chloride and cobalt chloride curves appear peculiar

in that they unexpectedly cross, a comparison of the relatively much lower zinc chloride curve with these indicates that the extent of any complex formation even in concentrated solutions of cobalt chloride must be small. The experimental fact that zinc chloride does not produce the color change phenomena is ascribed to the greater power of this salt to form its own complex ion, $ZnCl_4^{=}$.

By combining the results of spectral studies of cobalt chloride, in highly concentrated calcium chloride solutions, with some not too unreasonable approximations, Robinson and Brown found the following expression which holds quite constant but which is inconsistent with their suggested mechanism.

$$K = \frac{\alpha}{(1-\alpha)\,\gamma^3_{CoCl_2}\,[Cl]^2\,A^4_{H_2O}}$$

where α = fraction of Co in the blue form

$[Cl]$ = stoichiometric molality of chloride

γ = activity coefficient

A = activity

The water activity appears both to a different power and on the wrong side of the equation to represent the proposed dehydration reaction of these authors correctly. The expression does represent quite well the data obtained in this work, but if the water activity is ignored, the analgous mass expression fails to represent the experimental data successfully.

During a series of spectrophotometric studies of cobalt chloride in very highly concentrated lithium chloride solutions, it was noted in this laboratory[11] that the optical density of the characteristic pink entity at first increased and then decreased with increasing chloride concentration. Several workers[10,12] have observed such an increase in the optical density of $CoCl_2$

solutions, but as far as this author knows, the subsequent decrease in optical density has not been recognized and accounted for in the literature. One way in which the phenomena can be explained is by the assumption that a monochloro-complex is formed which superimposes its absorption on that of the hexahydrated ion, as the chloride concentration increases, in accord with the equation:

$$Co(H_2O)_6^{++} \rightleftharpoons Co(H_2O)_x\,Cl^{+} \rightleftharpoons Co(H_2O)_y\,Cl_2.$$

The possibility of the existence of this and other complex ions is indicative of the complexity of the aqueous solutions.

At this point it is convenient to point out that the complex ion and hydration theories really merge, depending on just what one means by a complex ion. For example in the chemical equation just given, a monochloroaquo complex ion is assumed to be responsible for the absorption. Thus hydration need not be excluded nor the complex ion theory be incorrect. Although the literature itself contains little specific agreement,[13] both theories would appear to be needed to explain the phenomena adequately. There are doubtless other complicating factors which bear consideration such as the ease of the various electronic transitions,[14] the effects of changes in viscosity, dielectric constant, etc., which make a complete explanation of the color changes difficult by any simple theory.

Activity Phenomena

It has been mentioned that chloride electrolytes having high activity coefficients in concentrated solution produce a marked color change from red to blue in $CoCl_2$ solutions, and correspondingly are good promoting agents for the extraction. A brief consideration of the present state of knowledge regarding the causes and theoretical interpretations of the behavior of activity coefficients of electrolytes which might have a bearing on the results

of this research would seem to be called for at this point.

I. Dilute Solutions

The mean ionic diameters, $\mathring{a}$, of various electrolytes in dilute solutions, as interpreted in the Debye-Hückel expression[15]

$$\log \quad = \frac{-AZ_+Z_-\sqrt{u}}{1+\beta \mathring{a}\sqrt{u}}^{*} \qquad (1)$$

have been calculated from measurements in several concentration ranges and the results are in general agreement. Thus for sodium chloride, values of $\mathring{a}$ from 3.6 to 4.4 Å have been reported.[16] This mean ionic diameter is in marked contrast to the sum of the crystallographic radii 2.76Å.[15] Therefore, it would appear that one or both of the ions are "hydrated" in the sense that an ion and some water act as a unit, increasing the effective diameters and the activity coefficients.

The Debye-Hückel theory has been frequently criticized for being inaccurate because of the approximation being made of regarding the ion as a point charge,[15] and the inclusion of only the first term in a mathematical series expansion.[17] Equation (1) embodying, however, only the latter approximation predicts an activity coefficient which is a decreasing function of the ionic strength, but this has been verified only for very dilute solutions. Actually an experimental minimum usually occurs, followed by a more or less rapid rise of the activity coefficient at high concentrations. Hückel[15] has explained this effect in terms of the change in dielectric constant of the

*See Appendix for the numbered mathematical equations used in this thesis.

solvent and was led to the expression

$$\log \frac{-AZ_+Z_-\sqrt{u}}{1+\beta \mathring{a}\sqrt{u}} + Bu \qquad (2)$$

Scatchard[18] has pointed out that Hückel assumed that the dielectric constant of the solution is given by $D = D_o - \delta 2c$ in which δ is a constant. With this assumption D is not truly a constant but a fraction of the concentration. However, equation (2) is of practical value for the extrapolation of standard potentials besides enabling calculation activity coefficients in very dilute solutions.[19] It usually fails to give even a reasonably accurate representation of observed activity coefficients at ionic strengths greater than unity. In overcoming this, arbitrary terms involving the concentration are used,[20] but such terms are of limited fundamental value to the theory of solutions.

II. Concentrated Solutions

In contrast to the theoretical treatment possible for very dilute solutions a comparable treatment of concentrated solutions is lacking. Stokes and Robinson[21] have recently employed a promising empirical approach based on Bjerrum's ideas[22] of ion solvation. They assume that for each mole of the salt, n moles of water will be bound in the hydration shells of the ions, thus effectively decreasing the free-water content of the solution. Thus, in order to treat concentrated solutions, especially in the case of 2:1 electrolytes, it has become increasingly clear that one must take into account the hydration of ions. As Robinson himself points out,[21] there seems to be no adequate alternative explanation for the very high activity coefficients of some solutions such as concentrated solutions of magnesium iodide, where the activity coefficient at 25°, in 5 m solution, is over 100.

In recognition of the importance of the hydration effect Scatchard[18] derived an equation,

$$\log \gamma_{\pm} = \frac{-A\sqrt{c}}{1+\beta\mathring{a}\sqrt{c}} + B\cdot c - \log (1-0.001 m w_1) - 0.5 \log a_w \qquad (3)$$

for dilute solutions of hydrochloric acid, in which the activity of water (a_w) was determined from that of acid by graphic integration. In this equation the effect of the ions upon the dielectric constant was taken into consideration (Bc). Stokes and Robinson,[21] however, disregarded the dielectric effect and from purely ion-solvent interaction derived an equation,

$$\log \gamma_{\pm} = -AZ_1Z_2 \sqrt{u} \; / \; (1 + \beta\mathring{a}\sqrt{u}) - n/\nu \; \log a_w - \log \left[1 - 0.018(n-\nu)m\right] \qquad (4)$$

which expresses the activity coefficients with remarkable accuracy for 36 electrolytes up to concentrations, in some cases, as high as 5 m using values of n ranging from 0.6 to 20. The value of n is not the conventional number of water molecules in the first layer around an ion, but is, they say, rather "a number introduced to allow for the average effect of all ion-solvent interactions," which may very well contain contributions from solvent molecules outside the first layer.

In a paper by Robinson and Levien[23] the activity coefficients of varying valence-type electrolytes are contrasted. In general, low values are characteristic of electrolytes wherein the anion is most highly charged, but more important is the fact that high values are characteristic for those electrolytes in which the high charge resides on the cation. This implies that hydration may be largely a cationic phenomenon, in general agreement with the hypothesis of Bernal and Fowler.[24]

The physical model thus presented while simple in nature is difficult to treat theoretically. Although there are many criticisms which can be made, the

apparent success of equation (4) is considered, according to Stokes and Robinson,[21] sufficient to "justify the decidedly ad hoc argurments" used in its development.

It is interesting to note that, according to Harned and Owen,[25] if the B values from equation (2) are plotted against $\sum \frac{1}{r_i}$, where r_i refers to the ionic radii, separate curves are obtained for the chlorides, bromides, and iodides of the alkali metals. This indicates that in concentrated solutions, activity coefficients are still some function of the ionic radii as they are in dilute solutions.

III. Very Concentrated Solutions

At very high concentrations, about 11 m for 1:1 and 7 m for 2:1 electrolytes, Stokes and Robinson[21] have found that the vapor pressure data conform to an equation of the type of the Brunauer-Emmett-Teller[26] adsorption isotherm as modified by Anderson.[27] They showed, for example, that plots of the experimental molalities as a function of the corresponding water activity versus the water activities give satisfactory straight lines for certain electrolytes such as calcium nitrate, calcium chloride, lithium chloride, hydrochloric acid, and sodium hydroxide. The very concentrated solution is then pictured as one in which the hydration number n is actually decreasing and the ions are tending to a "pseudo-crystalline" structure with some of the water molecules within the crystal lattice and some present as "free" solvent. It appears likely that such treatments of concentrated solutions and very concentrated solution will be found to be only special cases of a more general theory which will cover the whole concentration range.

IV. Mixed Electrolyte Solutions

In a very ambitious treatment of mixed electrolytes up to 5 m, Robinson

and Stokes,[28] using data obtained from the literature, have determined values for the hydration number n, as defined previously. These values are not all that could be wished. One difficulty found with the use of their proposed equation for calculating n is the lack of agreement of the differences between the n values for pairs of salts, each pair having two ions identical with those in the other salt-pairs being compared. For example, $n_{LiBr} - n_{LiCl} = 0.6$, $n_{NaBr} - n_{NaCl} = 0.65$, and $n_{KBr} - n_{KCl} = 0.15$. No adequate explanation is offered for this lack of agreement, although it might be pointed out that several simplifying approximations and omissions were made in developing their relation. For example, no allowance was made for any change in δ; in fact, it was completely ignored. Furthermore, values for the individual solute hydration numbers n_1 and n_2 were taken from the values found for the individual simple solutions and the dielectric change with concentration was disregarded.

Thermodynamic Survey

I. Simple Binary Solutions

In order to further clarify the two correlations pointed out by Garwin and Hixson (p. 2), it becomes convenient at this point to show curves for the activity coefficients of certain simple binary salts, taken from Harned and Owen.[25]

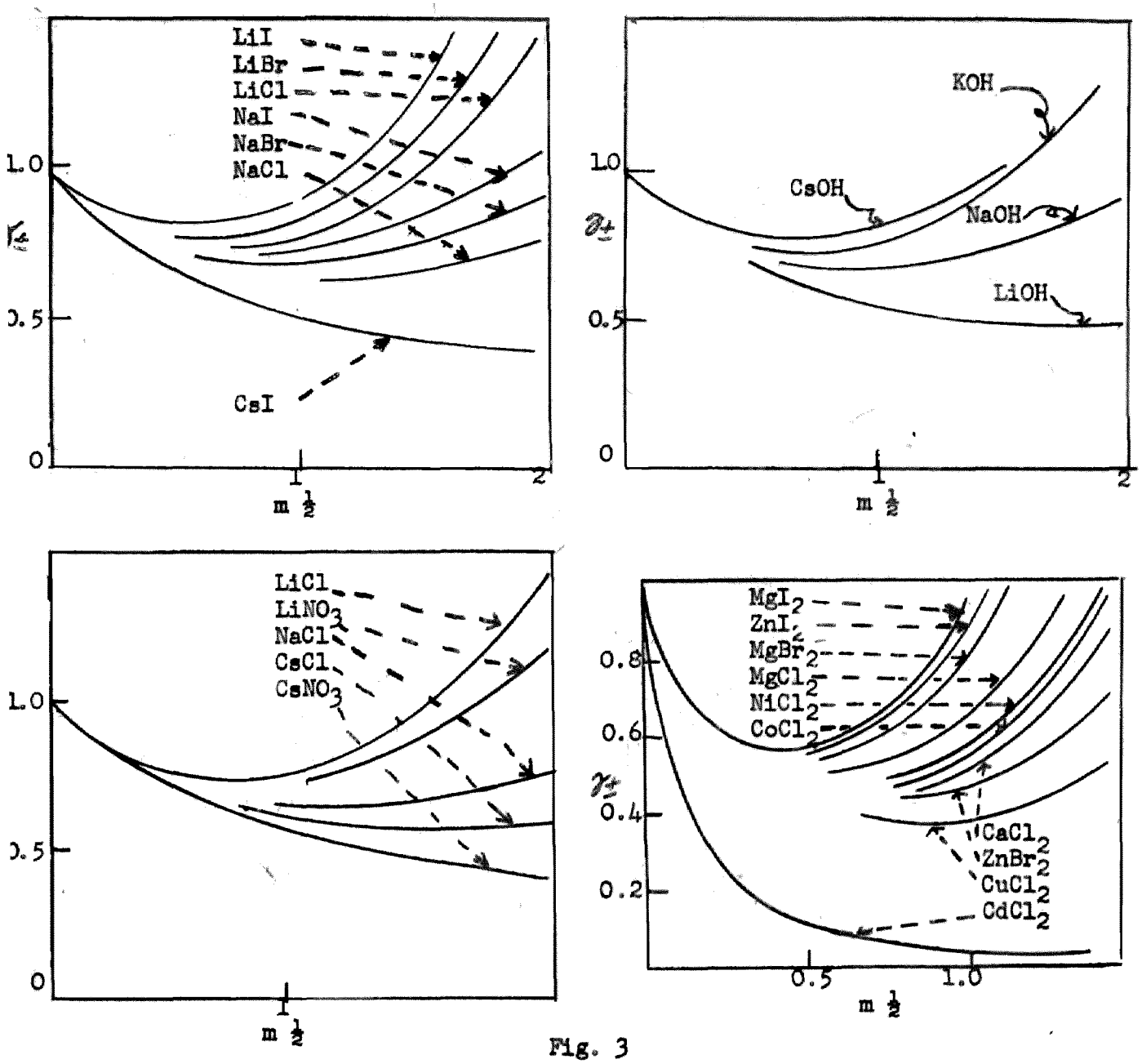


Fig. 3

Perhaps the most striking feature of the preceding plot is the wide range of activity coefficients and concentrations. Harned and Owen have made an extensive survey of experimental data of this type and certain specific behaviors should be pointed out. For the alkali halides the order of decreasing values of $\gamma_{\pm}$ for a given anion is Li > Na > K > Rb > Cs (with HCl > LiCl). These values, of course, are consistent with the radius of the unhydrated cation as determined by crystallographic measurements. For compounds of the proton-accepting type, i.e. the hydroxides, acetates, fluorides, etc., the order is reversed. Robinson and Harned[19] have explained both phenomena in terms of solvent interaction with the ions. Because of the more intense fields of smaller ions, the interaction with solvent dipoles will be stronger. In the absence of a likely proton acceptor, no further effect should be noted. Therefore, for the halides the activity coefficients should decrease in the order of decreasing hydration of the cation which is Li > Na > K > Rb > Cs. For the proton acceptors, a "localized hydrolysis" theory is proposed. This can be represented by

$$M^+ + H_2O + A^- \rightleftharpoons M^+ \ldots\ldots OH^- \ldots\ldots H^+ \ldots\ldots A^- \qquad (5)$$

which leads to a reduction of the number of "free" ions in solution by dipole interaction, thereby reducing the total ionic strength and decreasing the activity coefficient calculated in the usual way on the assumption of complete dissociation.

It is interesting to note that according to the ideas outlined above, cesium acetate and hydroxide should be normal, since the cesium ion is unlikely to be hydrated to an appreciable extent. The high activity coefficients of cesium hydroxide may then correspond to a high $\mathring{a}$ value, according to Robinson and Stokes,[28] perhaps meaning that the hydroxyl ion is hydrated. Further, the acetate ion may also be hydrated.[28]

The specific behavior of the alkaline earth electrolytes follows the same pattern.[29] Therefore, generally speaking, hydration increases the activity coefficient in two ways: (a) by increasing the "effective" mean ionic diameter or closest approach of the ions appearing in the Debye-Hückel theory and (b) by removing water as independent solvent which, in effect, increases the "apparent" or "effective" concentration of solute. Stokes[29] has made a general survey of the field and to discuss the phenomena further for other type salts seems unnecessary, not because of the completeness of the existing data, but because data for more salts are required before further progress can be made.

A rather curious phenomenon for both the alkali and alkaline earth electrolytes is that for a given cation, the order of decreasing values of the activity coefficients is with size of the anion reversed, i.e., the order of decreasing $\gamma_{\pm}$ for a given cation is that of decreasing anion radius, $ClO_4^- \lesssim I^- > Br^- > Cl^- > NO_3^-$. The explanation for this follows from the "cationic effect" explained above. For example, in an aqueous solution of lithium iodide, the negative iodide anion would not be expected to exert its field on lithium as much as the smaller bromide ion and water could still "get into" the so-called hydration sphere of the lithium. This again emphasizes the fact that hydration may largely be a cationic phenomenon. These common cation curves, then, would not show such a spread as the corresponding common anion curves. This is evident from a comparison of LiI and LiBr with LiI and NaI in Figure 3.

II. Mixtures of Electrolytes

In mixtures of electrolytes, the general behavior of the activity coefficients obtained from the existing data may be summarized by the two graphs of Fig. 4, reproduced from Harned and Owen,[25] and by the following two statements:

(a) "At a given ionic strength and acid concentration, the activity coefficient of a strong acid is greater in the solution of a salt, of a given valence type, which in pure solvent possesses the greater activity coefficient." Thus from Fig. 4

$$\gamma_{HCl(LiCl)} > \gamma_{HCl(NaCl)} > \gamma_{HCl(KCl)} > \gamma_{HCl(CsCl)}$$

and, from Fig. 3

$$\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl} > \gamma_{CsCl}.$$

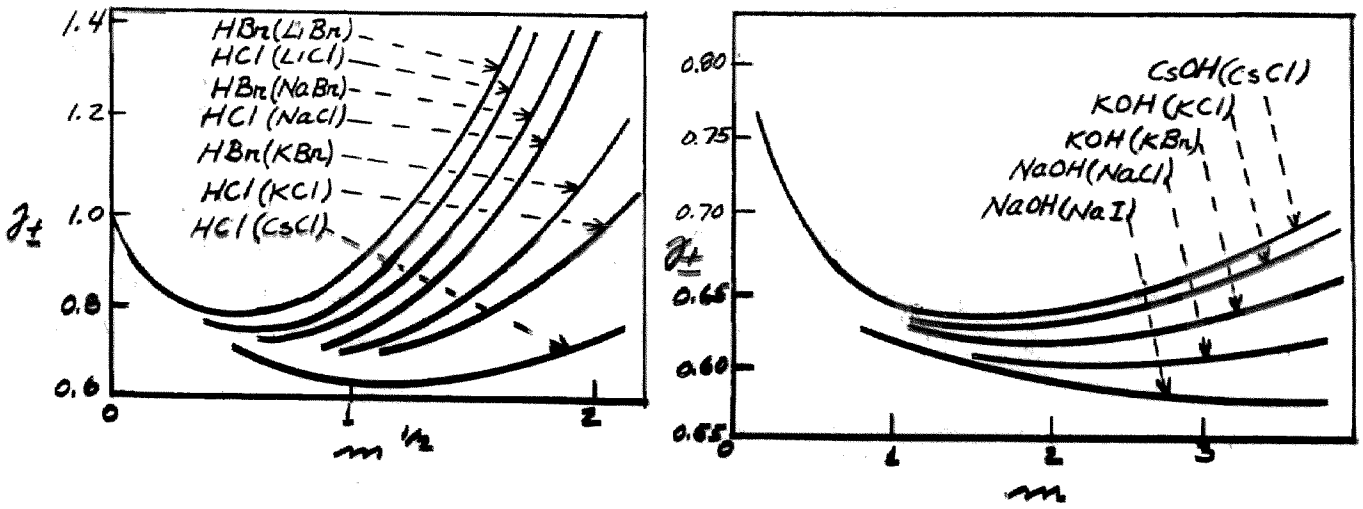


Fig. 4

(b) "Strong hydroxides in the halide solutions exhibit the opposite behavior." Thus from Fig. 4

$$\gamma_{MOH(CsCl)} > \gamma_{MOH(KCl)} > \gamma_{MOH(KBr)} > \gamma_{MOH(NaCl)}$$

Discussion of the behavior of hydrochloric acid in mixtures of higher

valence type salts will be postponed until later because a comparison will then be possible with results reported in this thesis (see p. 67).

III. Thermodynamic Difficulties

The problems involved in a thermodynamic study of the multicomponent system cobaltous chloride-nickelous chloride-hydrochloric acid-water-capryl alcohol are at present insurmountable not only because of the experimental difficulties involved, but also because there is no adequate extrathermodynamic theory which covers the entire system, especially at the concentrations where the extraction of the cobalt becomes appreciable. Even a three component system presents formidable difficulties in interpretation. As Lewis and Randall point out,[30] however, if one considers a solvent of two (or more) constituents in fixed proportion, a dilute solution of another substance in this mixed solvent will have many of the characteristics of a dilute solution in a pure solvent. An equation for a ternary mixture derived from the general Gibbs-Duhem equation is

$$N_1 \frac{(\partial \ln f_1)}{(\partial N_3)_{T,P,N_1,N_2}} + N_2 \frac{(\partial \ln f_2)}{(\partial N_3)_{T,P,N_1,N_2}} + N_3 \frac{(\partial \ln f_3)}{(\partial N_3)_{T,P,N_1,N_2}} = 0 \qquad (6)$$

It can be shown that provided component 3 is in infinitely dilute solution,

$$N_1 d \ln f_1 + N_2 d \ln f_2 = -dN_3 \qquad (7)$$

Thus according to Lewis and Randall the effect of adding solute (component 3) upon the fugacity (or activity) of each constituent of the solvent cannot be predicted from thermodynamics alone. According to these authors also this can be illustrated by the effect of adding benzene to a mixture containing equal parts of alcohol and water in contact with ice in a well-insulated vessel and observing the rise of the freezing point.

Darken[31] has recently developed a general, theoretical method of treating a single-phase, multi-component solution. With no extra-thermodynamic assumption other than Henry's law as a limiting law at infinite dilution, he has shown that it is possible to calculate the several extensive thermodynamic functions. The fundamental equation, written to correspond to equation (7), is for one of these functions, G,

$$G = (1-N_3)\left[\left[G_{N_3=0} + \int_0^{N_3} \frac{\bar{G}_3\, dN_3}{(1-N_3)^2}\right]\right]_{N_1/N_2} \qquad (8)$$

By choosing the standard state for each component as the pure component, this equation is made more useful. Briefly, however, its limitations are (a) the fact that the quantity under the integral must not approach infinity if accurate values are to be found, (b) it can be applied only where all components are completely miscible and the corresponding binary systems of component 3 with the other two components are miscible, (c) the particular extensive property determined must be determined for all compositions, i.e. $0 \leqslant N_3 \leqslant 1$, up to pure component 3, (this amounts to saying that the above method is similar to a triangular, three-component phase diagram in that the integrations can be made only if there are no miscibility gaps along the line connecting a particular extensive property and the pure component 3), and (d) only the extensive value of the property rather than the partial molal values can be obtained in this way. The limitations on this method are so severe, especially applied to aqueous solutions of electrolytes, that it is of restricted usefulness.

METHOD OF ATTACK

METHOD OF ATTACK

I. Preliminary Remarks

Although the results of measurements made on a ternary system such as $HCl-H_2O-CoCl_2$ are not equivalent to those made on a quaternary system of the type involved in the extraction equilibrium, e.g., $HCl-H_2O$-Octanol-2-$CoCl_2$, the simplification in experimentation and interpretation of results appeared to justify the study of the simpler system. A knowledge of the effect of salts upon the activity coefficient of hydrochloric acid in the three-component case might be expected to be applicable to the four-component case since the solubility of octanol in water is relatively small anyhow.

II. Reasons Governing Choice of Method

For a binary system there are several experimental methods for determining activities or activity coefficients. Thus activities are obtained from freezing point depressions, boiling point elevations, vapor pressures, E.M.F.

measurements, etc.[25] Any procedure which will quantitatively measure the "escaping tendency" may be used. The actual choice is a matter of suitability to a particular system. Robinson and Sinclair have discussed the general applicability of the more common methods[32] and references leading to more detailed discussions of the several methods may be found in the standard reference works on chemical solution thermodynamics.[25,30] Briefly, it may be said that both the boiling point elevation and freezing point depression methods suffer in that they usually require a difficult to evaluate temperature-correction term. Even so, as La Mer has pointed out,[33] the freezing point method is capable of very high accuracy in dilute solutions. The vapor pressure measurements of Lovelace, et al[34] are very accurate, but the experimental difficulties are many. Nevertheless, especially for concentrated solutions, vapor pressure methods have been widely used.[35] An extensive summary of activity coefficients from freezing points, boiling points, and vapor pressures may be found in Harned and Owen.[25]

There is general agreement that the E.M.F. method is capable of a high degree of accuracy in both dilute and concentrated solutions.[25,32] By using cells without transference in conjunction with a pair of electrodes reversible to the particular ions under investigation, various workers have studied a wide variety of systems.[17,25] The main criticism that might be made for the use of a similar E.M.F. method on the system HCl(1)-H_2O(2)-$CoCl_2$(3) is the fact that the silver-silver chloride (reversible to the chloride ion) electrode may actually dissolve if the chloride ion concentration is too high.[25] As Harned points out, this will manifest itself in that silver will deposit on the hydrogen electrode, thereby changing the observed E.M.F. Nevertheless, even if the chloride ion concentration is not appreciable, since the silver halide is slightly soluble in solutions containing the chloride ion, there

will be a slight concentration gradient which will give rise to a liquid junction potential. The methods used by others and by this author in minimizing this difficulty will be given more consideration in a subsequent section.

III Proposed Work

Although several alternative studies were given consideration and were, in the author's opinion, possibly more directly concerned with the extraction process, the system $HCl-H_2O-CoCl_2$ (or $NiCl_2$) merited study as pointed out in part I of this section, not only because it could throw some light on the extraction process, but because the literature contains, as far as this author knows, no really comparable comprehensive study. To be sure, certain systems such as $HCl-H_2O-LiCl$, $HCl-H_2O-CaCl_2$, $HCl-H_2O-AlCl_3$, etc.,[25] have been studied, but in each case the measurements were made at a single concentration of HCl in the dilute range.

The following work was therefore undertaken: a systematic study of the system $HCl-H_2O-CoCl_2$ (or $NiCl_2$) at several fixed concentrations of $HCl-H_2O$ with varying $CoCl_2$ or $NiCl_2$ (component 3). The concentrations studied cover the dilute, the concentrated, and the very concentrated regions.

A. Electromotive Force Measurements

The fundamental equations of the cells,

$$H_2 \mid HCl(m) \mid AgCl\text{-}Ag$$

$$H_2 \mid HCl(m_1)CoCl_2(m_2) \mid AgCl\text{-}Ag$$

are

$$E_{corr.} + 2k \log m = E^\circ - 2k \log \gamma_\pm \qquad (9)$$

$$E_{corr.} + k \log m_1(2m_2 + m_1) = E^\circ - 2k \log \gamma_\pm \qquad (10)$$

respectively. Since the standard potential E° has been determined by a number

of workers with considerable agreement,[25] $\gamma_{\pm}$ HCl can be readily calculated from the values of $E_{corr.}$ which are the observed E.M.F.'s corrected for pressure.

B. Spectrophotometric Measurements

In order to correlate the color change phenomena with the activity coefficient data, it was decided to make a series of paralleling spectrophotometric measurements. Further comments concerning these studies will be made in the Discussion of Results section.

EXPERIMENTAL

EXPERIMENTAL

A. Bridge Circuit

The first two runs (m_1 = 0.047 and m_1 = 0.0932) were made with a "Queens" type potentiometer, model E-3044-C manufactured by the Gray Instrument Company. This instrument has sufficient range (0 to 2.2 volts) and accuracy (slide wire accurate to ±0.1%) to permit reasonably accurate measurements to be made. The working standard cell (1.0179 volts at 25°) was prepared by Dr. H. M. Trimble of this institution.

All subsequent runs were made with a high precision Rubicon type B potentiometer (No. 54273). The range of this instrument is from 0 to 1.6 volts with an accuracy of ±0.01%. The working standard cell (1.0180 volts at 24°) used with this potentiometer was a low temperature coefficient Eppley type (No. 452495). Balancing of the circuit was noted through a wall-type Leeds and Northrup (No. 2239A) galvanometer (sensitivity 0.0079 μa/mm.). All connections were made with low resistance bell wire.

B. Temperature Control

Although Jones and Josephs recommend that oil be used in the bath,[36] a

kerosene and a water bath were both used for practical reasons. The kerosene bath was used for the "dilute" region readings (first two runs), and the water bath for the subsequent runs. The temperature bath was regulated to within 0.02°C. by a mercury thermoregulator connected through a Cenco-Gibson Electronic Relay (No. 99782) to an electric heater. An Eimer and Amend thermometer (No. 87266), which had been calibrated against a National Bureau of Standards thermometer (No. 90794), was used to measure the temperature.

C. Cells Employed

A total of six cells, all fundamentally the same, were used. The cells are shown in Figure 5.

D. Preparation of Solutions

I. Solvent ($HCl-H_2O$)

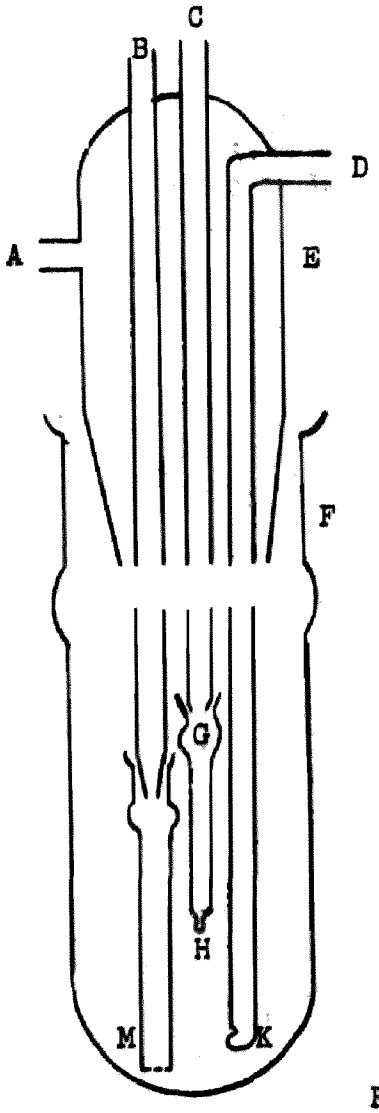
Constant boiling hydrochloric acid was prepared by the method of Bonner and Wallace.[37] In order to prevent superheating the reaction flask used contained several pyrex beads and a piece of platinum foil. The molalities of the hydrochloric acid were then determined from a table, given by the preceding authors, relating vapor pressures to percentages of hydrochloric acid:

Table A

Pressure (mm. Hg)	% HCl (Vacuum wt.)	gram solution/mole HCl
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.555

The observed barometric pressure was corrected to 0°, sea level, and 45° latitude by use of tables found in "Barometers and the Measurement of Atmospheric Pressure," published by the United States Department of Commerce.[38]

CELLS



A Hydrogen Outlet
B AgCl-Ag Electrode Inlet
C Hydrogen Electrode Outlet
D Hydrogen Gas Inlet
E 34/45 Pyrex Joint
F 34/45 Pyrex Joint
G 10/30 Pyrex Joint
H Hydrogen Electrode
K Hydrogen Bubbler
M Fritted Glass (Medium)

Fig. 5

The most concentrated hydrochloric acid used was prepared by dilution om Du Pont C.P. concentrated hydrochloric acid. This acid was then analyzed ve times by the silver chloride gravimetric method with the following results: .72, 10.81, 10.73, 10.69, 10.64 which average out to 10.7200$\pm$.005 According to erloff and Teare,[20] this high grade acid is sufficiently pure, as attested their work.

II. Solutes ($CoCl_2$ and $NiCl_2$)

The anhydrous salts were prepared from the hexahydrates. The latter were

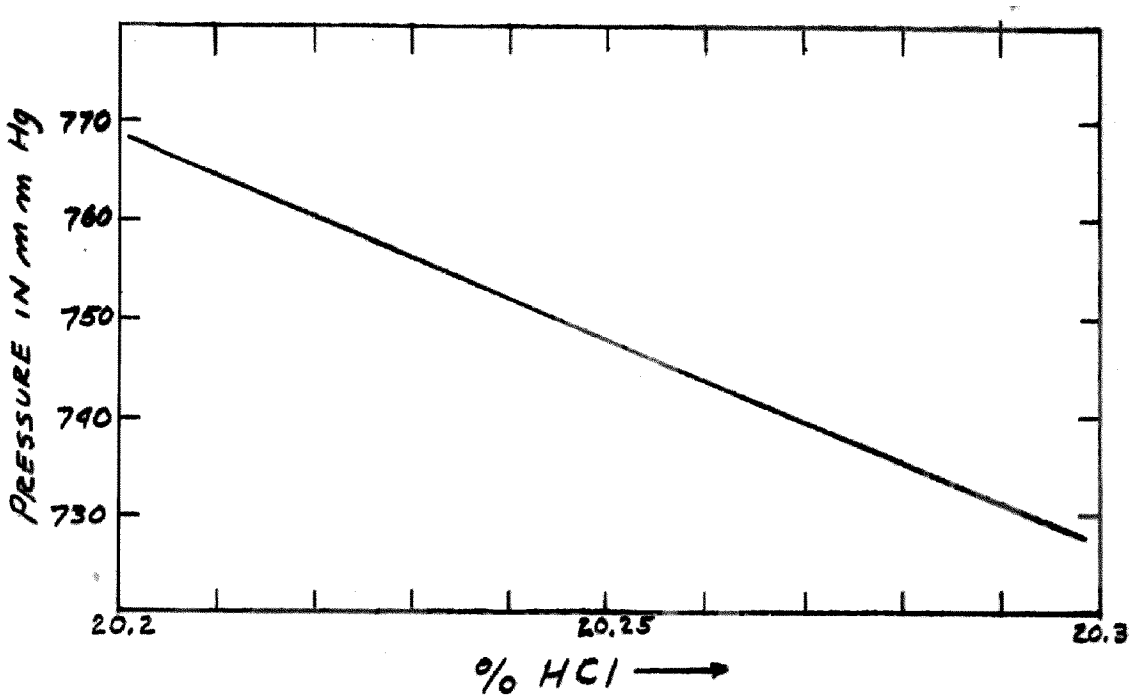


Fig. 6

Eimer and Amend C.P. grade containing the following significant impurities: 0.000% nickel in the cobalt salt; 0.18% cobalt in the nickel salt. Each of the hexahydrates was first partially dehydrated overnight in an oven at 100°; the residual material was then pulverized, and the fine powder was finally placed in the oven at 120° to 130° for complete dehydration. The anhydrous salts were kept at this temperature until used because of their great tendency to pick up moisture. The anhydrous salts were analyzed electrolytically according to the method given by Treadwell and Hall[39] using a Slomin Electro-Analyzer (No. 3325). The theoretical percentages of cobalt in cobaltous chloride and of nickel in nickelous chloride are 45.38 and 45.28% respectively. The analysis showed an average deviation from these

values of -.04 and -.12% respectively, which means that the analyses were well within experimental error, and the formation of any basic salts was negligible. Furthermore, the anhydrous salts dissolved completely in water.

III. Solutions

The solvent ($HCl-H_2O$) was weighed out into large glass-stoppered pyrex bottles by use of a Voland balance capable of an accuracy of ±0.005 g. The dry solutes were weighed by difference from a weighing bottle by use of a Eimer and Amend (No. 45792) chainomatic balance capable of an accuracy of ±0.0001 g. All glassware was washed with sulfuric acid-chromate "cleaning solution", rinsed with distilled water, and steamed for at least 15 minutes.

E. Preparation and Use of Electrodes

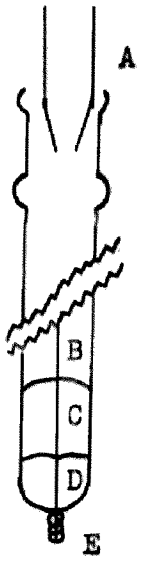
A thorough search of the literature revealed that there are many different techniques used in preparing both the hydrogen and the silver-silver chloride electrodes. Therefore, an experimental study of the two was made. It would be superfluous to give all the literature references on the subject, but mention of some previous workers findings will be given.

I. The Hydrogen Electrode

A critical experimental investigation of hydrogen electrodes has been made by Popoff, et al,[40] who claim that a thin coated electrode is preferable because equilibrium is attained much faster (order of 10 minutes). No advantage was found in reversing the current during the deposition of platinum black. Perley,[41] who has also made a critical study of hydrogen electrodes, comes to the conclusion that the use of the hydrogen electrode could be made more general if the confused state of affairs regarding its preparation were clarified. He recommends, as the preceding authors do, that the electrodes, after platinizing, should be washed thoroughly, then

placed in a weak sulfuric acid solution and electrolyzed with reversing polarity. This is supposed to remove any occluded gases. Perley further recommends that the hydrogen gas should be bubbled into the particular solution for about three minutes prior to the insertion of the hydrogen electrode. He claims that equilibrium is attained much faster this way.

The hydrogen electrodes used in this research were prepared in the usual manner by depositing a thin film of platinum black from a strongly acidified solution of platinum chloride on platinum wire (22 gauge) using a current of about 12 m.a. for twenty seconds. The details of the construction of the electrode are given in the following figure:



A 10/30 Pyrex Joint
B Platinum Wire, 26 gauge
C Mercury
D Pyrex Glass Bead
E Platinum spiral, 22 gauge, gently heated in oxygen flame until completely fused

Fig. 7

After platinizing, the electrodes were treated in the following manner: (a) they were washed with distilled water, (b) placed in a dilute sulfuric acid solution and electrolyzed with reversing polarity for about five minutes making sure that the hydrogen electrode was the cathode during the final electrolysis, and (c) after being washed again with distilled water, placed in a beaker through which water was kept continually running. It was later found

that step (b) of the preceeding treatment was unnecessary. Prior to use, the electrodes were compared against each other in the particular solvent to be used, and only those electrodes which showed a voltage difference less than ±0.0003 volts were used. The electrodes, treated as has been described, were used within four days. Before an actual run was begun, the particular solution to be used was placed in a cell and hydrogen gas passed through for twenty minutes to twelve hours, depending upon the concentration being studied. It was found to be absolutely necessary for the solution to be saturated with hydrogen gas before a reproducible reading could be obtained. More reproducible results were obtained by having the electrodes just touching the surface of the solution. Cells having errating readings or those showing a drift of more than three-tenths of a millivolt were discarded, and a new solution was made up and measured.

Matheson electrolytic hydrogen gas (99.9% pure) was passed through Tygon tubing into a bubbling tower containing solvent of the same concentration as that to be used in a particular run, with a gram or two of lead oxide to take out any sulfur.[42] Once the solution under investigation had become saturated, the rate of bubbling had no effect on the observed E.M.F.

II. The Silver-Silver Chloride Electrode (AgCl-Ag)

The preparation and use of the AgCl-Ag electrode was found more satisfactory than the hydrogen electrode. Perhaps the most comprehensive study of this particular type of electrode has been made by S. Jaques.[43] The literature does contain one particular point of agreement: AgCl-Ag electrodes made from platinum foil show erratic behavior; it is generally agreed that spirals should be used.[44] In this research both types were made, and in confirmation of the results reported by others the foil type of electrode

behaved in a rather erratic manner with time. This behavior may be due to the differential "strain" forces operating at the surface of the foil. The AgCl-Ag electrodes used in this research were prepared in the following manner: (a) The silver plating solution was prepared by dissolving about 10 grams of potassium silver cyanide, prepared by the method of Brown,[45] in a liter of distilled water, and free cyanide was reduced to a minimum by adding dilute silver nitrate until a faint cloud of silver cyanide became evident. After this had settled, the clear solution was decanted. It was found desirable to precipitate a little silver cyanide from the solution each time prior to use. (b) The electrodes were then silver plated by electrolysis as cathodes for two to six hours at a total current of 2 to 0.3 milliamperes, using a medium porosity glass disk to isolate the platinum anode from the main body of the solution, carefully washed with distilled water and then placed overnight in a beaker of running water. (c) Chlorodizing was carried out by electrolysis in hydrochloric acid of the same molality to be used in a particular run with the electrode being prepared serving as anode. After washing for three hours in running water the electrodes were placed in a beaker of distilled water, precautions being taken that direct illumination did not enter the beaker.

The electrodes were tested against each other in the solvent to be used. Any pair showing a difference of more than ±0.05 millivolts was discarded and new electrodes made. The electrodes prepared and tested as has been described were found to be very stable. New electrodes were prepared for each solvent used.

In order to overcome the difficulty with the solubility of the AgCl-Ag electrodes in solutions containing chloride ions, a medium glass frit was used (see M, Figure 5). The solution was aspirated up into B (Figure 5) so that the level inside B was higher than the level of the solution inside

the cell proper. The glass frits were tested with a solution of potassium permanganate inside B and diffusion was observed to be negligible if the levels were adjusted as has been described. It was experimentally found that the phenomena described by Harned and Owen[25] (reduction of silver at the hydrogen electrode, see p. 22) took place when the chloride molality was of the order of 4 m. which is in agreement with Jaques.[43] The liquid junction potential, caused by the introduction of the glass disk, was probably very small. (Jaques[43] has estimated the liquid junction in a similar experimental arrangement to be of the order of 0.1 millivolt.) Under any circumstances, the AgCl-Ag electrodes were not allowed to stay in any particular solution for over one minute. It should be added that without a glass frit, equilibrium was reached much faster.

AgCl-Ag Electrode

A Soft glass tubing, 3 m.m.
B Mercury
C Platinum wire, 26 gauge
D Platinum wire, 22 gauge

Fig. 8

F. Spectrophotometric Measurements

Spectrophotometric measurements were made with a Beckman model DU quartz

spectrophotometer (serial No. 22525) using one cm. Beckman silica absorption cells. Density values (reproducible to 0.002 density unit) were computed from percentage transmission readings. The cells were cleaned by using concentrated nitric acid and rinsing with distilled water and acetone.

G. Vapor Pressure Correction

The fundamental equation (9) can be put into the form

$$E^\circ - \frac{RT}{F} \ln A_H A_{Cl} = \left[E(p) - \frac{RT}{2F} \ln p_{H_2} \right] = E \text{ corr.} \qquad (11)$$

For dilute solutions of hydrochloric acid the correction factor takes the form

$$\frac{RT}{2F} \ln \frac{760}{P_B - p_{H_2O}} \qquad (12)$$

and for concentrated solutions

$$\frac{RT}{2F} \ln \frac{760}{P_B - p_{(H_2O+HCl)}} \qquad (13)$$

From the tables of the partial pressures of HCl and H_2O over aqueous solutions of hydrochloric acid compiled by Zeisberg[46] from all reliable sources, it is apparent that the vapor pressure of HCl becomes of consequence for the computation of the correction factor (Equations 12, 13) only at molalities greater than 4 m. The values used for the dilute solutions are given in Harned and Owen[25] and linear interpolation is satisfactory. A change of 0.5 mm. in p_{H_2O} affects the values by about 0.01 millivolt at ordinary temperatures. For the "concentrated" solutions ($>$ 4 m) the following table was worked out using the data compiled by Zeisberg.[46]

Table B

m_1 = 4.8428 (15.2% HCl), t = 30°, $p_{(H_2O+HCl)}$ = 24.0 mm.

P_B (corrected barometric pressure)mm.	Correction factor (volts x 10^5)
760	42
755	51
750	60
745	69
740	78
735	87
730	96

m_1 = 6.975 (20.3% HCl), t = 30°, $p_{(H_2O+HCl)}$ = 20.0 mm.

760	35
755	44
750	53
745	62
740	71
735	80
730	89

m_1 = 10.7 (28.0% HCl), t = 30°, $p_{(H_2O+HCl)}$ = 22.0 mm.

760	38
755	47
750	56
745	65
740	74
735	83
730	93

H. A Typical Experiment

Constant boiling hydrochloric was collected at a corrected pressure of 741.5 m.m. By interpolation from Figure 6, 179.7885 g. solution contained 36.465g. HCl. One gram of solution, then, contained 0.20282g. HCl. By use of the Voland balance, 2839.58g. HCl was weighed into a clean, dry 9 liter pyrex bottle. To this 997.60g. of distilled H_2O were added. For this stock solution, then, m_1 = 4.8428 or 1 gram solution contained 0.15009g. HCl.

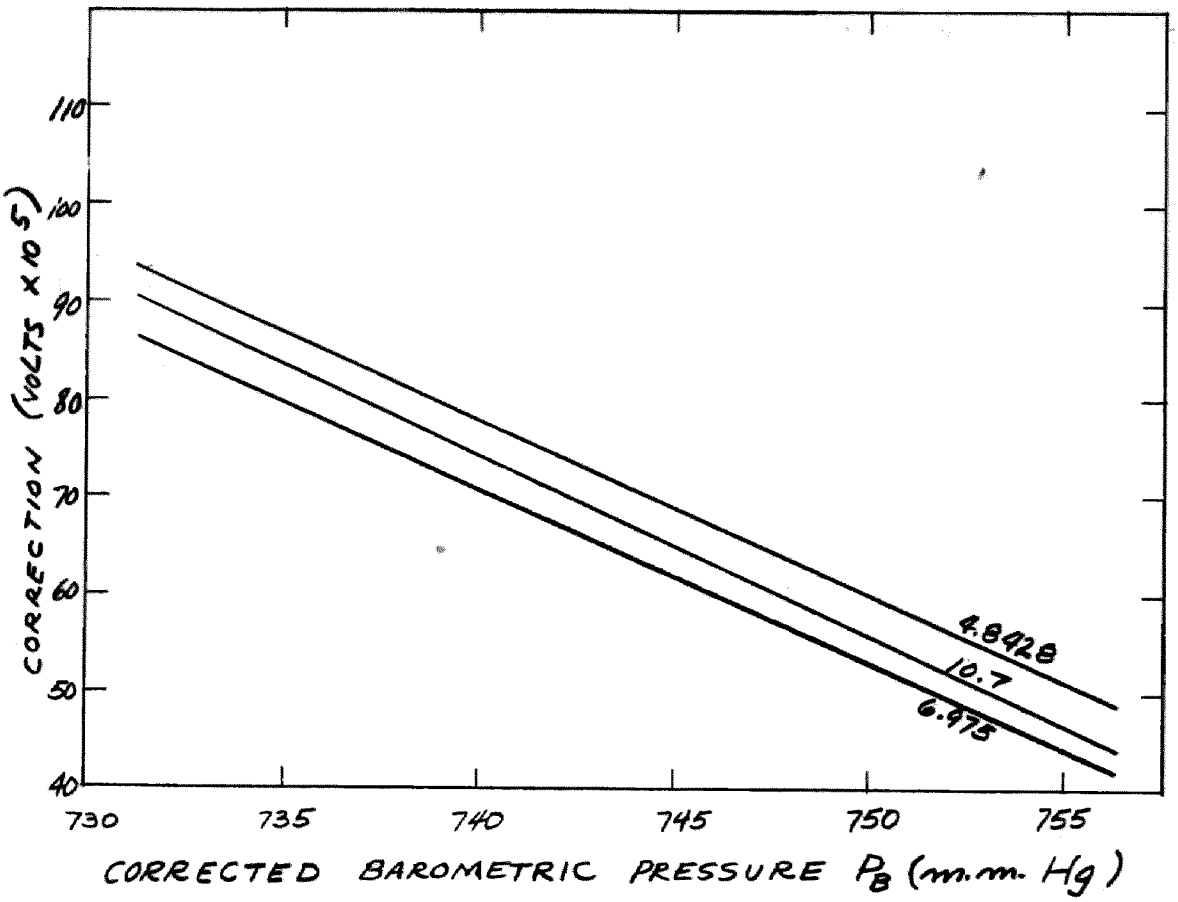


Fig. 9

Cobalt chloride (m_2) was then weighed by difference into weighing bottles containing solvent. For a typical point, m_2 = 0.3000.

Spectrophotometric measurements made at this particular concentration are given in Table XV and Figure 14.

The solution was placed in a cell and hydrogen gas bubbled in for about 3 hours. The hydrogen electrode was rinsed twice with solution and inserted. Solution was then aspirated up into the AgCl-Ag compartment (see B Fig. 5) until the level was slightly higher than in the solution proper. The bridge was then balanced against the standard cell. The temperature control was rechecked and the rinsed Ag-AgCl electrode inserted without delay. The first two readings, taken at intervals of about 15 minutes, usually showed a downward drift. The

third and fourth readings usually checked within 0.3 millivolt. For m_2 = 0.3000, the observed E.M.F. was 0.07369 volts. The corrected pressure was 745 m.m. which corresponds to 0.00069 volt (see Table B). From this E corr. was 0.07438. Insertion into equation (9), gives $\gamma_{\underline{t}}$ = 3.110 (see Table VII).

TABLES AND GRAPHS

E.M.F. DATA

Table 1

Run 1

$m_1 = 0.0470$, $t = 25^\circ$

$k = 0.05915$, $2k = 0.1183$

$E^\circ = 0.22239$ (Harned and Owen)

Equation for solvent: $E + 2k \log m = E^\circ - 2k \log \gamma_\pm$ (9)

Equation for solution: $E_{corr.} + k \log m_1(2m_2+m_1) = E^\circ - 2k \log \gamma_\pm$ (10)

$E_{corr.}$ (solvent) = 0.38976 $\gamma_\pm = 0.8187 \pm 0.021$

$\gamma_\pm = 0.8258$ (interpolated from Harned and Owen)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0052	0.38711	0.780	0.3950	0.33530	0.560
0.0131	0.38274	0.752	0.4172	0.33406	0.559
0.0175	0.38059	0.741	0.4981	0.32973	0.559
0.0393	0.37249	0.701	0.5543	0.32628	0.568
0.0594	0.36700	0.679	0.5832	0.32458	0.573
0.0650	0.36577	0.673	0.7230	0.31421	0.632
0.0932	0.36113	0.654	0.7551	0.31204	0.646
0.1032	0.35849	0.648	0.7984	0.31913	0.665
0.1643	0.35058	0.621	0.8740	0.30401	0.703
0.2000	0.34718	0.608	0.9537	0.29850	0.750
0.2675	0.34212	0.588	1.0184	0.29412	0.791
0.3141	0.33946	0.575	1.0621	0.29144	0.821 ± 0.01
0.3773	0.32622	0.562			

Table II

Run 2

m_1 = 0.0932, t = 25°

$E_{corr.}$ (solvent) = 0.35629 $\gamma_{\pm}$ = 0.792 ± 0.01

$\gamma_{\pm}$ = 0.790 (Harned and Owen)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$
0.0151	0.34934	0.788	0.6137	0.30093	0.618
0.0334	0.34339	0.777	0.6477	0.29973	0.617
0.0662	0.33769	0.766	0.6592	0.29938	0.616
0.1018	0.32947	0.748	0.6881	0.29853	0.617
0.1076	0.32868	0.745	0.7731	0.29538	0.618
0.1622	0.32244	0.723	0.8427	0.29270	0.625
0.1797	0.32087	0.716	0.8876	0.29063	0.635
0.2522	0.31532	0.693	0.9270	0.28868	0.646
0.3331	0.31084	0.672	1.0322	0.28221	0.696
0.3775	0.30885	0.661	1.1723	0.27698	0.725
0.4623	0.30567	0.642	1.2501	0.27338	0.754 ± 0.001
0.5424	0.30321	0.626			

Table III

Run 3

m_1 = 1.3825, t = 30°

k = 0.06014, 2k = 0.1203

E° = 0.21912 (Harned and Owen)

$E_{corr.}$ (solvent) = 0.20898

$\gamma_\pm$ = 0.878 ± 0.001

$\gamma_\pm$ = 0.864 (Harned and Owen)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0213	0.20875	0.869	0.6270	0.17310	1.264
0.0441	0.20847	0.860	0.6687	0.17014	1.317
0.0612	0.20810	0.856	0.8231	0.16002	1.515
0.0680	0.20793	0.855	0.9456	0.15240	1.686
0.0907	0.20698	0.858	1.0462	0.14785	1.827
0.1156	0.20580	0.864	1.1427	0.14116	1.975
0.1582	0.20314	0.886	1.3173	0.13227	2.237
0.1779	0.20202	0.895	1.3382	0.13099	2.281
0.2381	0.19826	0.930	1.3780	0.12889	2.352
0.3203	0.19374	0.972	1.3951	0.12798	2.383
0.3732	0.19026	1.013	1.4273	0.12648	2.434
0.4628	0.18479	1.080	1.4442	0.12548	2.471
0.5002	0.18169	1.128	1.4745	0.12392	2.528 ± 0.001
0.5263	0.17992	1.152			

Table IV

Run 4

m_1 = 2.2386, t = 30°

$E_{corr.}$ (solvent) = 0.17357

$\gamma_{\pm}$ = 1.068 ± 0.001

$\gamma_{\pm}$ = 1.054 (Harned and Owen)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$
0.0137	0.17308	1.072	0.3772	0.15867	1.229
0.0300	0.17246	1.076	0.3998	0.15732	1.251
0.0329	0.17234	1.078	0.4015	0.15682	1.263
0.0444	0.17186	0.082	0.4088	0.15688	1.258
0.0553	0.17141	1.087	0.5491	0.15090	1.350
0.0652	0.17098	1.901	0.6096	0.14777	1.408
0.0689	0.17073	1.094	0.8560	0.13884	1.563
0.0954	0.16901	1.121	0.9804	0.13416	1.658
0.0968	0.16952	1.107	1.1198	0.12830	1.755
0.1192	0.16901	1.115	1.3124	0.12087	1.987
0.1223	0.16841	1.119	1.5490	0.11052	2.313
0.1686	0.16637	1.143	1.6416	0.10637	2.462
0.1756	0.16614	1.145	1.8177	0.10151	2.619
0.2360	0.16499	1.144	2.1610	0.08835	3.188
0.2949	0.16130	1.202	2.5400	0.07686	3.806
0.3419	0.15906	1.234	3 2983	0.05544	5.159 ± 0.001

Table V

Run 5

m_1 = 3.7733, t = 30°

$E_{corr.}$ (solvent) = 0.12718

$\gamma_{\pm}$ = 1.540 ± 0.001

$\gamma_{\pm}$ = 1.579 (Akerloff and Teare)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_{\pm}$
0.0225	0.12614	1.562	0.9371	0.07824	3.213
0.0431	0.12527	1.580	0.9732	0.07651	3.300
0.0622	0.12434	1.600	1.0088	0.07513	3.368
0.1003	0.12231	1.648	1.0650	0.07266	3.497
0.1340	0.12045	1.693	1.1187	0.07051	3.611
0.2069	0.11641	1.797	1.1681	0.06844	3.725
0.3350	0.10869	2.023	1.1790	0.06793	3.756
0.4728	0.10078	2.283	1.2432	0.06509	3.925
0.5406	0.09734	2.404	1.3400	0.06093	4.187
0.7197	0.08853	2.746	1.4223	0.05731	4.431
0.7742	0.08574	2.867	1.4701	0.05515	4.585 ± 0.001

Table VI

Run 6

$m_1 = 3.7733$, $t = 30^\circ$

m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0127	0.12689	1.544	1.2233	0.07749	3.106
0.0343	0.12575	1.569	1.2522	0.07652	3.149
0.0550	0.12475	1.591	1.3086	0.07477	3.228
0.1221	0.12169	1.658	1.3275	0.07422	3.252
0.1596	0.11991	1.700	1.4074	0.07170	3.371
0.2234	0.11724	1.762	1.4251	0.07118	3.396
0.2568	0.11590	1.793	1.4676	0.06991	3.458
0.3072	0.11360	1.849	1.5124	0.06850	3.529
0.4325	0.10830	1.994	1.5850	0.06643	3.632
0.4521	0.10746	2.018	1.6432	0.06476	3.720
0.4975	0.10555	2.073	1.6678	0.06411	3.753
0.6963	0.09727	2.334	1.7600	0.06144	3.900 ± 0.001
0.9371	0.09768	2.682			

Table VII

Run 7

$m_1 = 4.8428$, $t = 30^\circ$

$E_{corr.}$ (solvent) = 0.09532

$\gamma_\pm = 2.207 \pm 0.001$

$\gamma_\pm = 2.170$ (Akerloff and Teare)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0411	0.08987	2.431	0.8317	0.05743	3.935
0.1078	0.08393	2.690	0.8751	0.05634	3.991
0.1976	0.07887	2.909	1.087	0.05010	4.360
0.3000	0.07438	3.110	1.285	0.04429	4.741
0.3454	0.07246	3.200	1.353	0.04253	4.859
0.3785	0.07132	3.251	1.455	0.03971	5.060
0.4959	0.06752	3.425	1.498	0.03851	5.150
0.5452	0.06563	3.523	1.531	0.03783	5.195
0.5962	0.06418	3.590	1.592	0.03608	5.331 ± 0.001
0.7120	0.06076	3.762			

Table VIII

Run 8

$m_1 = 4.8428$, $t = 30^\circ$

m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.1067	0.08782	2.495	0.5461	0.06900	3.302
0.1200	0.08676	2.540	0.5784	0.06767	3.369
0.1623	0.08390	2.661	0.6627	0.06540	3.470
0.1713	0.08358	2.672	0.7075	0.06346	3.575
0.1943	0.08193	2.746	0.8061	0.06062	3.717
0.2635	0.07888	2.873	1.0048	0.05474	4.037
0.3976	0.07427	3.063	1.0232	0.05399	4.084
0.4047	0.07382	3.085	1.3586	0.04559	4.580
0.4591	0.07144	3.198	1.5097	0.04258	4.756 ± 0.001
0.5118	0.06962	3.282			

Table IX

Run 9

$m_1 = 6.975$, $t = 30^\circ$

$E_{corr.}$ (solvent) = 0.04089

$\gamma_\pm = 4.345 \pm 0.001$

$\gamma_\pm = 4.180$ (Akerloff and Teare)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0194	0.03962	4.441	0.4269	0.01829	6.323
0.0228	0.03935	4.462	0.5243	0.01516	6.631
0.0512	0.03761	4.595	0.5815	0.01333	6.820
0.0819	0.03550	4.763	0.6402	0.01162	6.996
0.0998	0.03426	4.866	0.6875	0.01043	7.117
0.1097	0.03350	4.930	0.8617	0.00652	7.515
0.1133	0.03322	4.954	1.039	0.00304	7.873
0.1906	0.02829	5.387	1.214	-0.00013	8.210
0.2535	0.02505	5.682	1.400	-0.00314	8.528
0.3109	0.02260	5.911	1.502	-0.00460	8.681
0.3299	0.02180	5.987	1.688	-0.00697	8.918 ± 0.001
0.3601	0.02064	6.098			

Table X

Run 10

$m_1 = 6.975$, $t = 30^\circ$

m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0103	0.04039	4.382	0.4990	0.02135	5.910
0.0250	0.03958	4.441	0.6280	0.01819	6.178
0.0765	0.03686	4.644	0.6349	0.01810	6.184
0.0882	0.03619	4.697	0.9009	0.01278	6.636
0.0966	0.03580	4.726	0.9584	0.01177	6.722
0.1650	0.03265	4.973	1.123	0.00853	7.024
0.1889	0.03159	5.058	1.214	0.00693	7.172
0.2187	0.03047	5.147	1.306	0.00533	7.323
0.3212	0.02649	5.479	1.322	0.00505	7.350
0.4799	0.02187	5.865	1.498	0.00238	7.597 ± 0.001

Table XI

Run 11

$m_1 = 10.7$, $t = 30^\circ$

$E_{corr.}$ (solvent) = -0.03606

$\gamma_\pm = 12.35 \pm 0.001$

$\gamma_\pm = 11.70$ (Akerloff and Teare)

m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$	m_2 ($CoCl_2$)	$E_{corr.}$	$\gamma_\pm$
0.0105	-0.04095	13.56	0.4372	-0.05667	17.84
0.0130	-0.04139	13.67	0.4499	-0.05737	17.85
0.0314	-0.04518	14.67	0.5171	-0.05852	18.14
0.0514	-0.04740	15.28	0.7295	-0.06120	18.76
0.0937	-0.04991	15.97	0.7949	-0.06192	18.92
0.2441	-0.05407	17.06	0.8470	-0.06242	19.02
0.2794	-0.05482	17.25	0.0951	-0.06297	19.13 ± 0.001

Table XII

Run 12

$m_1 = 10.7$, $t = 30^{\circ}$

m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_{\pm}$	m_2 ($NiCl_2$)	$E_{corr.}$	$\gamma_{\pm}$
0.0062	-0.03893	13.05	0.4867	-0.05728	17.76
0.0535	-0.04766	15.36	0.5137	-0.05766	17.85
0.0718	-0.04884	15.68	0.5395	-0.05798	17.92
0.0930	-0.04981	15.94	0.5888	-0.05857	18.05
0.1014	-0.05014	16.03	0.7222	-0.06001	18.35
0.1832	-0.05241	16.62	0.7520	-0.06034	18.42
0.4537	-0.05686	17.67	0.8185	-0.06099	18.55 ± 0.001

SPECTROPHOTOMETRIC DATA

Table XIII

Run 5

$CoCl_2$ in 3.7733 m HCl (Run V), m_2 = 0.2514, 0.5624, 0.6193

Extinction Coefficient (ϵ) = log I_o/I

	ϵ		
λ (millimicrons)	0.2514	0.5624	0.6193
440	0.402	0.845	0.971
460	0.818	1.703	1.883
480	1.129	2.087	
490	1.269	2.347	
500	1.407	2.420	
510	1.511	2.585	
520	1.539	2.658	
530	1.469	2.769	
540	1.274	2.420	
560	0.724	1.694	1.921
580	0.359	0.910	
600	0.221	0.633	0.740
610	0.213	0.688	0.818
620	0.217	0.740	0.886
630	0.222	0.783	0.939
640	0.213	0.759	0.919
650	0.217	0.796	0.959
660	0.245	0.947	1.155
670	0.249	0.967	1.174
680	0.237	0.932	1.139
700	0.197	0.800	0.987
720	0.078	0.240	0.333
740	0.035	0.096	
780	0.025	0.063	

Table XIV

Run 6

$NiCl_2$ in 3.7733 m HCl, m_2 = 0.0224, 0.3302, 0.4722, 1.1098

	ϵ			
λ (millimicrons)	0.0224	0.3302	0.4722	1.1098
385	0.936	1.442		
390	1.654	1.606		
400	1.620	1.678		
410	1.607	1.431		
420	1.824	1.047		
430	1.592	0.646		
440		0.398		
450	1.530			
560	0.005	0.089	0.142	0.300
580	0.006	0.126	0.196	0.412
600	0.018	0.199	0.302	0.652
620	0.023	0.325	0.478	1.064
640	0.032	0.472	0.697	1.556
660	0.042	0.595	0.873	1.983
680	0.043	0.611	0.903	
700	0.045	0.656	0.971	
710	0.046	0.686	1.018	
720	0.050	0.703	1.041	
730	0.050			
740	0.049	0.697	1.028	
760	0.044	0.616	0.917	
780	0.034	0.502	0.750	1.821
800	0.028	0.402	0.602	1.485
820	0.021	0.306	1.458	1.144
840	0.015	0.267	0.345	0.860

Table XV

Run 7

$CoCl_2$ in 4.8428 m HCl, m_2 = 0.0453, 0.1018, 0.3000, 0.3785

	ϵ			
λ (millimicrons)	0.0453	0.1018	0.3000	0.3785
440	0.0697	0.157	0.465	0.633
460	0.139	0.325	0.959	1.322
480	0.194	0.458	1.351	1.928
500	0.243	0.588	1.747	
520	0.266	0.654	1.947	
530	0.247	0.614	1.848	
540	0.203	0.523	1.604	
560	0.114	0.309	0.974	1.368
580	0.054	0.163	0.535	0.752
600	0.033	0.124	0.452	0.666
620	0.033	0.167	0.690	1.046
640	0.031	0.173	0.734	1.108
660	0.034	0.227	0.975	1.462
670	0.035	0.229	0.997	1.513
680	0.033	0.224	0.979	1.502
685	0.033	0.227	1.000	1.501
700	0.026	0.188	0.833	1.157
720	0.034	0.058	0.237	0.535

Table XVI

Run 8

$NiCl_2$ in 4.8428 m HCl, m_2 = 0.1623, 0.2635, 0.4047, 0.5118

λ (millimicrons)	ϵ 0.1623	0.2635	0.4047	0.5118
385	0.597	0.827	1.224	
390	0.678	0.945	1.396	
400	0.733	1.036	1.532	
410	0.642	0.903	1.353	
425	0.373	0.527	0.799	
430		0.407	0.616	
560	0.026	0.039	0.058	
600	0.080	0.112	0.163	
620	0.135	0.118	0.276	
640	0.201	0.280	0.411	
660	0.261	0.351	0.520	0.745 (650)
680	0.264	0.368	0.545	0.836 (670)
700	0.280	0.391	0.577	0.886 (690)
720	0.293	0.409	0.599	0.928 (700)
740	0.283	0.395	0.573	0.987 (720)
760	0.254	0.350	0.506	0.975 (740)
800	0.181	0.249	0.356	0.870 (760)
820	0.152	0.208	0.298	0.572 (800)

Table XVII

Run 9

$CoCl_2$ in 6.975 m HCl, m_2 = 0.0194, 0.0512, 0.0998

	ϵ		
λ (millimicrons)	0.0194	0.0512	0.0998
440	0.029	0.073	0.125
460	0.061	0.150	0.256
480	0.094	0.232	0.398
500	0.127	0.318	0.545
510	0.142	0.354	0.607
520	0.151	0.380	0.654
530	0.155	0.387	0.674
540	0.141	0.354	0.611
560	0.104	0.262	0.455
580	0.098	0.253	0.445
600	0.212	0.550	0.991
620	0.506	1.322	
640	0.553	1.438	
660	0.801		
670	0.815	1.967	
680	0.807	1.932	
685	0.833	1.979	
700	0.740	1.726	
720	0.232	0.541	

Table XVIII

Run 10

$NiCl_2$ in 6.975 m HCl, m_2 = 0.0765, 0.1650, 0.1889, 0.3212

λ (millimicrons)	ϵ 0.0765		0.1650	0.1889	0.3212
380	0.308		0.377	0.636	0.987
385	0.338	(390)	0.519	0.889	1.409
400	0.410		0.572	0.979	1.553
410	0.373		0.526	0.889	1.409
425	0.229	(420)	0.398	0.692	1.125
440	0.102			0.283	0.470
590	0.039	(580)	0.031	0.062	0.098
610	0.080	(600)	0.072	0.134	0.217
630	0.129	(620)	0.126	0.220	0.361
650	0.173	(640)	0.173	0.301	0.493
670	0.201	(660)	0.220	0.387	0.638
690	0.211	(680)	0.246	0.420	0.699
700	0.212	(700)	0.243	0.423	0.688
720	0.205	(730)	0.236	0.408	0.654
740	0.188	(770)	0.184	0.323	0.523
760	0.159	(800)	0.124		0.414
800	0.110	(820)	0.091	0.166	0.276
820	0.094				

Table XIX

Run 11

$CoCl_2$ in 10.7 m HCl, m_2 = 0.0105, 0.0514, 0.0937

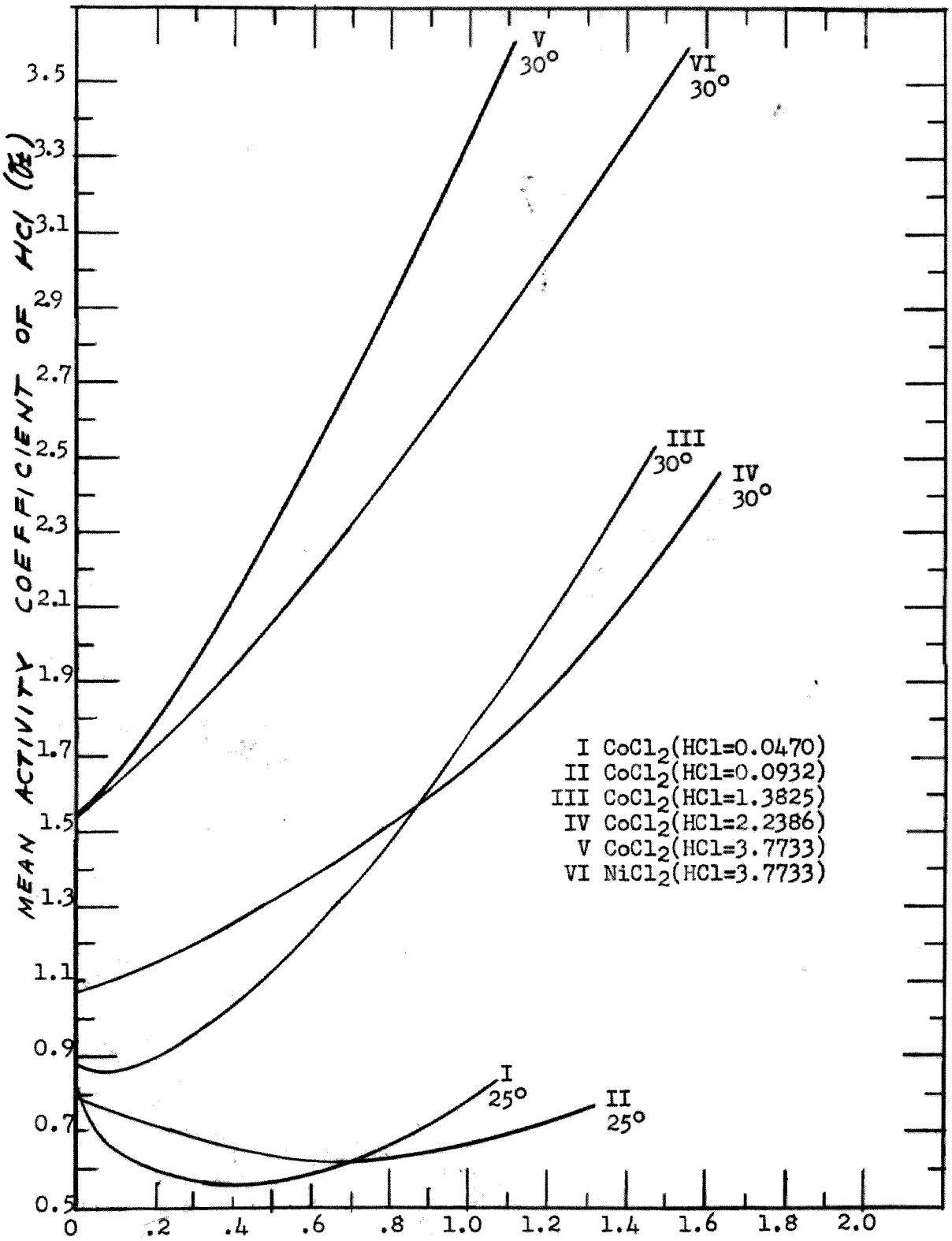
λ (millimicrons)	ϵ 0.0105	0.0514	0.0937
440		0.067	0.124
460	0.015	0.055	0.106
480	0.021	0.090	0.179
500	0.046	0.199	0.367
520	0.074	0.301	0.542
530	0.096	0.409	0.750
550	0.079	0.345	0.650
600	1.060	2.658	
620	2.699	2.796	
640	2.745	3.000	
680	3.301	3.523	
700	2.824	2.824	
720	1.184	2.620	

Table XX

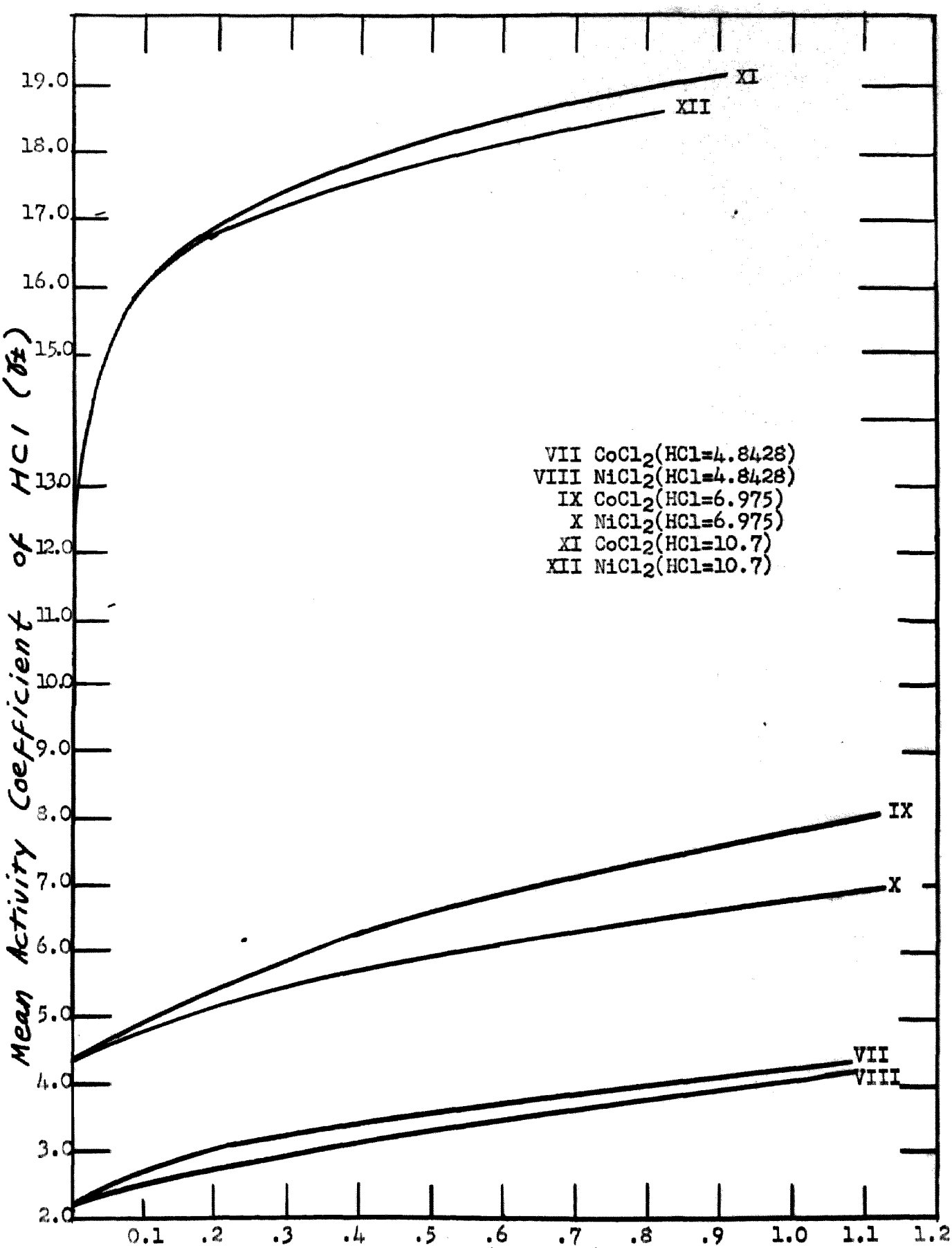
Run 12

$NiCl_2$ in 10.7 m HCl, m_2 = 0.0535, 0.1014, 0.4537, 0.7222

	ϵ			
λ (millimicrons)	0.0535	0.1014	0.4537	0.7222
400	0.248	0.352	2.284	2.301
420	0.312	0.440	2.658	2.699
440	0.205	0.292	2.222	2.237
640	0.128	0.184	1.178	1.209
660	0.189	0.281	1.807	1.866
680	0.205	0.307	2.046	2.114
690	0.228	0.341	2.276	2.337
700	0.212	0.319	2.046	2.081
720	0.137	0.196		



Activity Coefficients of Hydrochloric Acid in Salt Solutions
Fig. 10



Activity Coefficients of Hydrochloric Acid in Salt Solutions
Fig. 11

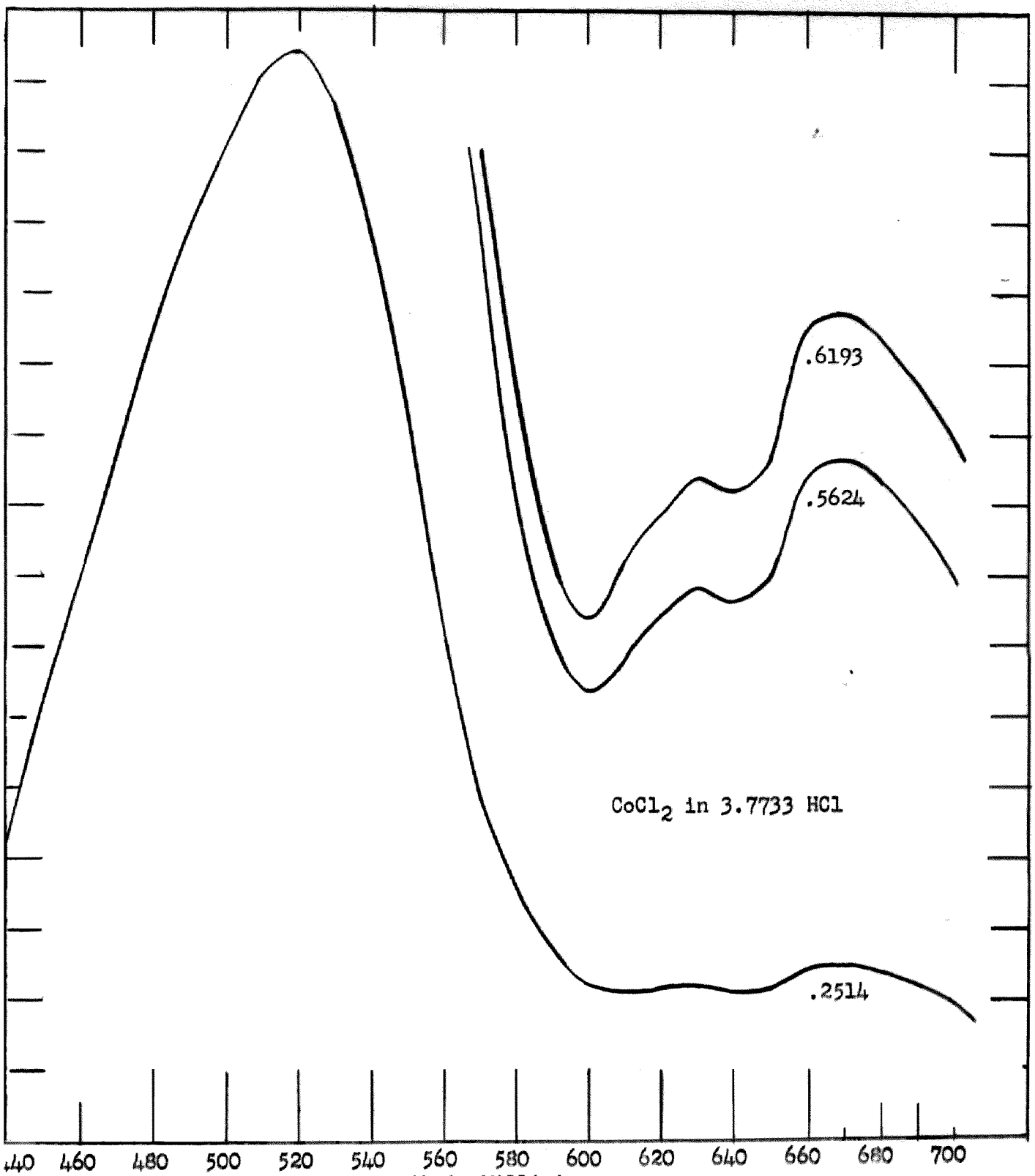

.6193
.5624
$CoCl_2$ in 3.7733 HCl
.2514
440 460 480 500 520 540 560 580 600 620 640 660 680 700
Wave Length in Millimicrons

Fig. 12

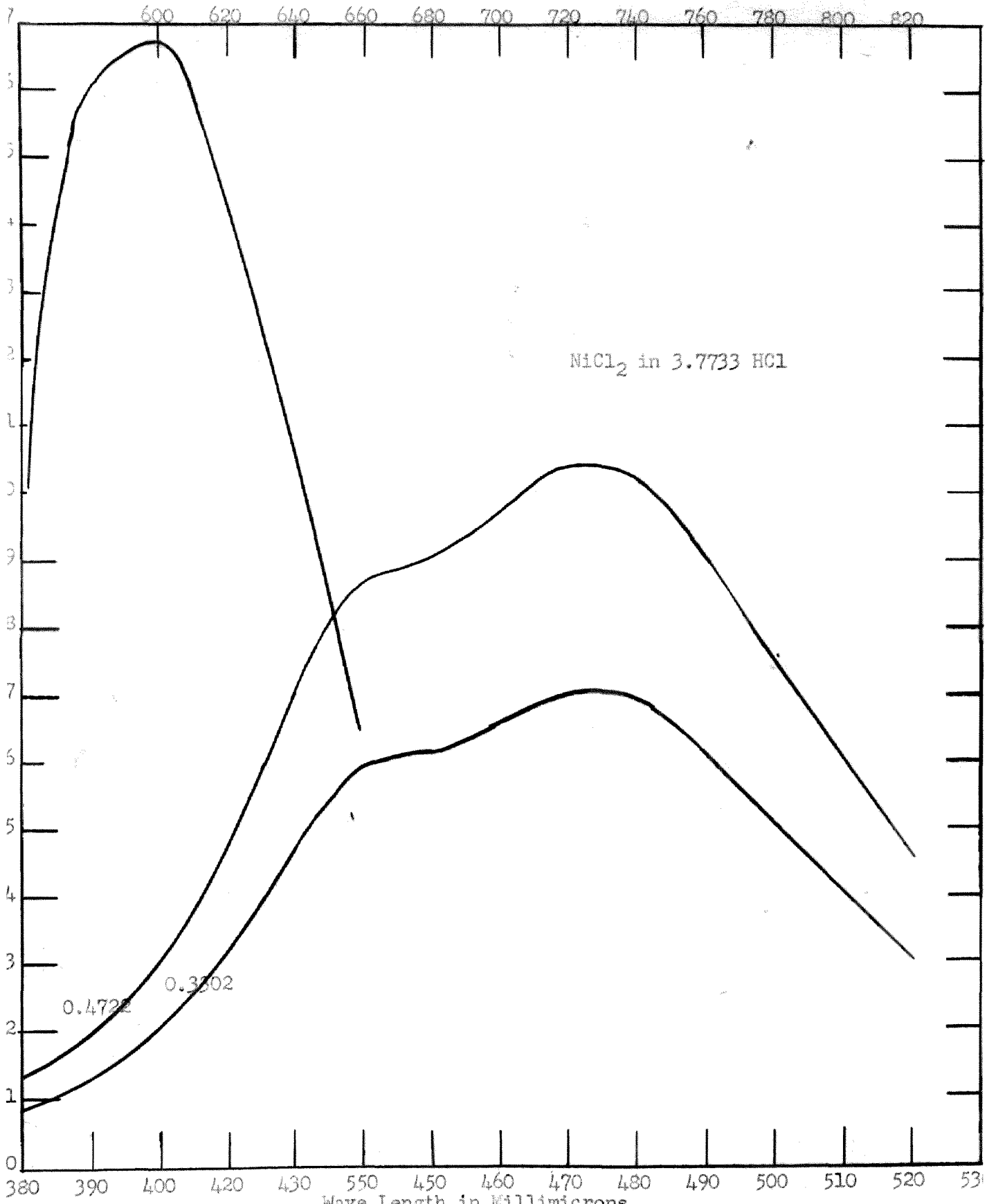
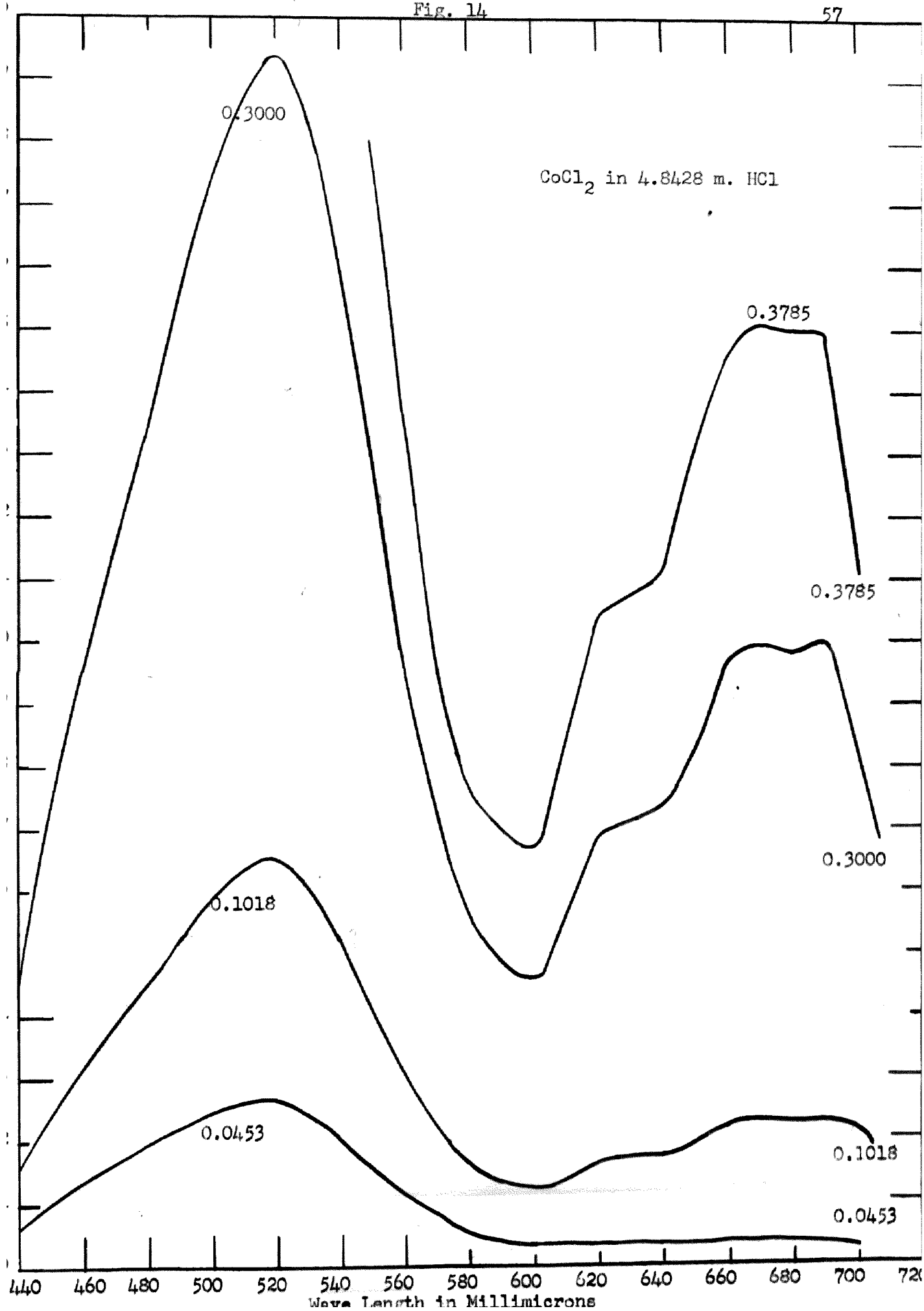

600
620
640
660
680
700
720
740
760
780
800
820
NiCl2 in 3.7733 HCl
0.4722
0.3302
0
1
2
3
4
5
6
7
8
9
380
390
400
420
430
550
450
460
470
480
490
500
510
520
Wave Length in Millimicrons

Fig. 13

Fig. 14


$CoCl_2$ in 4.8428 m. HCl
0.3000
0.3785
0.3785
0.3000
0.1018
0.1018
0.0453
0.0453
440
460
480
500
520
540
560
580
600
620
640
660
680
700
Wave Length in Millimicrons

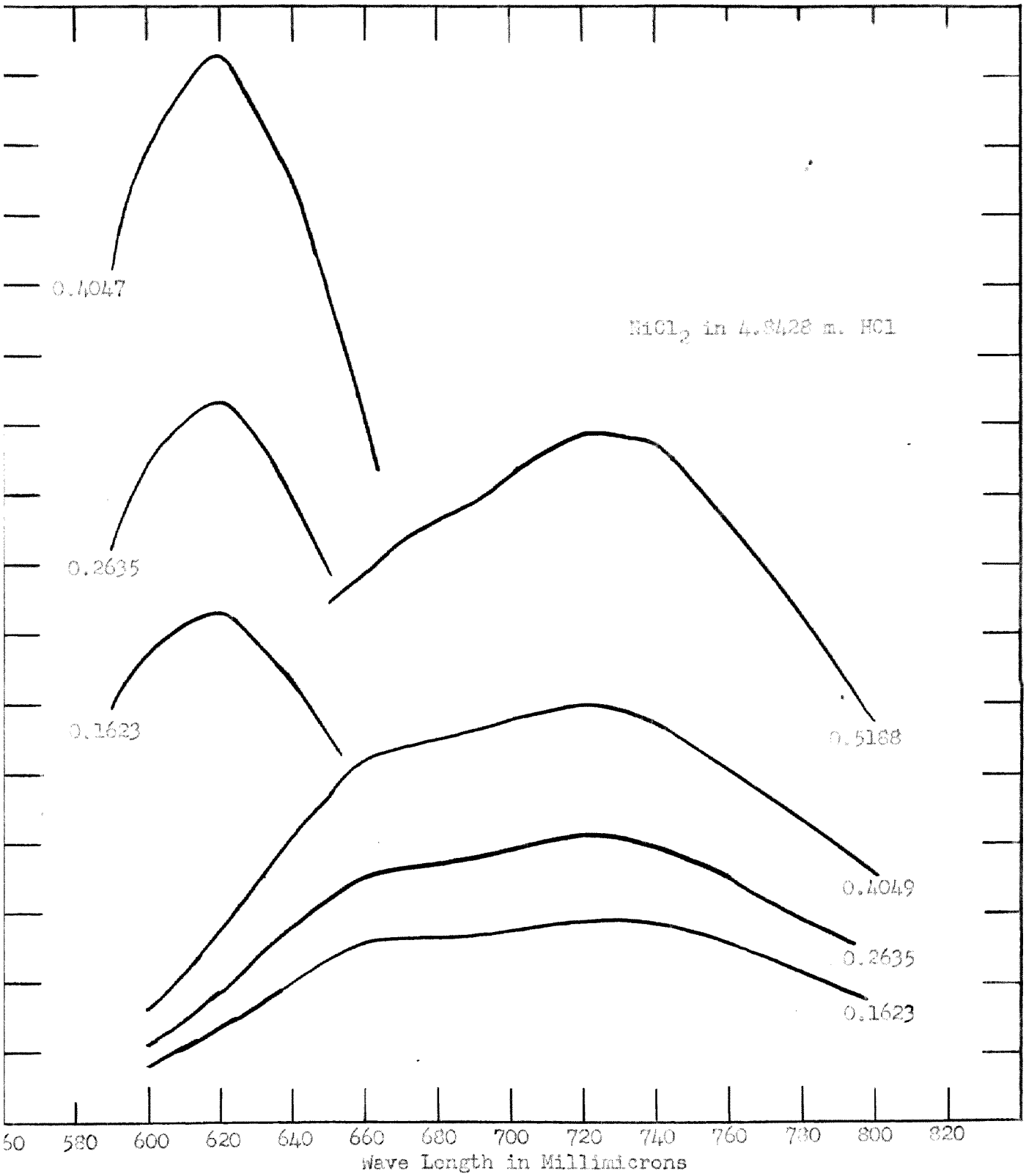
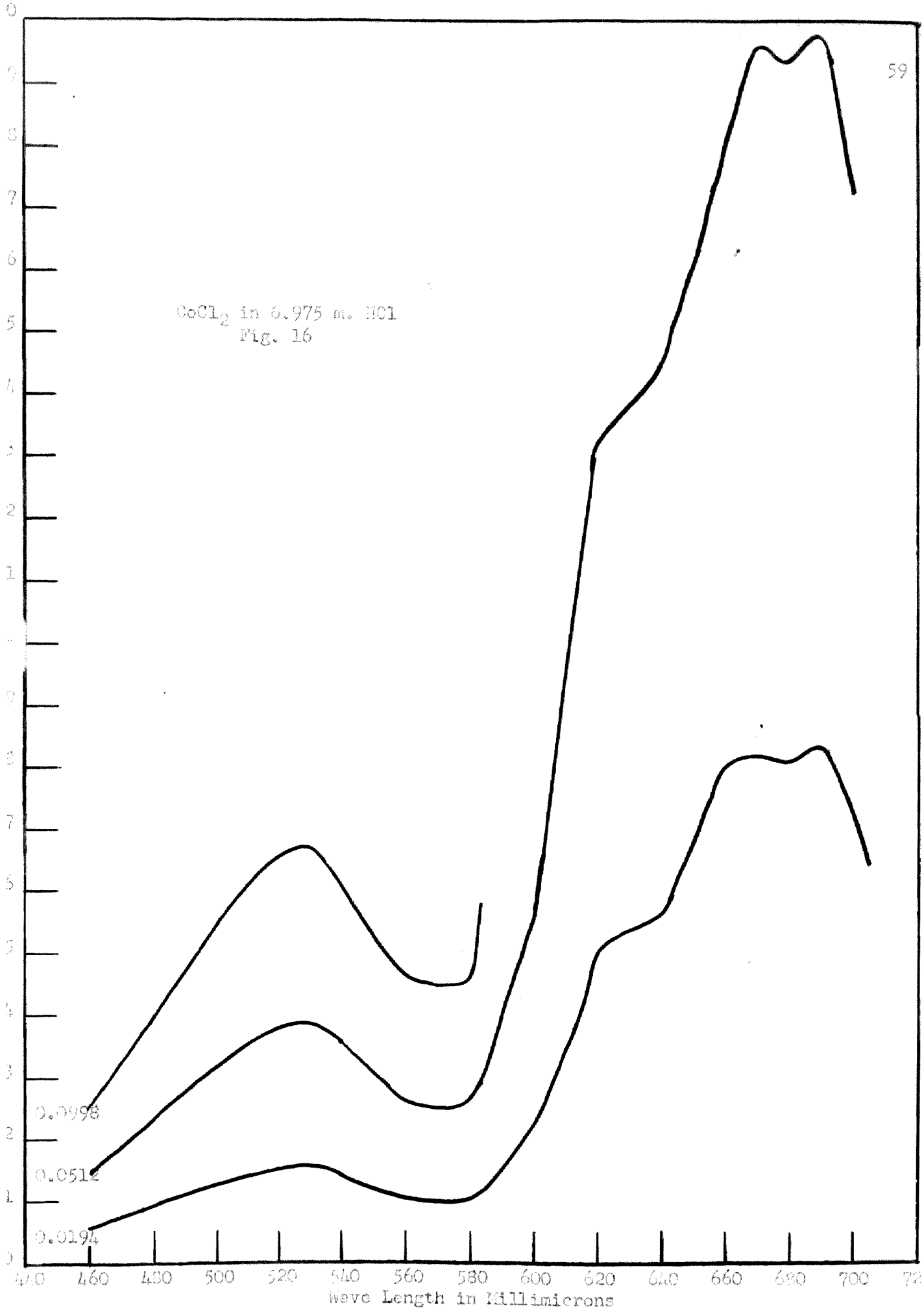

0.4047
$NiCl_2$ in 4.8428 m. HCl
0.2635
0.1623
0.5188
0.4049
0.2635
0.1623
560
580
600
620
640
660
680
700
720
740
760
780
800
820
Wave Length in Millimicrons

Fig. 15

$CoCl_2$ in 6.975 m. HCl
Fig. 16



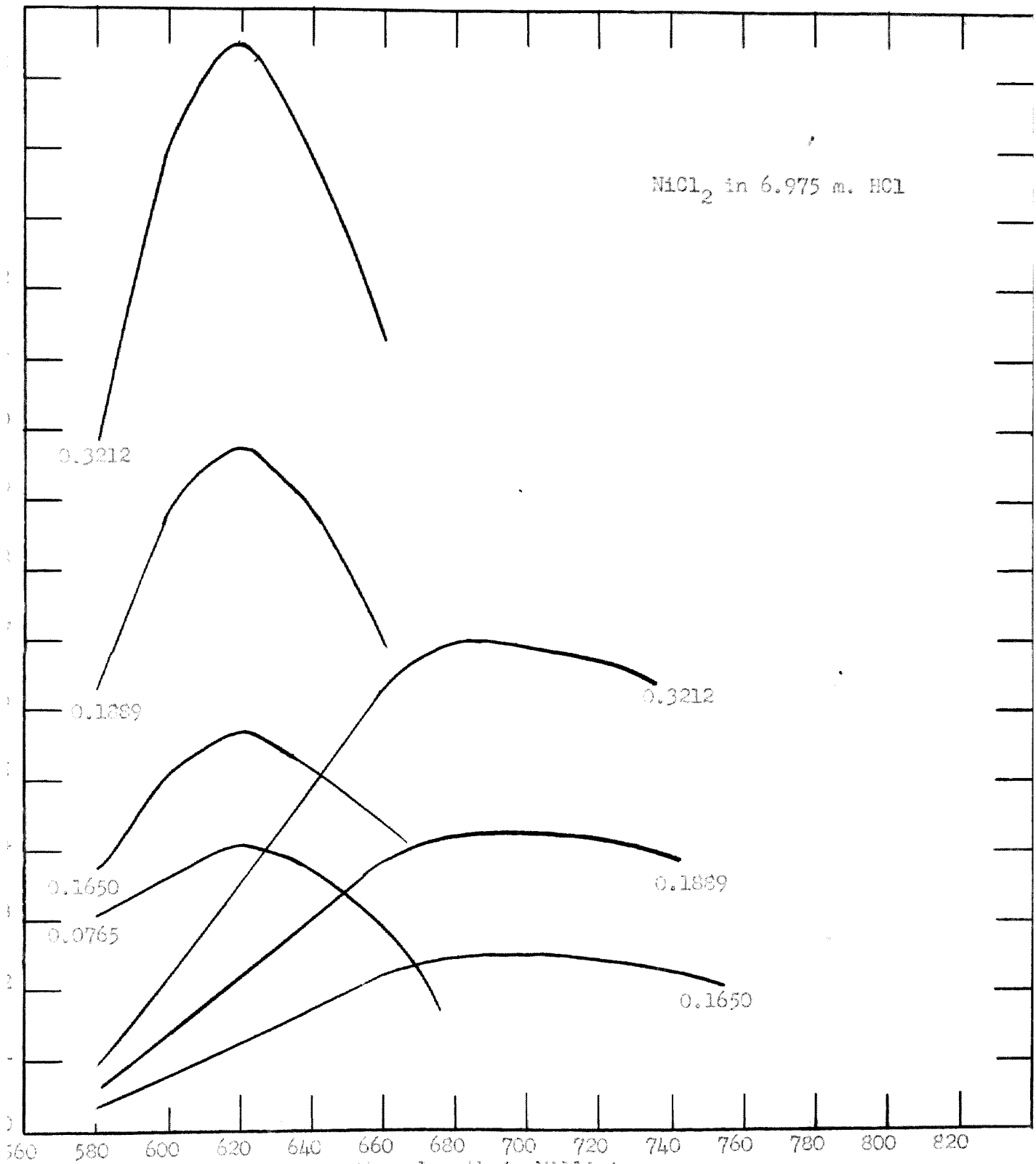
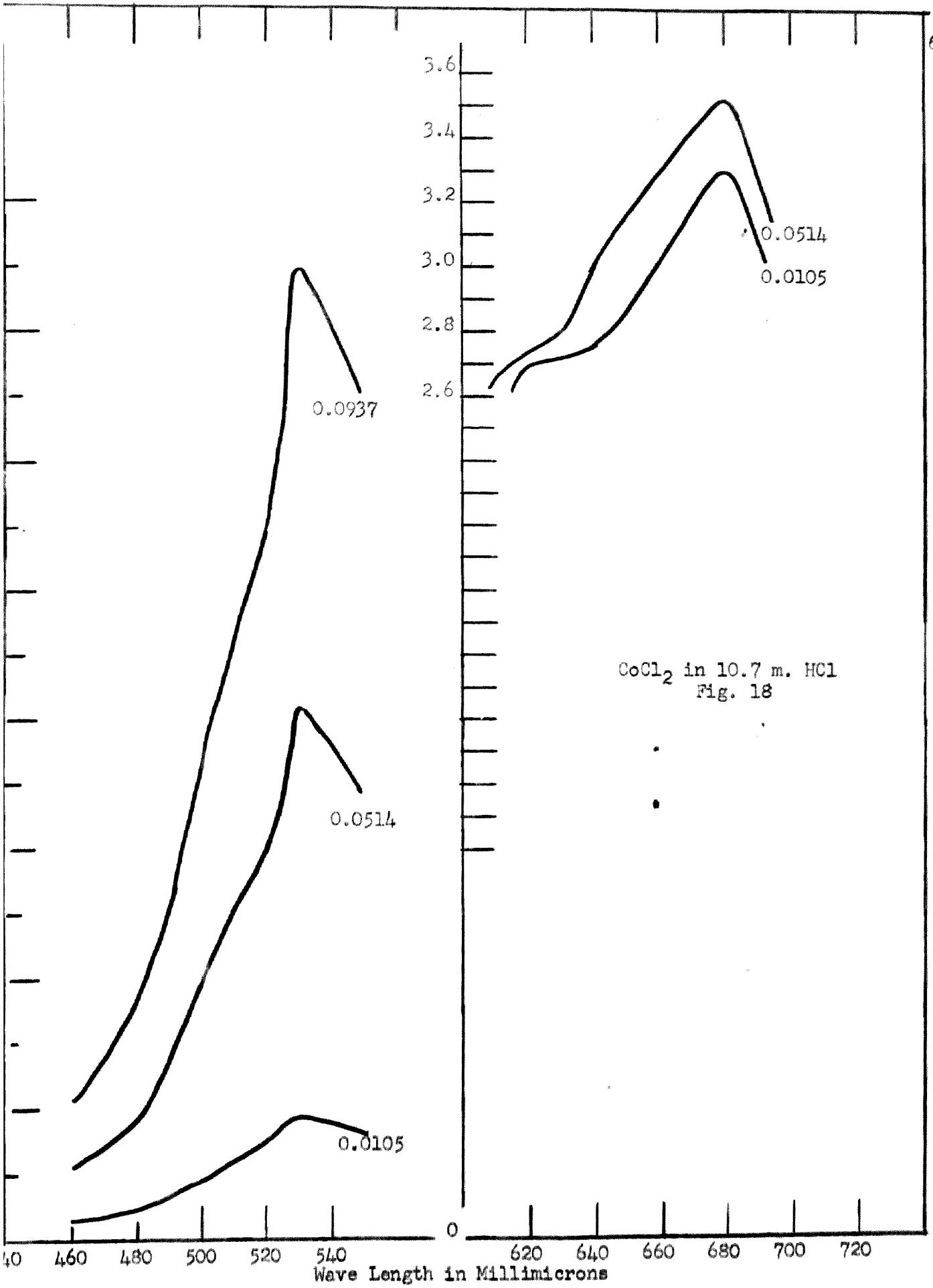
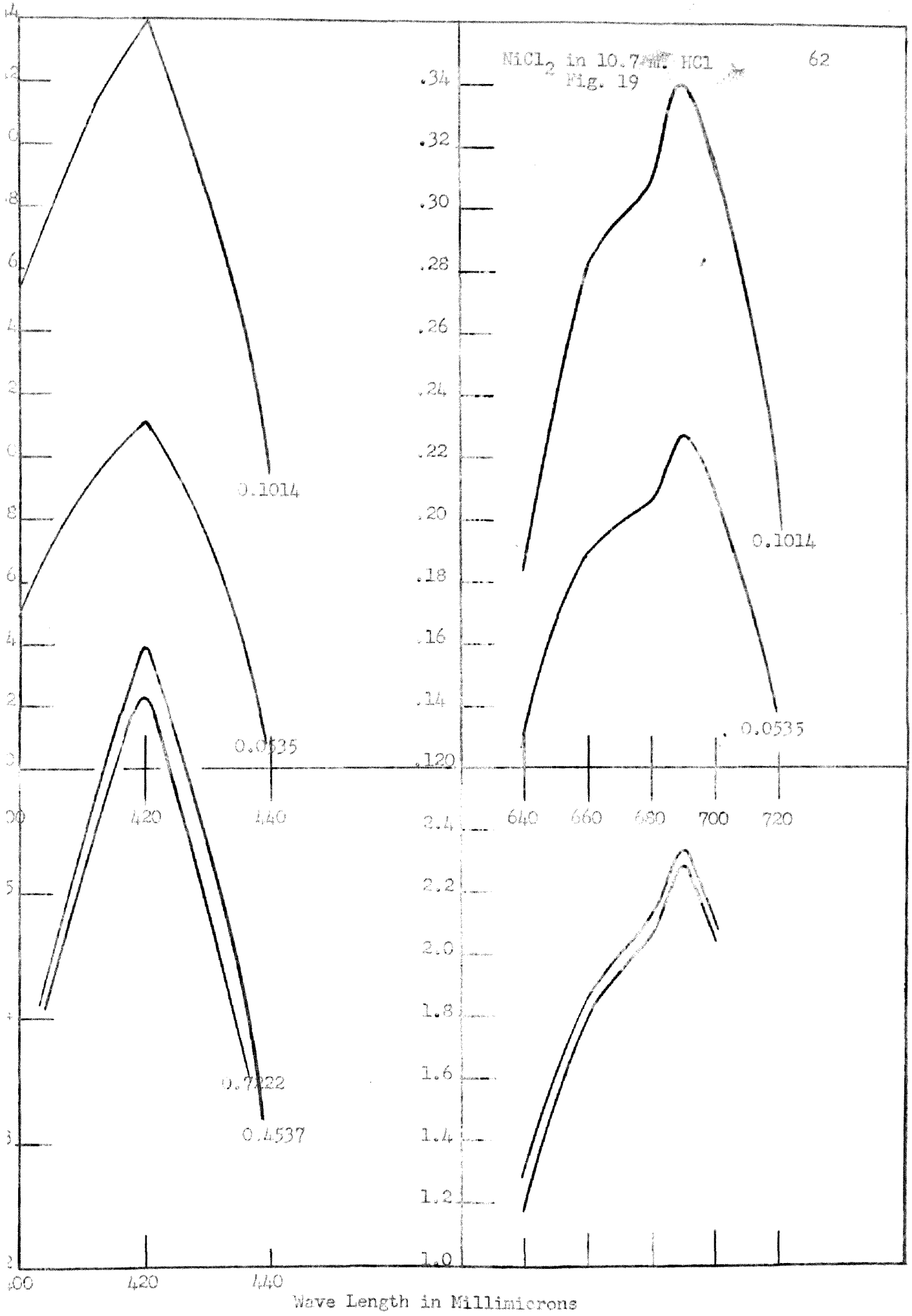

NiCl2 in 6.975 m. HCl
0.3212
0.1889
0.3212
0.1650
0.1889
0.0765
0.1650
560
580
600
620
640
660
680
700
720
740
760
780
800
820
Wave Length in Millimicrons

Fig. 17



$CoCl_2$ in 10.7 m. HCl
Fig. 18

$NiCl_2$ in 10.7 M. HCl
Fig. 19



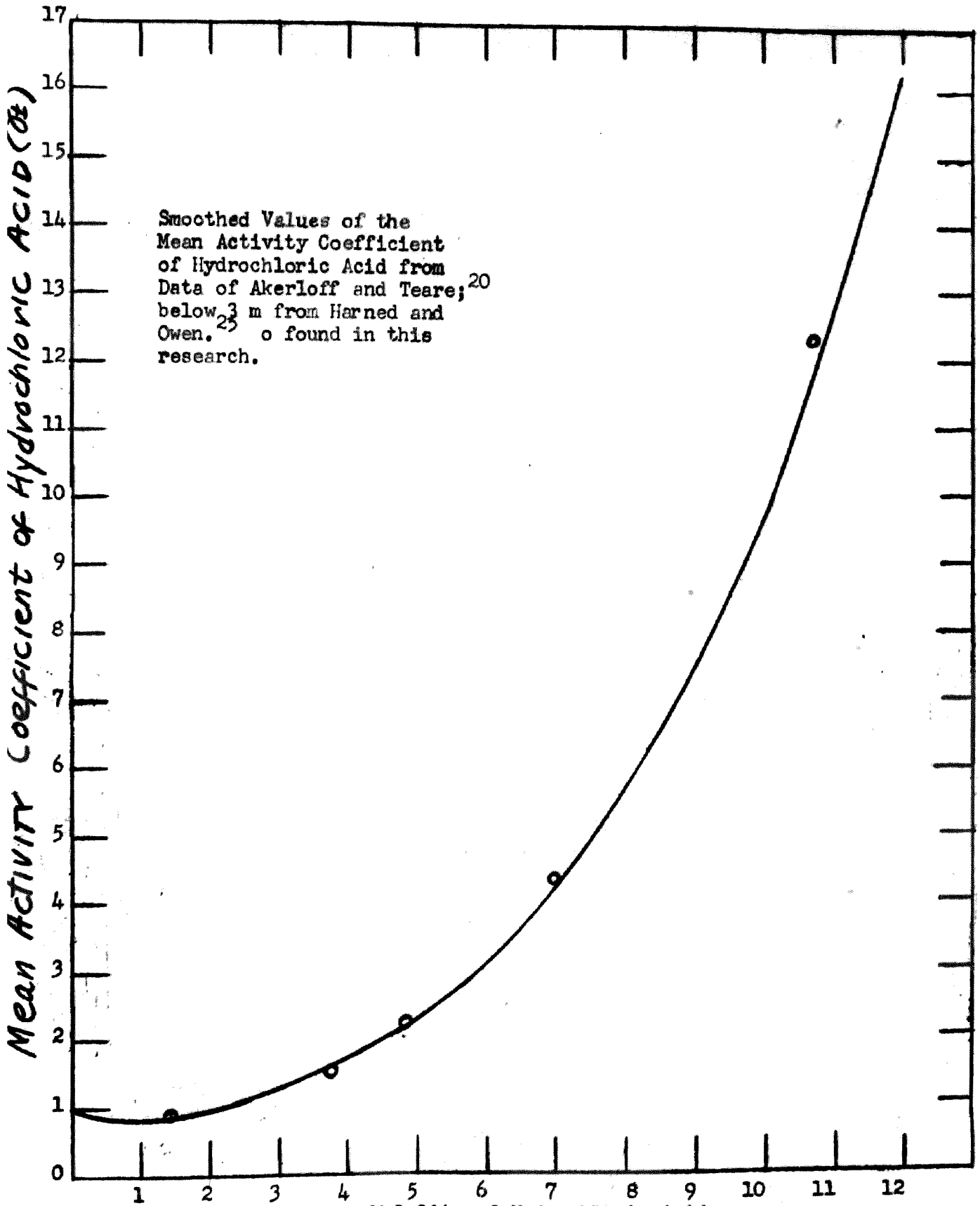

Mean Activity Coefficient of Hydrochloric Acid (Oz)
Smoothed Values of the Mean Activity Coefficient of Hydrochloric Acid from Data of Akerloff and Teare;[20] below 3 m from Harned and Owen.[25] o found in this research.
Molality of Hydrochloric Acid

Fig. 20

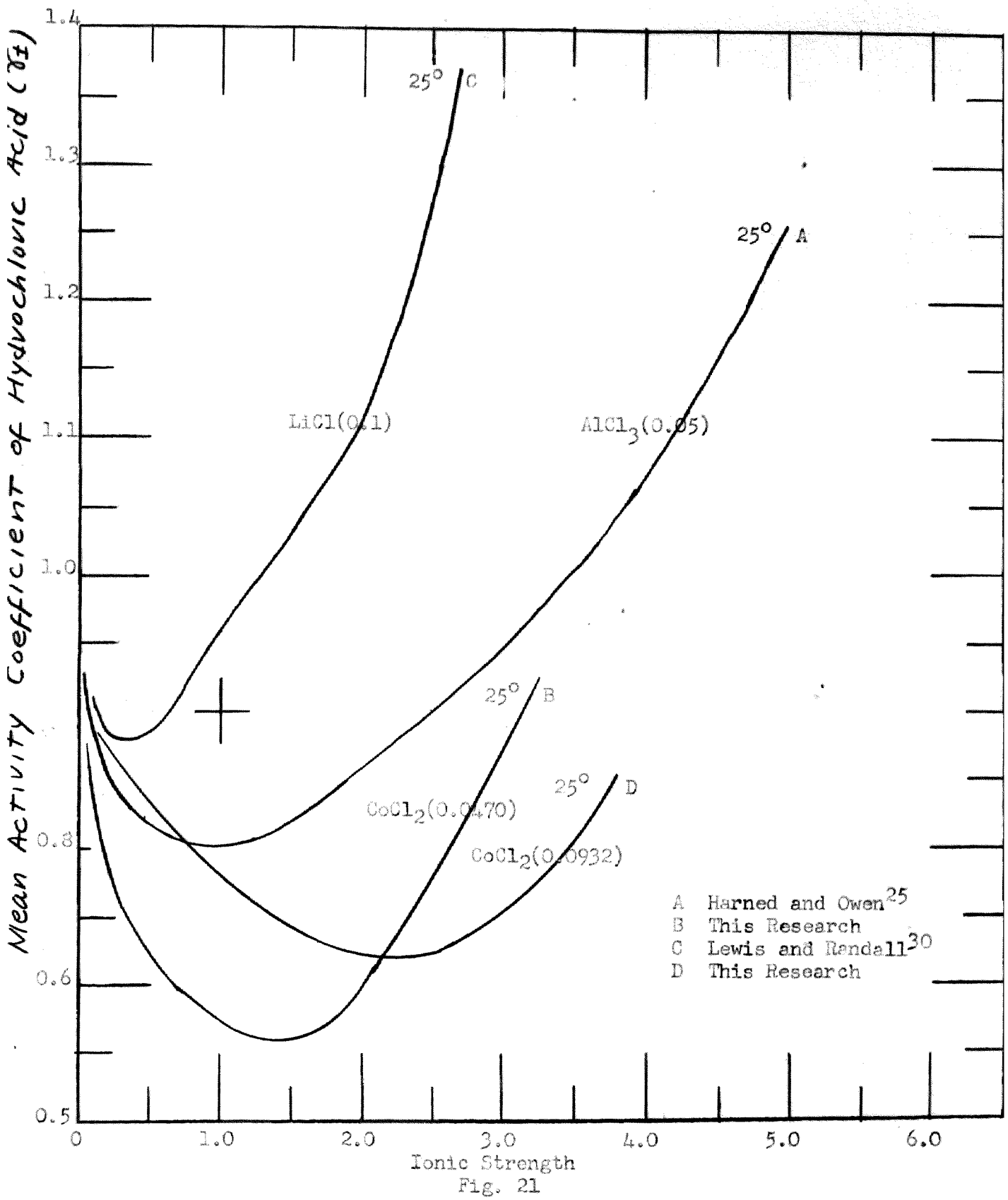

Mean Activity Coefficient of Hydrochloric Acid (γ±)
1.4
1.3
1.2
1.1
1.0
0.8
0.6
0.5
0
1.0
2.0
3.0
4.0
5.0
6.0
Ionic Strength
25° C
LiCl(0.1)
25° A
AlCl3(0.05)
25° B
CoCl2(0.0470)
25° D
CoCl2(0.0932)
A Harned and Owen[25]
B This Research
C Lewis and Randall[30]
D This Research

Fig. 21

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

I. Relation of $\gamma\pm$ HCl to the Extraction Process.

According to the data of Garwin and Hixson (Fig. 2) high separation factors are obtained when the molality of the hydrochloric acid is 4 or greater. This result should be compared to the shape of the activity coefficient curves obtained in this study (Figs. 10 and 11). It will be noted that with increasing concentrations of hydrochloric acid (m_1) in the presence of cobalt and nickel chlorides (m_2) the shape of the curves change from concave upward to convex upward. It can be seen further that the effect of cobalt chloride on the values of $\gamma\pm$ HCl is greater than that of nickel chloride although both markedly increase the $\gamma\pm$ HCl values at higher salt concentrations even when the hydrochloric acid molality is low.

The relation between the increase in the extraction of cobalt and nickel chlorides and the effect of these salts on $\gamma\pm$ HCl cannot be simply explained. Increase in HCl activity would normally be expected to increase the extraction of the acid into the nonaqueous phase. This increase in acid concentration in the organic phase may or may not be advantageous to the salt extraction depending upon additional factors. For example if extensive chlorocomplexing occurs in this phase, it would be an aid to extraction, and it seems not improbable that the increased extraction of cobalt relative to that of nickel is due to the difference in complexing of these substances in the nonaqueous phase rather than solely to the effect of the acid on the

the acid on the aqueous-phase activity coefficients of cobalt or nickel chlorides.

Perhaps the significance of this study to the extraction process will be made much clearer when supporting thermodynamic data on all components in both phases are available.

II. E.M.F. Data.

It is possible to postulate for $CoCl_2$ in HCl solution a series of chloro-aquo-complex ion equilibria of the type

$$\left[Co(H_2O)_x\right]^{++} \rightleftharpoons \left[Co(H_2O)_{x-1}Cl\right]^{+} \rightleftharpoons \left[Co(H_2O)_{x-2}Cl_2\right] \rightleftharpoons \left[Co(H_2O)_{x-3}Cl_3\right]^{-} \rightleftharpoons \left[Co(H_2O)_{x-4}Cl_4\right]^{=}$$

in which associated water is replaced in the cobalt coordination sphere by chloride ions. If one supposes the formation of the double charged cation to be predominate in the more dilute solutions followed by increasing amounts of the higher chloro-complexes in the more concentrated solutions of HCl, the qualitative features of the activity coefficient data become more understandable.

In the dilute region ($m_1 = 0.0470$ and $m_1 = 0.0932$) the initial lowering of $\gamma_{\pm}$ HCl by $CoCl_2$ would seem to be primarily an interionic-attraction effect and would follow the Debye-Hückel type of expression for the change in activity coefficients with electrolyte concentration. However, as the $CoCl_2$ concentration rises the important factor becomes the effect of the salt in decreasing the amount of effectively "free" solvent. This latter behavior is characteristic of the effect of high concentrations of several other salts upon hydrochloric acid. While no data was obtained to support this conclusion, probably the $\gamma_{\pm}CoCl_2$ also increases in this range much as it does in concentrated aqueous solutions alone. Such a mutual effect is to be expected if one can assume the rise in activity coefficients of both the acid and salt is

the result of a tying up of solvent by the ions of the salt.

In the intermediate concentration range (m_1 = 1.383 and m_1 = 2.239) the shapes of the $\gamma_{\pm}$(HCl) curves are similar to those found at lower acid concentrations. The minimum is much less pronounced at the lower concentration of HCl and has disappeared at the higher, however.

Still higher concentrations of HCl (m_1 = 3.773 and m_1 = 4.843) give spectrophotometric evidence for a change in the nature of the cobalt-containing entity as a blue color is developed in the solutions. A comparison of the activity coefficient curves for these two solutions shows that in the more concentrated one there is a tendency to level out which is interpreted as indicative of chloro-complex formation by the added $CoCl_2$. At the highest concentrations (m_1 = 6.975 and m_1 = 10.70) the initial sharp rise of HCl, presumably caused by the effect upon the "free" water of the salt ions, is replaced by a very distinct flattening or bending over of the curves. The expression for the formation of the neutral complex in the case of calcium chloride and cobalt chloride found by Robinson and Brown[10] has been commented upon earlier, and a comparable expression doubtless could be set up for the HCl-$CoCl_2$ system were the necessary data available.

The effect of $NiCl_2$ on $\gamma_{\pm}$ HCl was found to be less than that of $CoCl_2$ at the same concentration of salt. This result may be compared with the relative mean activity coefficients of the salts alone in water and with the applicability of Harned's rule[25] which states that at a given ionic strength and acid concentration, the activity coefficient of a strong acid is greater in the solution of a salt, of a given valence type, which in the pure solvent possesses the greater activity coefficient.

At molalities of about 4 m $\gamma_{\pm}$ $NiCl_2$ in aqueous solution is about 26%

larger than $\gamma_{\pm}CoCl_2$ and at the concentrations of added salts (m_2) studied in this research (up to about 1 m on the average) $\gamma_{\pm}NiCl_2$ is about 1% larger than $CoCl_2$.[29] Therefore, according to Harned's rule, $\gamma_{\pm}$ HCl in the presence of $NiCl_2$ should be higher than in the presence of $CoCl_2$ at the same concentration. Since this empirical rule of Harned's was developed for HCl mixtures with alkali and alkaline earth chlorides at low ionic strengths (about 1.5), it cannot be considered general, especially at higher concentrations where the usefulness of the "ionic strength" in correlating activity coefficients with electrolyte concentrations has become questionable. For example, Olson and Simonson[47] have expressed their doubts as to utility of the ionic strength in correlating "salt" effects upon reaction rates. In a number of ionic reactions studied by these authors, reaction rates and equilibrium constants (and thus $\gamma_{\pm}$) seem to be a function of the concentration of ions of opposite charge rather than of the "ionic strength". Other workers have developed theoretical equations[48] which indicate that at appreciable concentrations reaction rates should vary in a linear manner with "ionic strength" instead of with its square root. Therefore, these curves are not experimentally nor theoretically compatible with the behavior encountered in dilute solutions of hydrochloric acid in the presence of the alkali and alkaline earth chlorides. Such incompatibility, however, might be expected since both nickel and cobalt are transition-series elements. Rather, this emphasizes that in concentrated solutions, it is the specific nature of the ions involved which determines behavior.

In Figs. 21 and 4 the activity coefficient data are compared with data on other mixtures available in the literature. The comparison given in Fig. 21 does follow the general pattern expected by the Harned rule,

but due to the restricted number of cases studied, no statement can be made regarding the applicability of this rule to all systems.

The observed differences between the effects of the two salts were most noticeable at the higher concentrations of the salts at all acid molalities investigated. This result, in the cases where appreciable leveling out of the curves occurs, would indicate an association reaction in the case of nickel chloride analogous to that of cobalt chloride with hydrochloric acid. No determined investigation seems to have been made of this point since, unlike the cobalt case, no striking color change occurs in the solution. However, all the evidence points to the much greater tendency of cobalt to complex chloride ions relative to that of nickel. This is shown, for example, by the relative stabilities of the chloro-complexes in media of low dielectric constant,[49] by the activity coefficient curves of the pure salts in water, and by the behavior reported by Kraus[50] for these salts with anion exchange resins.

The complete explanation of the relative effects of these salts cannot be given, therefore, simply on the basis of chloro-complex formation alone and probably involves the effects of these salts on water activities also.

The values for the probable errors in $\gamma\pm$, calculated by the method of Worthing and Geffner,[51] are included for the E.M.F. data. Values taken for the probable errors (P), of which $\gamma\pm$ is a function, were: $P_{m_1} = \pm 0.001$ (for all solutions except $m_1 = 10.7$ for which $P_{m_1} = \pm 0.03$); $P_{m_2} = \pm 0.001$; $P_E = \pm 0.0003$; $P_{E^0} = \pm 0.0002$; and $P_T = \pm 0.02$. Except for the most dilute and most concentrated solutions, the overall error in $\gamma\pm$ is of the order of 0.2%.

III. Spectrophotometric Data.

Spectrophotometric studies of aqueous $CoCl_2$ and $NiCl_2$ in the presence of HCl (and other electrolytes) have been made previously.[52] No completely convincing evidence has been presented by the "complex ion" or "dehydration" adherents in favor of either theory used to explain the observed spectra. For example, even among the "complex ion" advocates there is disagreement as to the probable formula of the complex. Since the nature of the problem has been covered for $CoCl_2$, the nickel chloride situation may be briefly stated. The more recent data seem to agree that a complex nickel entity $(NiCl_4)^{=}$ is formed ($\lambda \simeq 700$ mμ.) in aqueous solutions of $NiCl_2$. The molecular extinction maxima for both $CoCl_2$ and $NiCl_2$ in the presence of HCl are in agreement with the spectrophotometric data obtained in this research. For $CoCl_2$, the absorption maxima of the pink and blue entities occur at wavelengths of $\lambda \simeq 520$ and $\lambda \simeq 670$ millimicrons respectively. For the nickel entities the absorption maxima occur at $\lambda \simeq 400$ and $\lambda \simeq 700$ millimicrons.

Since it is not the object of this paper to enter into a discussion of the various factors involved in explaining the shapes of the spectrophotometric curves, this aspect can be dismissed with the statement that these curves by no means solve the question concerning complex ions or dehydration. It may be pointed out that most of the literature contains too little direct, positive experimental evidence to assign confidently a specific formula to either the cobalt or a nickel entity.

IV. Future Work.

This author is of the opinion that there are at least three things which are absolutely necessary for the further elucidation of the $CoCl_2$ (or $NiCl_2$)-H_2O-HCl-capryl alcohol system. These are: First, the

determination of the identity of the molecular or ionic species in both the aqueous and organic phases, possibly by a spectrophotometric method; second, the determination of the activity of the water in the aqueous phase; and third, the evaluation of the activity of "$CoCl_2$" and "$NiCl_2$" in the aqueous phase in the presence of the promoting electrolyte (HCl). The latter two parameters may be amenable to a vapor pressure method of measurement.

The E.M.F. measurements were well underway when a theoretical equation, applicable to the determination of the activities of non-volatile solutes in a volatile solvent, was suggested.[53]

$$-\int_{a_3'}^{a_3''} d \ln a_3 = \frac{n_1}{n_2} \int_{\phi'}^{\phi''} d(\phi) \qquad (14)$$

where ϕ is the function, $\log p_1 p_2^k$

This equation offers intriguing possibilities and difficulties which are discussed in the Appendix of this thesis. It is only necessary to point out here that if accurate data could be obtained for the vapor pressures in the system $HCl-H_2O-CoCl_2$ (or $NiCl_2$), a graphical integration of the quantity on the right-hand side of the equation could be performed. This quantity would then not only indicate the effect of adding hydrochloric acid (several runs at constant $HCl:H_2O$) upon the activity of cobalt chloride (or nickel chloride), but would also be a measure of the water activities. Further, at concentrations (< 7 m.) where the vapor pressure of hydrochloric acid becomes very small, the E.M.F. data obtained in this research could be combined with the vapor pressure data to determine the necessary parameters to perform the required integration.

SUMMARY

SUMMARY

The activity coefficient ($\gamma \pm HCl$) of hydrochloric acid at several fixed concentration ratios ($HCl:H_2O$) has been determined in the presence of varying amounts of cobalt chloride ($CoCl_2$) and nickel chloride ($NiCl_2$) by an E.M.F. method. Although measurements were taken in both the dilute and concentrated acid ranges, the study was essentially concerned with the concentrated range ($m > 1$). Paralleling spectrophotometric measurements were made to correlate, if possible, the activity coefficient data with light absorbing species in solution.

The data show that in relation to the more favorable extraction of cobalt in the system $CoCl_2$ (or $NiCl_2$)-H_2O-HCl-octanol-2, the hydrochloric acid should be partitioned into the alcohol phase to a greater extent by $CoCl_2$ than by $NiCl_2$. Such an event would probably favor the greater extraction of cobalt relative to that of nickel in the event of stronger chloro-complexing in the alcohol phase by the cobalt.

The shapes of the activity coefficient curves are such as to indicate a greater effect for cobalt than for nickel in decreasing the effectively free water. At the highest HCl concentrations a leveling off of the curves with increasing salt concentrations is found and this result is discussed relative to the formation of chloro-complexes by both salts. A mechanism for the tie-up of chloride ions is suggested in which the initial step is the formation of a singly charged cation. The curves are interpreted in

relation to changes in ionic radii and dielectric constant of the medium, dehydration, and complexing.

Further work is suggested to determine values of $\gamma\pm$ $CoCl_2$ (or $\gamma\pm$ $NiCl_2$) in the presence of HCl and an evaluation of water activities. More information about the nature of the species in solution is needed to complete an understanding of the data obtained in this research.

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APPENDIX

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quations:

1) Debye-Hückel Equation[15]

$f_{\pm}$ = rational activity coefficient or more properly, the stoichiometric mean ionic mol fraction activity coefficient.

A = a constant for a given solvent at a specified temperature which is given by

$$A = \frac{N\epsilon^2}{2.303R}\left(\frac{2\pi}{1000}\right)^{1/2}\frac{1}{(DT)^{3/2}}$$ where N = 6.023×10^{23}, $\epsilon = 4.802 \times 10^{-10}$ e.s.u., D = the dielectric constant of the solvent medium, and R = 8.314×10^{7} ergs.

Z = the valence of an ion regardless of sign or more properly, for example, $Z_- = |Z_-|$ where $|Z_-|$ is the absolute value of Z_-, i.e. $|-2| = 2$.

u = the ionic strength[30] = $\frac{1}{2}\sum M_i Z_i^2 \approx \frac{1}{2}\sum C_i Z_i^2$

$$\beta \cdot u^{\frac{1}{2}} = K = \left[\frac{4\pi\epsilon^2 \sum n_i Z_i^2}{DkT}\right]^{\frac{1}{2}}$$ where n_i = the number of ions per c.c. and k = R/N.

2) Debye-Hückel Equation with Dielectric term added[15,25]

Bu = a linear term which was necessary if there were a linear decrease in the dielectric constant of the solvent medium with concentration.

3) Scatchard's added terms for a 1-1 electrolyte[18]

$\gamma_{\pm}$ = the practical activity coefficient or more properly,[25] the stoichiometric mean ionic molal activity coefficient.

w_1 = molecular weight of the solvent.

a_w = activity of water.

$\log f_{\pm} = \log \gamma_{\pm} + \log (1 + m\nu M_1/1000)$[25] where m = molality, and ν = total number of ions into which an electrolyte dissociates.

(4) Stokes and Robinson[21] thus use n as the second adjustable parameter in place of the Hückel B.

(5) See ref. 25.

(6) Gibbs-Duhem Equation for a ternary mixture[15,25,30]

f_1 = fugacity of component (1), etc.

N_1 = mole fraction of component (1), etc.

(7) See ref. 30.

(8) See ref. 31.

(9) Fundamental equation of cell containing only solvent:[25]

$k = RT/nF$ where $R = 8.314$, $n = 1$, and $F = 96{,}500$.

E° = the standard potential of the AgCl, Ag electrode

$E_{corr.}$ = the corrected observed E.M.F. (see eqs. 11, 12, 13).

(10) Fundamental equation of cell containing mixture[25] (either $CoCl_2$ or $NiCl_2$); since this equation refers to HCl, the mean molality $m_{\pm}$ is given by $m_1(2m_2+m_1)$, i.e. m_1 contains the contribution to the hydrogen ion and the quantity $(2m_2+m_1)$ is the total contribution to the chloride ions.

(11), (12), (13) See reference 25.

(14) Since this equation[53] is not found in standard reference works a brief derivation is presented:

(a) $u_1 = u_1^{\circ} + RT \ln a_1$, where $a_1 = f_1/f^{\circ} = p_1/p_1^{\circ}$

(b) The general Gibbs-Duhem equation for a three component system is

$$n_1\, du_1 + n_2\, du_2 + n_3\, du_3 = 0$$

($n_1 = H_2O$, $n_2 = HCl$, $n_3 = CoCl_2$ or added non-volatile electrolyte)

(c) $$du_1 + k\, du_2 + n_3/n_1\, du_3 = 0$$

Now by varying component (3) and holding (1) and (2) constant, i.e., letting $n_2/n_1 = \alpha/\beta = k$

(d) $$(\partial u_1/\partial n_3)_{n_1,n_2,\,T,P}\, dn_3 + k\,(\partial u_2/\partial n_3)\ldots dn_3 + n_3/\beta\,(\partial u_3/\partial n_3)\cdot dn_3 = 0$$

By substituting (a) into (d), eliminating RT, and leaving component (3) in the form of a_3, we have

(e) $$(\partial \ln p_1/\partial n_3)\, dn_3 + k\,(\partial \ln p_2/\partial n_3)\, dn_3 + n_3/\beta\,(\partial \ln a_3/\partial n_3)\cdot dn_3 = 0$$

Now define $\phi = \ln p_1 p_2^{\,k} = \ln p_1 + k \ln p_2$ and

(f) $$d\phi = \partial \ln p_1/\partial n_3)\, dn_3 + k\,(\partial \ln p_2/\partial n_3)\, dn_3$$

$$\therefore\ d\phi = -\, n_3/n_1\,(\partial \ln a_3/\partial n_3)\cdot dn_3$$

(g) $$\beta/n_3 \int_{\phi'}^{\phi''} d\phi = -\int_{a_3'}^{a_3''} d \ln a_3$$

The single primes refer to the standard state. The solvent (H_2O + HCl) composition remains constant (n_2/n_1) and it can be defined as the pure solvent. When the HCl molality is changed we have a new standard state. For a particular series one has:

(h) $$-\log a_3'' + \log a_3' = \beta/n_3 \int_{\phi'}^{\phi''} d(\phi)$$

which requires a graphical integration of the integral on the right. We are forced by the customary choice of a standard state to integrate from ϕ' where $n_3 \cong 0$ and this gives us no accurate value of a_3'' because the curve approaches the y - axis asymtotically. Since we have chosen (H_2O+HCl) as the standard state for the solvent, we note that $a_3' = 0$ since $n_3 = 0$ at this hypothetically infinitely dilute solution, i.e. there would be no component (3) present. Of course, it is possible to choose some other standard state, say at 0.5 m with respect to (3), which would be more amenable to an experimental treatment. Perhaps then a suitable graphical integration could be performed.

THESIS TITLE: The Mean Activity Coefficient of Hydrochloric Acid in the Presence of Cobalt Chloride and Nickel Chloride

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The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

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