THE STUDY OF TRANSPORT PHENOMENON OF

COBALTOUS CHLORIDE IN ANHYDROUS

n-BUTANOL

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INTRODUCTION

Discussion of Transport Numbers

The passage of electric current through an electrolyte solution is effected by the motion of ions of opposite charge moving in opposite directions under an applied potential. The fraction of current carried by the positive ions is called the transport or transference number of the positive ion. Likewise, the fraction of current carried by the negative ion is called the transport number of the negative ion. In the classical example of potassium chloride in water, the transport numbers of potassium and chloride ions are 0.489 and 0.511 or simply the chloride ion carries a slightly larger portion of the current than does the potassium ion. This results in a small concentration shift between the anode and cathode compartments in a Hittorf transference cell experiment. By measuring the concentration change in either of the electrode compartments and knowing the electrode reactions and the total amount of current passed through the cell, it is possible to determine the transport numbers for the ions present in this case.

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History and Related Work

Transference numbers and transport phenomenon were first observed by Hittorf (1) in 1853. Hittorf's first apparatus was crude by present day standards, but was of extreme importance in that it was a new approach to the study of the properties of electrolyte solutions. Research workers such as Jones (2), Dole (2,3), MacInnes (3), and Washburn (4) did extensive transport work and made important improvements in apparatus and technique. Washburn's modification of the Hittorf cell is the classical design used in transport work even to the present time.

At least two other standard methods for determining transport numbers have been developed in recent years, but neither the moving boundary method nor the method based upon the emf of concentration cells with liquid junction are generally adaptable to non-aqueous solutions. It appears that any hope of obtaining any considerable amount of transport number data in non-aqueous solutions lies with the less accurate Hittorf method. The Hittorf method is limited by two main factors: (a) at least one and preferably both the electrode reactions must be reversible and (b) extreme accuracy is needed in the analysis of the solution (5). The Hittorf method also assumes that the solvent remains stationary and does not move with the solute.

Work has been done by Amis (6-11) and co-workers using ethanol and ethanol-water mixtures as solvents. Transference numbers and hydration numbers were determined in the mixed solvents for uranyl chloride, potassium chloride, silver perchlorate, lithium chloride, and sodium chloride. Amis also added sucrose as an "inert" reference substance in order to determine the true transference number. Since the ions transport solvent molecules during electromigration, the result is a dilution of the solution around one electrode and a decrease in solvent concentration near the other electrode. This has a marked effect on the value of the Hittorf transference number. Transference numbers obtained using the "inert" reference material are thus "corrected" for the movement of the solvent, and have been called the "true" transference numbers (12). This technique was first used by Nernst (13) and associates in 1900.

The procedure employed is essentially that of a Hittorf measurement. However, a second solute, such as sucrose or raffinose, is added to the solution, and instead of referring the changes of salt concentration to the solvent, as in the calculation of Hittorf transference numbers, the changes both of salt and of water are referred to the added solute. Collet (14,15) disagrees with Nernst and most early workers and gives evidence to show that the

"inert" reference is not stationary as Nernst assumed but also migrates with the ions.

A. M. Sukhotin (16-19) and his Russian co-workers have done extensive work with alkali metal halides and calcium chloride in ethanol, and n-butanol-hexane mixtures. These solvents have dielectric constants in the range of 4.77 to 2.16. Their data shows the ionization of calcium chloride in such solvents to be: $CaCl_2 \rightleftharpoons CaCl^+ + Cl^-$. Their conductance data indicates the absence of any ion triplets, such as $CaCl_3^-$, formed from a neutral molecule and a simple ion.

Statement of the Problem

This study had a threefold objective: (a) the development of a suitable apparatus and proper experimental techniques for the investigation of material transfer in the electrolysis of salts in non-aqueous solution; (b) the determination of transport numbers in the anhydrous cobaltous chloride-n-butanol system; and (c) a determination of the extent of hydration of the ion constituents present when the above system contained small amounts of water.

The basic experimental problem was the accurate determination of the ratio of water to ion constituent present in each compartment before and after electrolysis. From the results of the water analysis and from the transference num-

ber data it is possible to calculate the moles of water transferred per mole of solute transferred. In an experiment of this kind, however, one can only determine the average difference in hydration of the cationic and anionic species.

Transport numbers besides representing the fraction of current carried by each ionic species are directly related to the size and mobility of the ions present in solution and hence are dependent on temperature, concentration, viscosity of the solution, solvation of the ions and charge on the ions. However, the effect of small temperature, and concentration changes are usually negligible while the extent of solvation of the ions has by far the greatest effect on the transport numbers.

EXPERIMENTAL

Equipment

The transference cell was a Washburn modification (4) of the Hittorf cell (Figure 1). The cell was constructed of 25 mm i.d. glass tubing with a total length of approximately 150 centimeters. Its volume was 700 milliliters. The cell was divided into three compartments by two large hollow stopcocks. The middle compartment was 100 centimeters in length with each of the end compartments 25 centimeters long. The bore of the stopcocks was the same as the inside diameter of the glass tubing so there would be no turbulence or restriction in the stopcocks. All of the bends in the tubing were well rounded and annealed so that the inside of the cell was as smooth as possible. There was a standard-taper ground-glass joint at each end of the cell through which the electrodes were placed. The middle compartment had a ground glass opening near its center to allow withdrawal of the solution from the middle compartment. The stopcocks and the standard-taper joints were lubricated with Apiezon type N stopcock grease, which was found to be very resistant to attack by n-butanol.

The silver electrodes were made from 18-gauge high-purity silver wire. The wire was rolled into a coil so that approximately 100 cm, or about 40cm^2 surface area of

the wire was in contact with the solution.

A 50-gallon kerosene bath was maintained at $25^\circ C \pm 0.1^\circ C$. The bath was stirred continuously by circulating the kerosene with a pump. It was found that the temperature was uniform throughout the bath.

Two standard platinum dish silver coulometers were used. One was connected ahead of the cell and the other following the cell in the circuit to check for electrical leaks.

The D.C. power supply could supply up to 5000 volts. Its maximum current output was 30 milliamperes.

Materials

Solutions were prepared from reagent grade n-butanol and anhydrous reagent grade cobaltous chloride. Anhydrous n-butanol was prepared from reagent grade n-butanol by boiling off the minimum boiling azetrope. All solutions were made as close to 0.20 molal as possible by adding the calculated amount (25.97 grams) of anhydrous cobaltous chloride (dried at 150° C in vacuum oven for 24 hours) to each 974.03 grams of n-butanol. The solutions were stirred for 24 hours with a magnetic stirrer. The solutions were then allowed to stand for at least 24 hours in order to permit any insoluble residue to settle out. The top portion only was siphoned off and used since the bottom portion sometimes contained apparently undissolved cobaltous chloride. The solutions

were kept as anhydrous as possible. Water was added immediately before each electrolysis so that the desired water-to-cobalt mole ratio was obtained.

Analysis for water was done with Karl Fisher Reagent which had been standardized directly against water that same day.

Procedure

The cell and stopcocks were washed with hot soapy water and thoroughly rinsed with de-ionized water and acetone. Fresh Apiezon-N grease was applied to the stopcocks which were gently heated in order to spread the grease evenly over the stopcock. The cell was then dried by blowing dry air through it while the outside was flammed with a torch. The cell was stoppered immediately in order to keep it as dry as possible.

The electrode which was to serve as the anode was put into place and the cell filled with the desired Butanol-$CoCl_2$ solution. All the air bubbles were removed from the cell, the cathode put into place, and the cell securely mounted on a lucite frame. The lucile frame was designed to hold the cell rigid while in the constant temperature bath. The cell was then totally submerged in the thermostat for at least one hour in order to bring it to a temperature of $25^{\circ}C$.

The platinum dishes which served as cathodes in the silver coulometers were cleaned, dried, and placed in the coulometers. The lead wires were then connected in such a manner that the platinum dishes in both coulometers served as the cathodes (negative). The positive lead from the power supply was connected to the anode in the cell and the negative lead to the cathode.

The power supply was then turned on and the voltage adjusted so that the current was 7.0 milliamperes. It was necessary to pass about 500 coulombs of electricity which for a current of 7 ma required about 20 hours at 1500 to 4000 volts, depending on the amount of water in the solution.

Upon completion of an electrolysis, the stopcocks were carefully closed while the cell was still in the bath. Great care was taken to avoid shaking the cell and stirring the solution while closing the stopcocks.

The solution from the anode and cathode compartments are quantitatively transferred to previously weighed beakers. The beakers and solutions were then weighed to determine the weight of the anode and cathode solutions. Each solution was next transferred to a glass stoppered flask and stored for analysis. The anode and cathode compartments were washed with ethanol and the washings from each compartment saved for analysis. This is necessary in order to determine the total weight of solution present in each compartment.

The solution in the middle compartment was poured into a glass stoppered flask and saved for analysis. It is not necessary to know the total amount of middle solution, but most of the solution should be kept to insure uniform sampling.

Analyses for chloride were made in triplicate using standard gravimetric procedures. Precise chloride analyses

were needed for the anode, cathode, middle, anode wash, and cathode wash solutions.

In a preliminary check of the apparatus, aqueous potassium chloride solution was used and the transference numbers measured at 25°. The results are compared below with those reported by MacInnes (20).
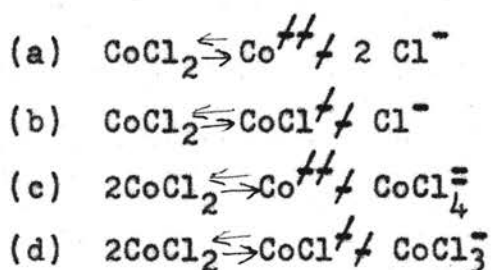
Molality	t+(this research)	t-(literature)
0.5	0.489	0.489
0.5	0.493	0.489

DISCUSSION OF RESULTS

Transference number data cannot tell how much of the total current has been carried by each individual ionic species present in a solution; however, it can give a qualitative answer to the question of what the predominate species present may be. If the ions present in a solution of a completely dissociated salt are relatively simple, the values of the transference numbers, t_+ and t_-, would be expected to be nearly equal to each other ($t_+ \approx t_- \approx 0.5$). As the ions in solution become more complex, the value of t_+ often approaches zero and the value of t_- approaches unity. This can be caused by the ordinarily positive metal ion becoming a part of a complex negative ion, and the metal then being transported toward the anode. This phenomenon can even cause an apparent negative transport number for the metal ion constituent if the predominating anionic species contains the metal ion. For example, in the case of potassium chloride where the ions may be considered simple, the reaction at the silver anode would be: $Ag + Cl^- \rightarrow AgCl + e^-$. The change in chloride ion concentration in the anode compartment per Faraday of current passed is obtained by considering that t_- equivalents of chloride

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ions enter and one equivalent of chloride deposits on the silver anode. The net change in equivalents of chloride ions in the anode compartment is a loss of $1-t_-$. Since the total current is carried by both the positive and negative ions, $t_+ + t_- = 1$, and therefore, $\Delta Cl = t_+$.

In the case of potassium chloride ($t_+ = 0.489$), there was a loss of chloride in the anode compartment. In the anhydrous cobalt chloride n-butanol system, however (Table I), an increase in chloride concentration in the anode compartment was found. Since the same type of silver anode was used as with potassium chloride, the anode reaction was again $Ag + Cl^- \rightarrow AgCl + e^-$. Since the reaction at the anode for both salts was the same, a gain of chloride in the anode compartment can only be explained if some or all of the negative ion constituent is present as complex ions such as $CoCl_3^-$ or $CoCl_4^=$. In order to maintain electrical neutrality, the corresponding positive ions likely would be $CoCl^+$ or Co^{++}. Some possible ionization processes can be represented by:

(a) $\quad CoCl_2 \rightleftharpoons Co^{++} + 2 Cl^-$

(b) $\quad CoCl_2 \rightleftharpoons CoCl^+ + Cl^-$

(c) $\quad 2CoCl_2 \rightleftharpoons Co^{++} + CoCl_4^=$

(d) $\quad 2CoCl_2 \rightleftharpoons CoCl^+ + CoCl_3^-$

As previously mentioned, it is impossible from the
experimental data to select from the above any pair of
ions and be certain that they are the only ionic species
present. All that one can do is to select those which
are most likely to predominate and see if the data can be
reasonably interpreted on the basis of such a choice.

Equation (a) can be eliminated as providing the prin-
cipal species since the negative value for t_+ indicates
complex negative ions containing cobalt present rather than
the simple ions of Co^{++} and Cl^-.

Equation (b) shows a complex positive ion, but not the
complex negative ion necessary for negative transference
numbers.

It would be possible also to have an apparent increase
in chloride concentration near the anode if the ionic species
present were $CoCl^+$ and Cl^- and if the cation were much more
highly solvated than the anion. The result would be a dilu-
tion near the cathode with a corresponding apparent increase
in chloride concentration near the anode. This is not be-
lieved to be the case for two reasons. First, there is no
evidence indicating the cation is much more highly solvated
in n-butanol than the anion. Secondly, one would expect
any water present in the solution to be transported out of
the anode region as cation hydrate water before the n-butanol
would be transported out with the cation. This would result

in a large drop in the water-to-cobalt mole ratio in the
anode compartment. Table II shows the water-to-cobalt mole
ratio of the solution in the original solution and in the
anode compartment after electrolysis. Analysis of this
data shows that some water and possibly some butanol is
transported with the solute; however, the amount trans-
ported is not sufficient to account for the gain in chloride
concentration in the anode compartment. If one assumes the
ionic species to be only $CoCl^+$ and Cl^-, then the net gain
in chloride ions near the anode would be: (a) one equivalent
of chloride ions deposited on the silver anode; (b) a loss
of t_+ equivalents of chloride transported toward the cathode;
and (c) a gain of t_- equivalents of chloride transported into
the anode region. The net result would be $\Delta Cl = t_- - 1 - t_+$
equivalents of chloride gained, since charge transfer requires
that $t_+ + t_- = 1$. The real transport numbers calculated in
this way still have values near zero and unity for the cation
and anion. Since these values still are not very reasonable,
consideration should be given to equation (c).

Equation (c) contains a complex negative ion but seems
an unlikely reaction when one considers the low dielectric
constant of the n-butanol solvent. Water has a dielectric
constant of 78.3 (21) at 25 C which is ten times that of
n-butanol (22). It is improbable that one will find an
appreciable concentration of bi-valent ions in a 0.2 molal
solution in a solvent of such low dielectric constant (23).

Equation (d) represents the most probable reaction. Both of the ions are univalent and the anion contains the necessary chloride to account for the observed increase in chloride in the anode compartments. Spectrophotometric study of $CoCl_2$ has also provided evidence for disproportionation of this type in methanol.

When the apparent transport number for the positive ion constituent $t_{\not}$ is plotted against the mole ratio of water-to-cobaltous chloride, the curve divides itself into three regions with "breaks" near mole ratios of 3:1 and 6:1 (Figure 2). These breaks can be accounted for by assuming the ions in the solution to be $CoCl^{\not}$ and $CoCl_3^-$ in equilibrium with $CoCl_2$.

$$2CoCl_2 \leftrightharpoons CoCl^{\not} \not\!\!+ CoCl_3^-$$
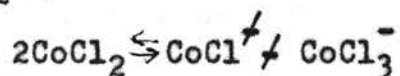
If the structure of the $CoCl^{\not}$ ion is assumed to be octahedral and the $CoCl_3^-$ ion assumed to be tetrahedral, the reaction

$$(e) \quad 2CoCl_2 \not\!\!+ 6H_2O \leftrightharpoons Co(H_2O)_5Cl^{\not} \not\!\!+ Co(H_2O)Cl_3^-$$
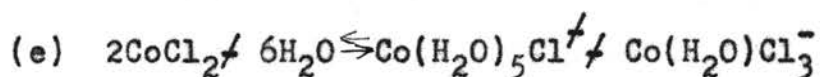
would account for the break at the 3:1 mole ration. When the mole ration of water to cobalt reaches 3:1 as in equation (e), any additional water added will occupy secondary coordination sites rather than primary sites in the octahedron or tetrahedron. The change in relative values of the transference numbers up to a 3:1 ratio then may be regarded as arising from changes in the mobility of the aquocomplexes relative to

the corresponding butanol complexes. This would also account for the flat region between mole ratios of 3:1 and 6:1. Any increase in the water-to-cobalt ratio above 6:1 would, of course, have an effect on the solvent causing the dielectric constant to increase rapidly and the solvent to become more like water. The relative hydration of $Co(H_2O)_5Cl^+$ and $Co(H_2O)Cl_3^-$ would also help explain the water that was observed to be transported to the cathode compartment during electrolysis (Table IV).

Previous discussion has dealt with the experimentally measured apparent transport number whose values are near zero and unity for t^+ and t_-. A theoretically more meaningful transport number can be calculated as for $CoCl^+$ and Cl^- by again assuming only $CoCl^+$ and $CoCl_3^-$ to be present (Table III), (Figure 3).

The reaction at the anode as before is: $Ag + Cl^- \rightarrow AgCl + e^-$ which results in the removal of one equivalent of chloride ion per Faraday of current. Owing to transference, there are t_- equivalents of $CoCl_3^+$ entering the anode compartment which results in $3t_-$ equivalents of chloride entering. Likewise, there are t_+ equivalents of $CoCl^+$ leaving the anode compartment due to transference. The net result is a gain of chloride represented by: $\Delta Cl(gain) = 3t_- - t_+ - 1$ equivalents per Faraday of current. Solving for t_+

$$t_+ = - \frac{\Delta Cl + 2}{4}$$

A sample calculation is shown in Appendix A.

Examination of (Table III) (Figure 3) shows that as the amount of water increases in the solution, the values for t^+ and t_- become more nearly equal. This is the expected behavior since the solute becomes more ionized with the addition of water.

As a part of the experiment, a determination was made by Karl Fisher analysis of the amount of water in the original solution and also of the amount of water left in each compartment after electrolysis. It was found, however, because of the small amounts of solute transferred to the anode compartment and the small total amounts of water present, the differences in the two sets of measurements were comparable to uncertainty in the analytical data. The same type of measurement using the middle compartment and the cathode compartment showed an increase in the amount of water transported into the cathode compartment with an increase in water concentration in the original solution (Figure 4). This increase represents the difference in the amount of water entering the cathode compartment and the amount of water leaving the cathode compartment. This is in agreement with the concept that positive ions are more highly hydrated than negative ions.

If one attempts to assign absolute hydration numbers, one must arbitrarily assume the hydration number of one ion

in order to calculate the hydration number of the other ion.
In view of the low accuracy of the measurements, this was
not attempted; it may be pointed out, however, that as the
amount of water in the solution increases the difference
in the amount of water transported by the cation and anion
increases. This seems reasonable if one pictures the water
being carried by the negative ion as primarily tightly
bound water and the water carried by the positive ion as
tightly bound water plus additional loosely bound secondary
water. With better data, it would be possible to test the
hypotheses regarding the disproportionation into

$$Co(H_2O)_5\ Cl^+ \quad and \quad Co(H_2O)\ Cl_3^-.$$
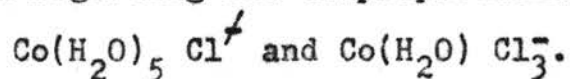
SUMMARY

This study involved (a) adapting the Hittorf Cell to non-aqueous solvents; (b) the determination of transference numbers of cobaltous chloride in n-butanol; and (c) the determination of the predominate ionic species present in the solution.

The Washburn modification of the Hittorf Cell was shown to be applicable to both aqueous and non-aqueous solutions.

The value of t_+, the transference number of the positive ion in solution, was a small negative number. This result can only be explained by assuming $CoCl^+$ and $CoCl_3^-$ to be the predominate ions present in solution.

The moles of water transferred per mole of cobalt chloride transferred increased linearly with increasing mole ratios of water to cobalt chloride. The moles of water transferred toward the cathode ranged from 1.3 to 2.5 as the mole ratio of cobalt chloride in the original solution increased from 2 to 7.38.

TABLE I

TRANSFERENCE NUMBERS OF COBALT CHLORIDE IN ANHYDROUS n-BUTANOL AT 25° C.

$H_2O/$ $CoCl_2$ Mole Ratio	Grams Butanol in Anode	Grams $CoCl_2$ in Anode	Grams $CoCl_2$ in Middle	Grams $CoCl_2$ Transferred	Equiv. $CoCl_2$ Transferred	Faradays Current	Apparent t_+	$*t_+$	Molality of Original Solution
0.06	75.405	2.0964	2.0534	0.0430	0.000662	0.006303	-0.105	0.474	0.2107
1.01	75.145	1.7632	1.7351	0.0281	0.000432	0.005995	-0.072	0.482	0.1782
2.04	75.782	1.9322	1.9117	0.0203	0.000312	0.006378	-0.049	0.488	0.1944
2.93	75.792	2.0437	2.0267	0.0170	0.000261	0.006776	-0.039	0.490	0.2055
4.53	75.891	2.0294	2.0108	0.0186	0.000286	0.00730	-0.038	0.491	0.2039
5.36	75.379	1.6934	1.6793	0.0141	0.000217	0.00573	-0.038	0.491	0.1720
5.58	75.553	2.0887	2.0774	0.0113	0.000174	0.00485	-0.036	0.491	0.2114
7.10	75.358	1.9971	1.9924	0.0047	0.000072	0.00638	-0.011	0.497	0.2040
7.38	75.872	2.0061	1.9978	0.0023	0.000035	0.00489	-0.007	0.498	0.2035

*Calculated assuming only $CoCl^+$ and $CoCl_3^-$ ions

TABLE II

MOLE RATIOS OF WATER TO COBALT CHLORIDE IN ORIGINAL
SOLUTIONS AND IN ANODE AFTER TRANSFERENCE

Mole Ratio of Water to Cobalt Chloride in Original Solution	Mole Ratio of Water to Cobalt Chloride in Anode After Transference
7.38	7.34
7.10	7.10
5.58	5.62
5.36	5.25
4.53	4.43
2.93	2.88
2.04	2.00

TABLE III

COMPARISON OF TRANSFERENCE NUMBERS OF COBALT CHLORIDE IN n-BUTANOL ASSUMING THE IONS PRESENT TO BE $CoCl^+$ AND $CoCl_3^-$ OR $CoCl^+$ AND Cl^-

Mole Ratio of Water to $CoCl_2$	Apparent t_+	t_+ Assuming $CoCl^+$ and $CoCl_3$	t_- Assuming $CoCl^+$ and $CoCl_3^-$	t_+ Assuming $CoCl^+$ and Cl^-
0.06	−0.105	0.474	0.526	−0.053
1.01	−0.072	0.482	0.518	−0.036
2.04	−0.049	0.488	0.512	−0.025
2.93	−0.039	0.490	0.510	−0.020
4.53	−0.038	0.491	0.509	−0.019
5.36	−0.038	0.491	0.509	−0.019
5.58	−0.036	0.491	0.509	−0.018
7.10	−0.011	0.497	0.503	−0.006
7.38	−0.007	0.498	0.502	−0.004

TABLE IV

MOLES OF WATER TRANSFERRED PER MOLE OF
TRANSFERRED COBALT CHLORIDE

Mole Ratio of Water to $CoCl_2$	Moles of Water Transferred	Moles of $CoCl_2$ Transferred	Moles of Water Transferred Per Mole of $CoCl_2$ Transferred
7.38	0.005540	0.002245	2.47
7.10	0.006570	0.002780	2.36
5.58	0.007022	0.002400	2.93
5.36	0.005370	0.002890	1.86
4.53	0.007610	0.003950	1.93
2.93	0.005040	0.003890	1.30
2.04	0.005330	0.003510	1.52

FIGURE I

HITTORF TRANSFERENCE CELL

PLUG

Ag ELECTRODE

EXTRACTION
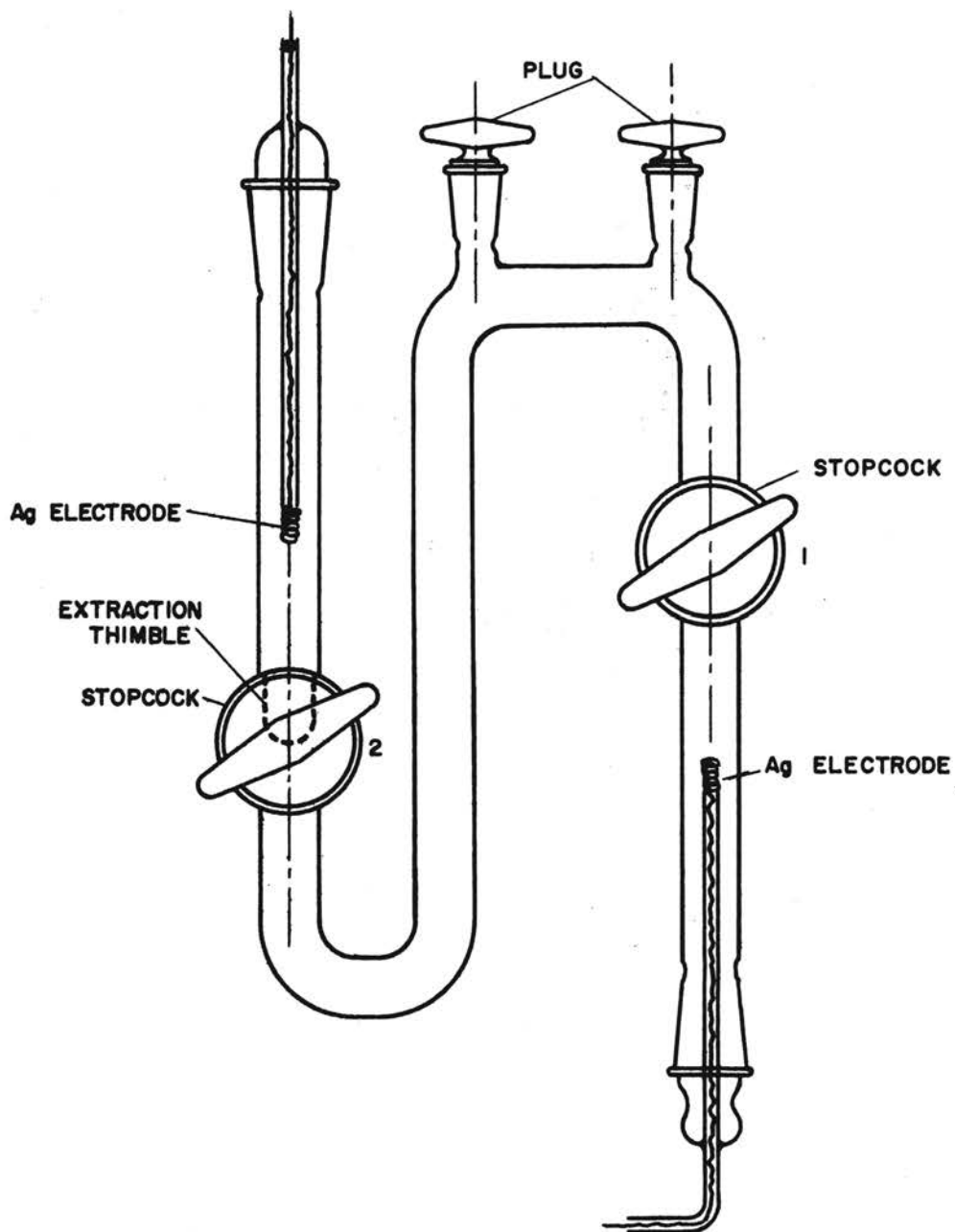THIMBLE

STOPCOCK

STOPCOCK

Ag ELECTRODE

FIGURE 2

APPARENT TRANSFERENCE NUMBERS
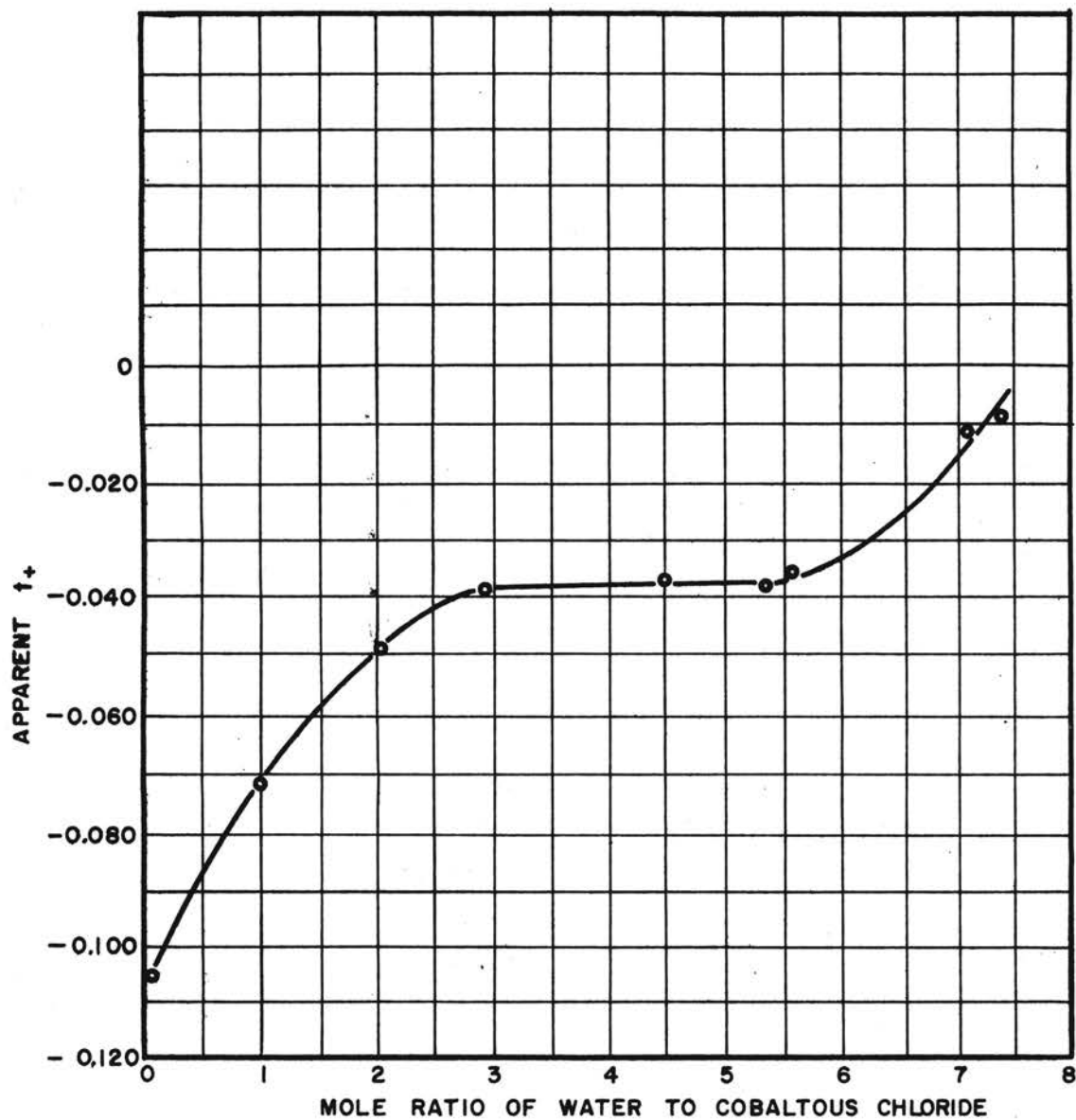## FOR COBALT CHLORIDE IN n-BUTANOL AT 25°C.

FIGURE 3

TRANSFERENCE NUMBERS FOR COBALT CHLORIDE
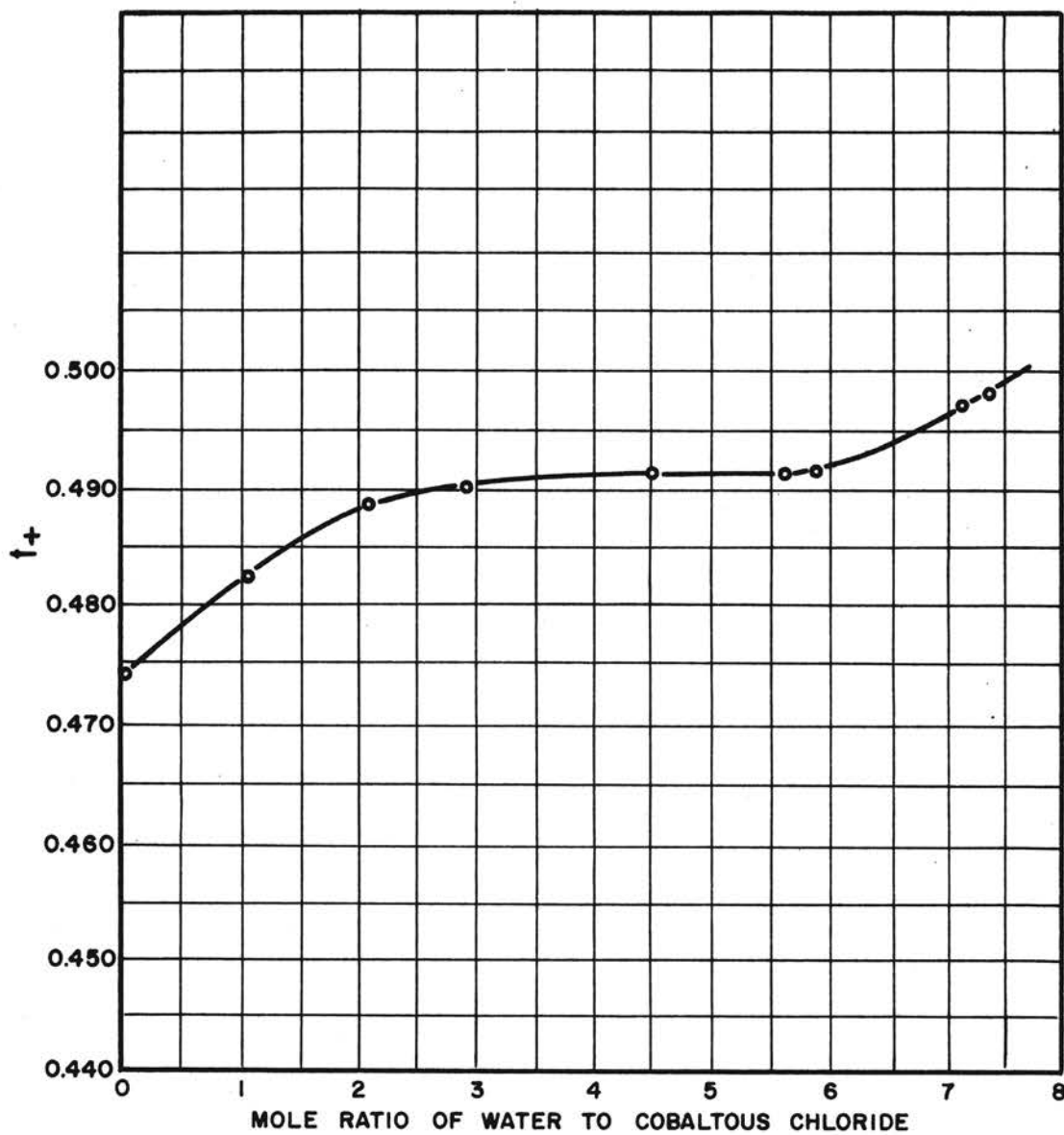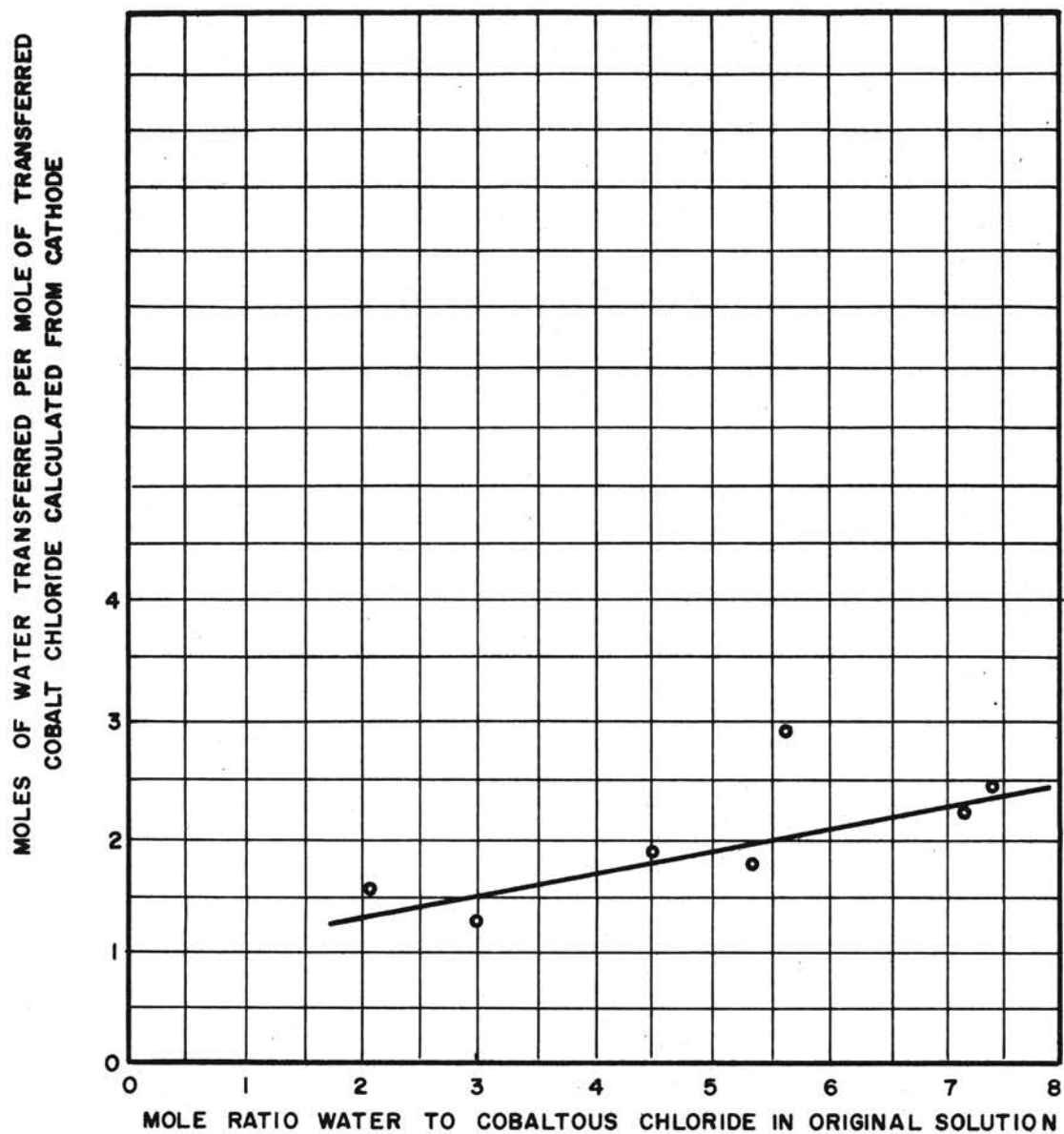## IN n-BUTANOL ASSUMING $CoCl^+$ AND $CoCl_3^-$, AT 25°C.

FIGURE 4

MOLES OF WATER TRANSFERRED PER MOLE OF TRANSFERRED COBALT CHLORIDE VERSUS MOLE RATIO OF WATER TO COBALT CHLORIDE IN ORIGINAL SOLUTION AT 25°C.

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APPENDIX A

The general procedure is to calculate the total
weight of solvent present in the anode compartment and
the total amount of solute associated with it. The
weight of solute associated with this same amount of
solvent in the middle compartment is calculated. The
equivalents of solute transferred are calculated and
divided by the number of Faradays of current passed.
For example: The AgCl precipitate from a 8.7359 gram
sample of anode solution weighed 0.4796 grams. This is
equivalent to 0.2172 grams of $CoCl_2$ $(0.4796 \times \dfrac{129.85}{2(143.34)})$
AgCl = 143.34; $CoCl_2$ = 129.85.

The weight of the anode solution was 76.55 grams;
therefore, the weight of $CoCl_2$ in the anode solution is
1.9035 grams. Since a small portion of the anode solution
could not be weighed directly, the anode compartment was
washed with ethanol and the weight of the $CoCl_2$ in the
washings was added to the weight of $CoCl2$ in the bulk of
the solution. 1.9035 $\neq$ 0.0287 = 1.9322g $CoCl_2$(Total)
The total amount of anode solvent containing the total
$CoCl_2$ would be:

$$\text{wt anode solvent} = \dfrac{(76.55 - 1.9035)(1.9322)}{1.9035} = 75.782.$$

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In the middle compartment, the AgCl precipitate from an 8.8749g sample weighed 0.4822g. This is equivalent to 0.2184g of $CoCl_2$.

The total weight of $CoCl_2$ in 75.782g of middle solvent is $\frac{(0.2184)(75.782)}{(8.8749-0.2184)} = 1.9119g$ $CoCl_2$.

Since there is 1.9322g of $CoCl_2$ associated with 75.782 grams of solvent in the anode compartment and 1.9119g of $CoCl_2$ associated with the same weight of solvent in the middle compartment, the net change in $CoCl_2$ is a gain of 0.0203g of $CoCl_2$ in the anode compartment. (1.9322 - 1.9119 = 0.0203g $CoCl_2$) or 0.000312 equivalents of chloride.

There were 0.6878g of silver deposited in each coulometer. This is equivalent to 0.006378 Faradays of current. Since $t\neq = \frac{\triangle Cl}{F}$, the transference number for the positive species is $\frac{-0.000312}{0.006378} = -0.049$.

Assuming the ions present to be $CoCl^{\neq}$ and $CoCl_3^{-}$, the values for $t\neq$ and $t-$, using $\frac{-\triangle Cl\neq2}{4} = t\neq$, are

$\frac{-0.000312 \neq 2(0.006378)}{4(0.006378)} = 0.488 = t\neq;$

$t\neq \neq t- = 1$; therefore, $t- = 0.512.$

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