NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

THE DEPENDENCE OF MEASURED CHARGE SEPARATION UPON THE NATURE AND POLARIZATION OF THE BASE DURING FREEZING OF DILUTE AQUEOUS SOLUTIONS

by

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The author wishes to express his appreciation to the many members of the Faculty and Research Division of New Mexico Institute of Mining and Technology for their assistance and suggestions; the writer is especially grateful to Dr. E. J. Workman for suggesting the problem, Dr. Marks Brook for many interesting discussions, and to Dr. Walter Drost-Hansen for his direction of this research.

CHAPTER I

INTRODUCTION

In the fall of 1946, Workman and Reynolds[1] discovered that potentials were developed when dilute aqueous solutions were frozen. The potentials were measured between an unfrozen solution and a metal freezing base. They found this phenomenon occurred only when freezing was taking place, and no potential could be detected if the freezing stopped (or melting began); further, the sign and magnitude of the potential depended upon the concentration and nature of the solute. The potentials were capable of maintaining currents through an external resistance up to about one microampere.

Workman and Reynolds[1] tested many substances and found that some compounds produced a positive and others a negative potential of the liquid phase in relation to the solid phase. They found that the behavior of ammonium and fluoride ions was most outstanding and offered suggestions to explain the behavior of these ions. They suggested that the charge separation was the result of the selective incorporation of either the anion or cation into the ice.

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[1] E. J. Workman and S. E. Reynolds, "Electrical Phenomena Occurring During the Freezing of Dilute Aqueous Solutions and Their Possible Relationship to Thunderstorm Electricity," Phys. Rev., 78, 254 (1950).

Workman and Reynolds[1], Schaefer[2], and Gill[3] have shown that there is an "optimum concentration" which produces maximum freezing potential under open circuit conditions. Optimum concentration is defined in this work as that concentration of electrolytes which gives the maximum potential when solutions of different concentrations are frozen under otherwise identical conditions. Carlin and Drost-Hansen[4] have shown that the optimum concentration which results in maximum measured charge separation (over a wide range of external currents) coincides with the optimum concentration which results in maximum potentials within the experimental error.

Carlin and Drost-Hansen[4] have measured optimum concentrations for forty compounds and have noted a relationship between optimum concentration and entropy of the substances in solution. They have also noted a relationship between the incorporability of an ion and its ionic radius. The incorporability of an ion is defined as the tendency of an ion to be taken into the ice relative to a particular ion chosen as a standard.

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[2] Vincent J. Schaefer, "A Confirmation of the Workman-Reynolds Effect", Phys. Rev., 77, 721 (1950).

[3] E. W. B. Gill, "Electrification by Freezing", British Journal of Applied Physics, Supp. #2, p. S16 (1953).

[4] J. T. Carlin and W. Drost-Hansen, (unpublished report) (1955).

Most of the studies of these phenomena have involved the formation of ice on a solid substrate. Reynolds, Brook and Gourley[5], and Drost-Hansen[6] have noted anomalous results when the freezing bases have been pretreated by electrolysis. At the suggestion of Dr. E. J. Workman, the author undertook a series of investigations to establish a possible relationship between the charge separation efficiency and the nature and polarization of the material on which the ice forms. The results of these studies are presented in this thesis.

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[5] New Mexico Institute of Mining and Technology, "Thunderstorm Electricity", U. S. Army Signal Corps Research Project 172-B, Report No. 9 (1955).

[6] Walter Drost-Hansen (Personal Communications).

CHAPTER II

EXPERIMENTAL PROCEDURES

The equipment used in this investigation is similar to that described by Workman and Reynolds[1]. The equipment, materials and methods of measurements are outlined below:

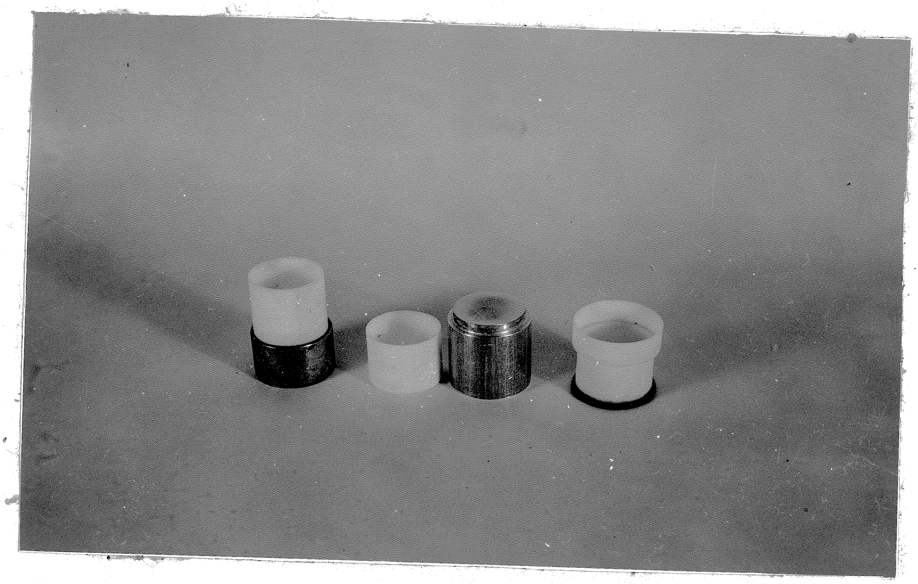
Equipment and Materials.

Preparation of Solutions.

Chemicals used in these experiments are commercially prepared compounds meeting A.C.S. standards. The solutions are prepared by weighing the compound and dissolving in ion exchange water (2-3 megohm cm resistivity) to make one liter of 10^{-2} M solution. Other concentrations are made by diluting the 10^{-2} M stock solution using ion exchange water.

Freezing Cups.

The freezing cups used in this work were designed so as to have a flat freezing base of a thermal and electrical conducting material with walls of a chemically inert, electrical non-conducting material. In these experiments, teflon was used for the walls of the freezing cups. The bases were made of solid copper, solid aluminum,



FREEZING CUPS

FIGURE 1

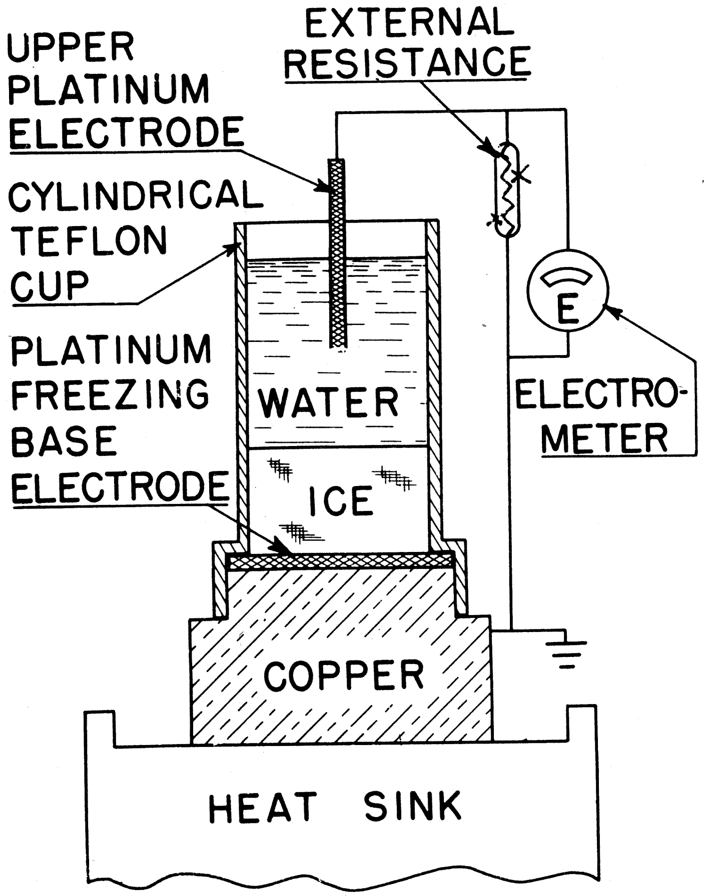
solid carbon, nickel (plated on copper) and gold (plated on copper). Figure 1 is a picture of some typical freezing cups.

Refrigeration.

Two refrigerators were used in these tests. Each refrigerator is fitted with a large copper rod in good contact with the refrigerating surfaces and extending to the top of the refrigerator where it is used as the freezing block. One freezing block was maintained at a temperature of approximately -20° C. and the other at a temperature of approximately -65° C.

Apparatus for Measuring Potentials and Charge Separation.

The apparatus for measurements of potentials and charge separation is shown in Figure 2. It consists of a vacuum tube electrometer, shunt resistance, and a Brown recorder. The magnitude of the shunt resistance was chosen such that the resultant voltages to be measured were relatively large compared to thermal and contact potentials. Thermal and contact potentials are rarely larger than one-half volt.



APPARATUS FOR MEASURING FREEZING POTENTIALS.

Figure 2

Measurements.

Potentials.

The measurement of freezing potentials is performed under open circuit conditions, i.e., infinite external resistance. This measurement gives the potential difference between the unfrozen solution and the metal freezing base. The electrometer used has an input resistance of approximately 10^{14} ohms.

Charge Separation.

To measure the amount of charge separation, a shunt resistance is added to the circuit allowing an external current to flow. The potential difference across the known resistance then permits the calculation of the current in the external circuit.

Concentration of Alkali Ions.

The concentration of the alkali metal ions in both the liquid and solid phase was determined using the Model B. Beckman Flame Spectrophotometer. The standard procedure of comparing the solution of unknown concentration with standard solutions was followed. It proved impractical to attempt to measure the halide concentration by ordinary analytical means at these concentrations.

attempt to measure the halide concentration by ordinary analytical means at these concentrations.

RESULTS

Dependence of the Optimum Concentration on the Freezing Base Material.

A series of measurements were made to determine whether the material on which the ice formed had any effect on the optimum concentration. Using solutions of potassium chloride, runs were made with freezing cups having bases of nickel, gold, aluminum, copper and carbon. These runs were made using the same freezing block at approximately -60° C. The bases, made of different materials and different lengths, had different thermal conductivities. The calculated thermal conductances are tabulated in Table I.

The results of these measurements are shown in Figure 3. Table I is the summary of the charge separations and optimum concentrations measured in these experiments. These measurements were made with a shunt resistance of 1000 megohms.

CHAPTER III

RESULTS

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A series of measurements were made to determine whether the material on which the ice formed had any effect on the optimum concentration. Using solutions of potassium chloride, runs were made with freezing cups having bases of nickel, gold, aluminum, copper and carbon. These runs were made using the same freezing block at approximately -20° C. The bases, made of different materials and different lengths, had different thermal conductivities. The calculated thermal conductances are tabulated in Table I.

The results of these measurements are shown in Figure 3. Table I is the summary of the charge separations and optimum concentrations measured in these experiments. These measurements were made with a shunt resistance of 1000 megohms.

OPTIMUM CONCENTRATION FOR DIFFERENT FREEZING BASES

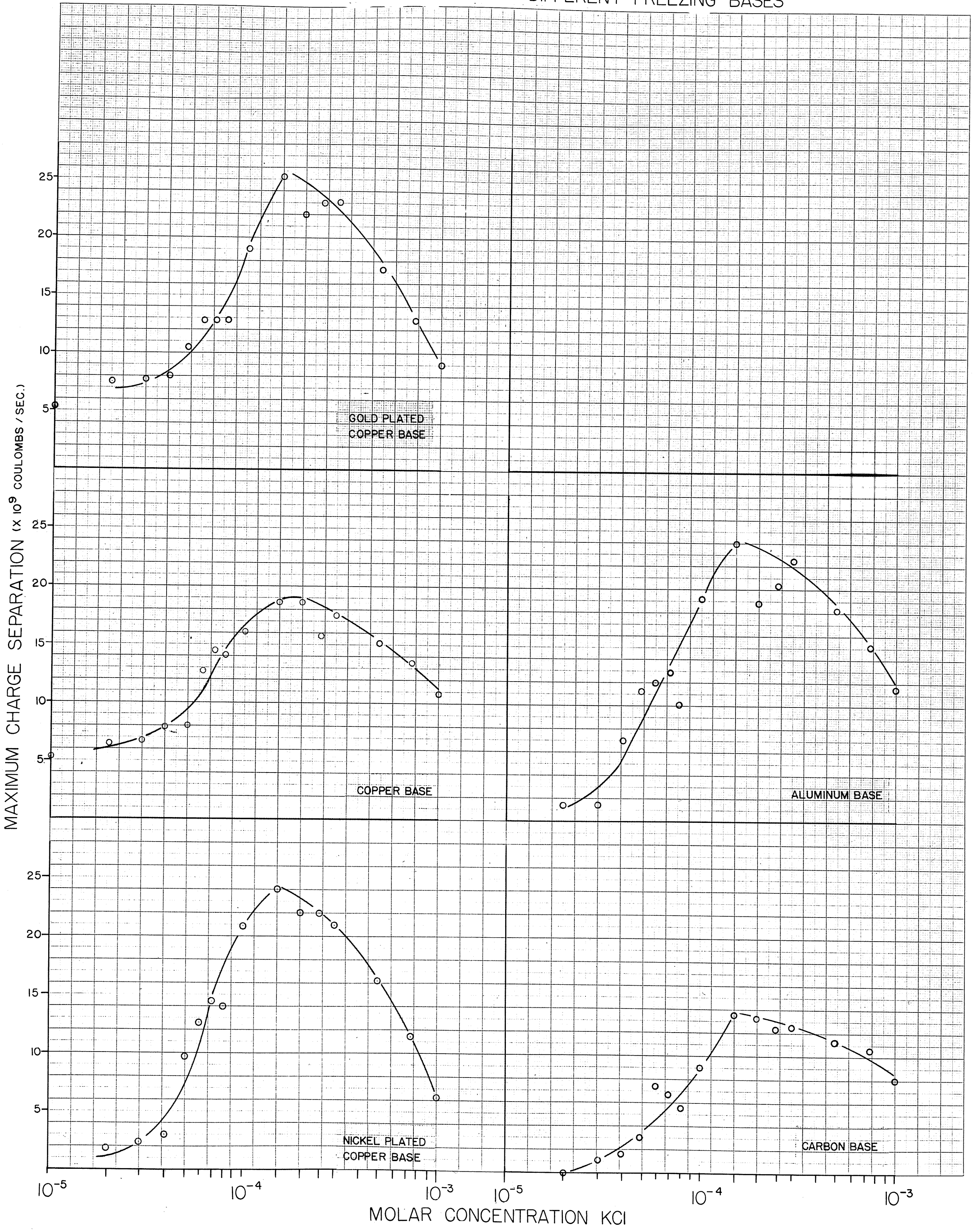


FIGURE 3

Table I - Optimum Concentration and Maximum Measured Charge Separation for Different Freezing Bases.

BASE	THERMAL CONDUCTANCE* cal/cm^2 sec deg	FREEZING RATE gmole ice/min.	OPTIMUM CONCENTRATION	MAXIMUM CHARGE SEPARATION Coulombs/sec.
Carbon	.475	0.060	1.5×10^{-4}	13.5×10^{-9}
Aluminum	1.192	0.055	1.5×10^{-4}	24.0×10^{-9}
Copper	2.81	0.061	1.5×10^{-4}	18.5×10^{-9}
Gold plated on copper	3.18	0.068	1.5×10^{-4}	26.0×10^{-9}
Nickel plated on copper	1.96	0.057	1.5×10^{-4}	24.0×10^{-9}

*Thermal conductivity coefficient/length of freezing base. Freezing block approximately -20° C.

Dependence of Optimum Concentration on the Freezing Rate.

The heat conductivities of the freezing bases vary, resulting in different freezing rates; it was of interest, therefore, to study the effect of the freezing rate upon the optimum concentration. Runs were made using solutions of potassium chloride on freezing blocks at different temperatures. Using a nickel plated copper base and a freezing block temperature of about -20° C., an initial freezing amounting to about 0.104 gmole ice during the first minute was observed, while for a temperature of about -65° C., using the same freezing cup, an initial freezing amounting to about 0.167 gmole of ice during the first minute was measured. The results of these runs are plotted in Figure 4. It can be seen from this graph that the optimum concentration changes from 3×10^{-4} at the lower freezing rate to 7×10^{-5} for the higher freezing rate. At the same time, the maximum measured charge separation increases from 0.134 to 0.349 microcoulombs/second.

To investigate the amount of potassium ion incorporated into the ice for different freezing rates, a solution of 10^{-4} M potassium chloride was partially frozen at two different freezing rates. The ice and the unfrozen solution were separated and the concentration of potassium in both phases was determined with a flame spectrophotometer. The results of these runs are plotted in Figure 5. It can be seen from Figure 5 that, as more ice forms, the concentration of potassium in the solid phase decreases. Also from Figure 7, we see that as more ice forms the freezing rate decreases. Thus, the decrease in potassium concentration in the solid phase must depend upon the freezing rate.

The total measured charge separation for each freezing was calculated and plotted against the amount frozen. The calculations were made for both freezing rates, and the results are plotted in Figure 6. It is evident from the graph that the total charge separation is directly proportional to the amount frozen; the proportionality constant is determined by the freezing rate.

To see if the addition of ammonium ions would influence the concentration of the potassium ions incorporated into the ice, a 10^{-4} M solution with respect to both potassium chloride and ammonium carbonate was frozen. Although the addition of the ammonium ion to the potassium chloride caused a large change in both the sign and magnitude of the measured charge separated during freezing, the concentration of potassium ion in the solid phase did not materially change. It appears that the presence of ammonium ion in the solution does not influence the amount of potassium ion incorporated into the ice.

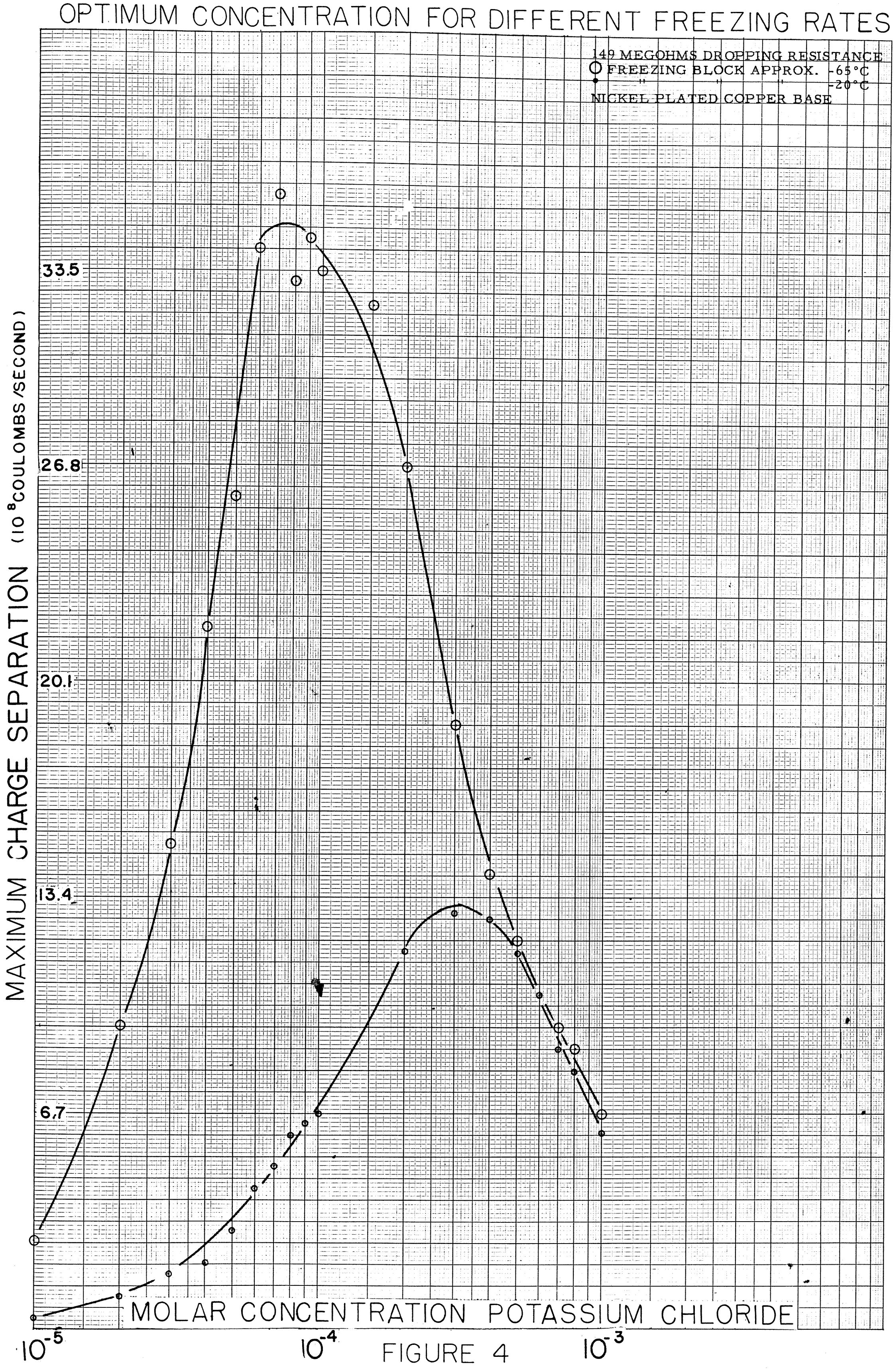

OPTIMUM CONCENTRATION FOR DIFFERENT FREEZING RATES
149 MEGOHMS DROPPING RESISTANCE
○ FREEZING BLOCK APPROX. -65°C
● " " " -20°C
NICKEL PLATED COPPER BASE
MAXIMUM CHARGE SEPARATION (10⁸ COULOMBS/SECOND)
33.5
26.8
20.1
13.4
6.7
MOLAR CONCENTRATION POTASSIUM CHLORIDE
10⁻⁵
10⁻⁴
10⁻³

FIGURE 4

CONCENTRATION OF POTASSIUM FOR DIFFERENT FREEZING RATES

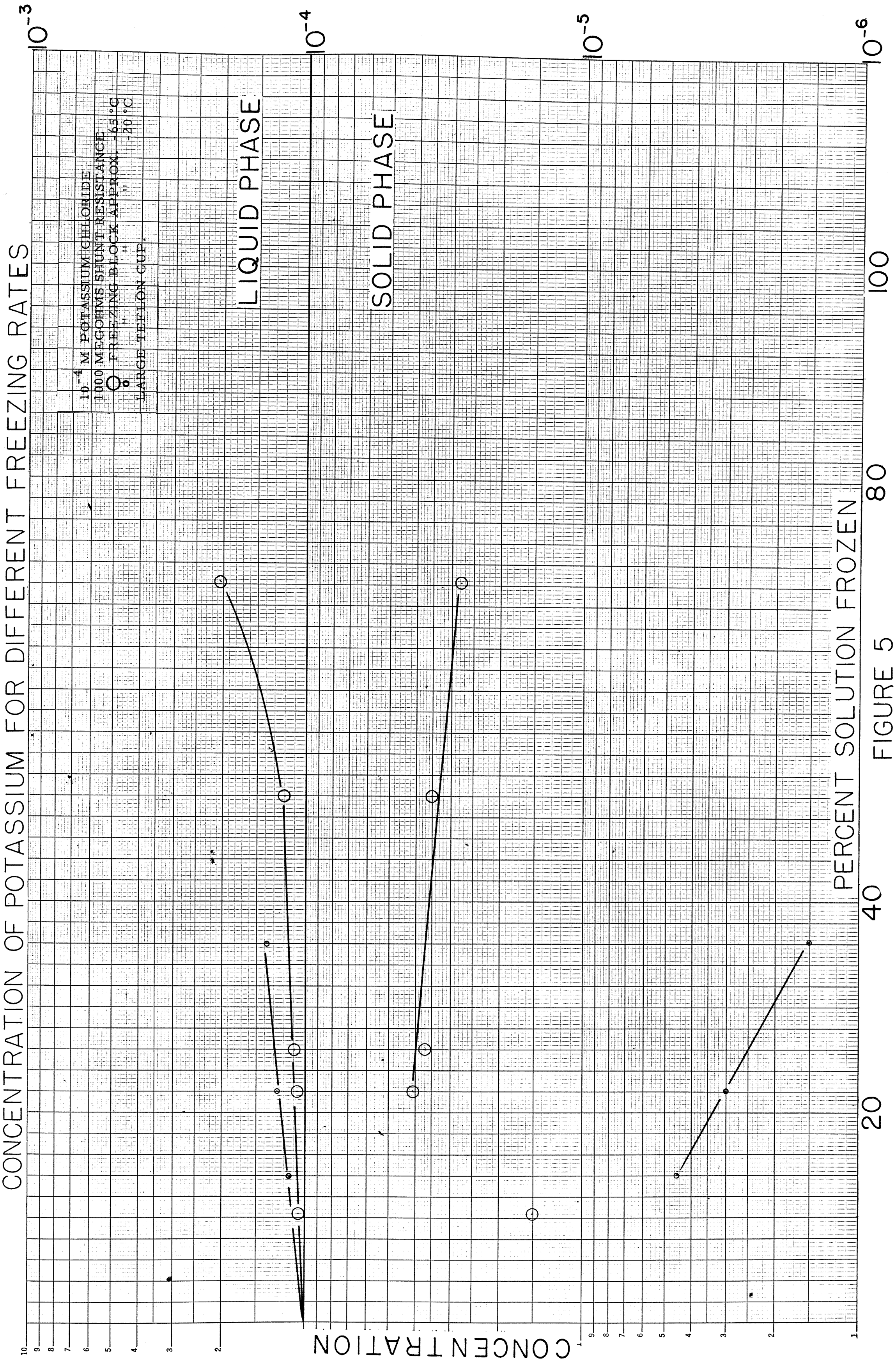


FIGURE 5

TOTAL CHARGE SEPARATION FOR DIFFERENT FREEZING RATES

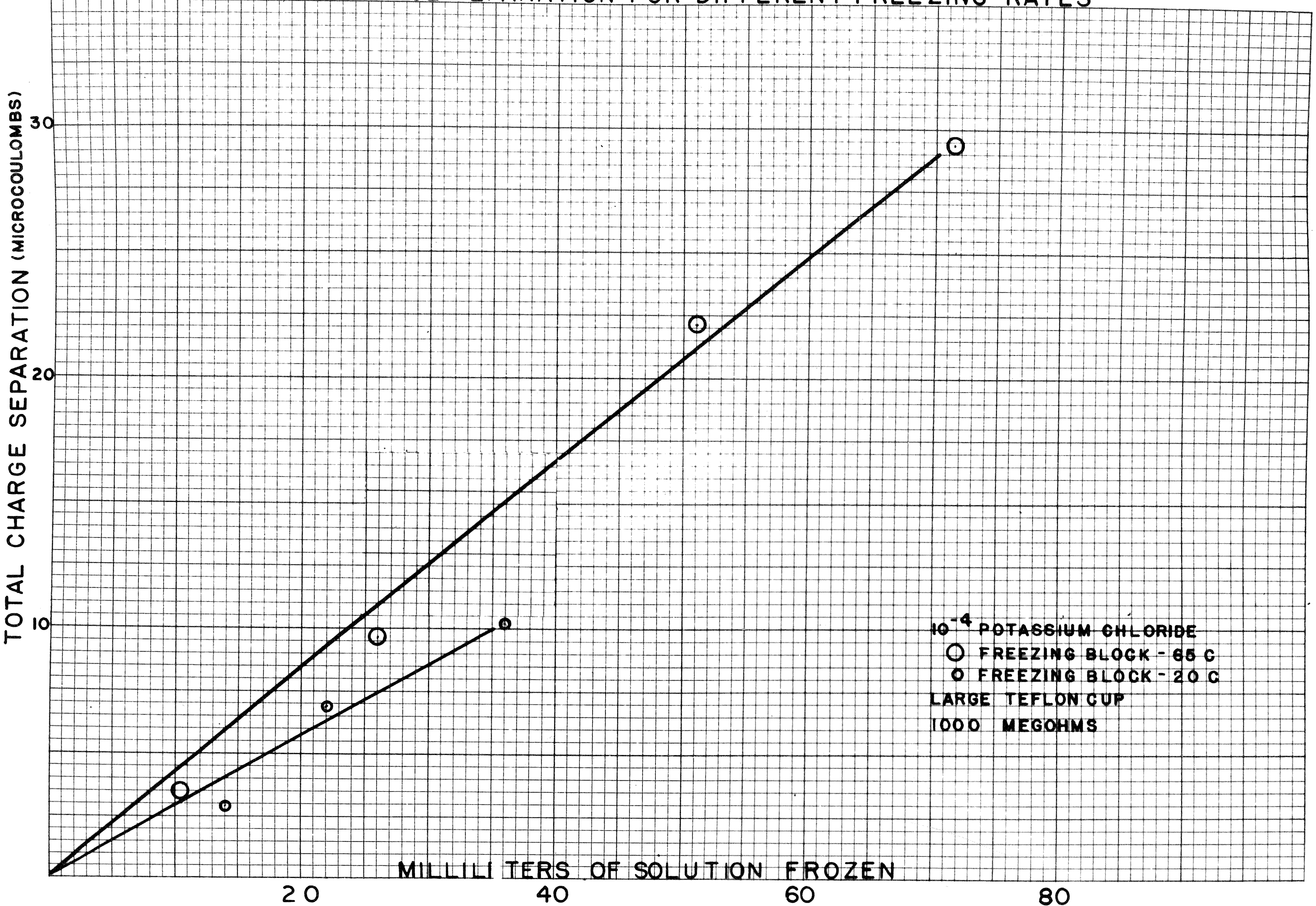


FIGURE 6

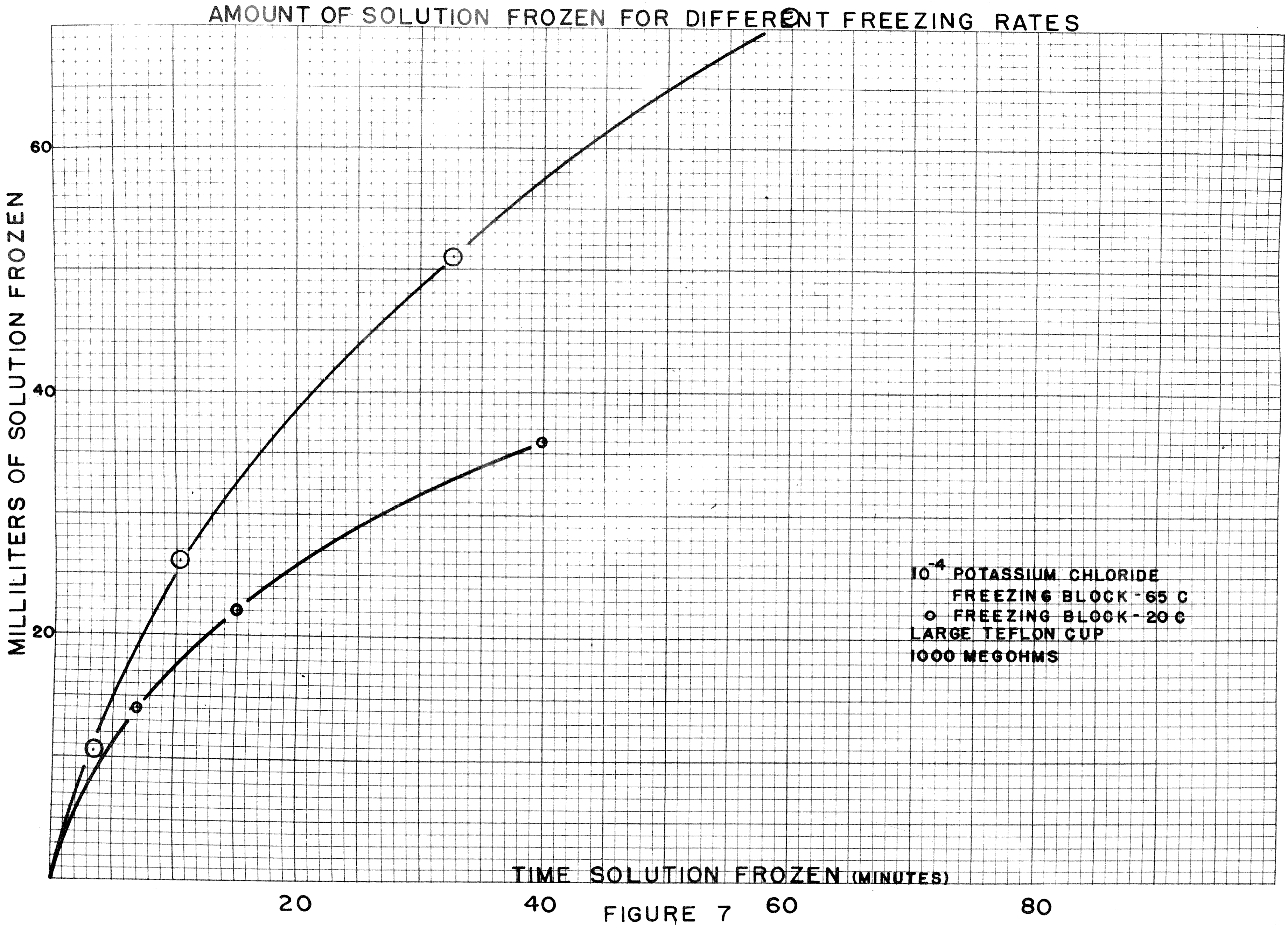
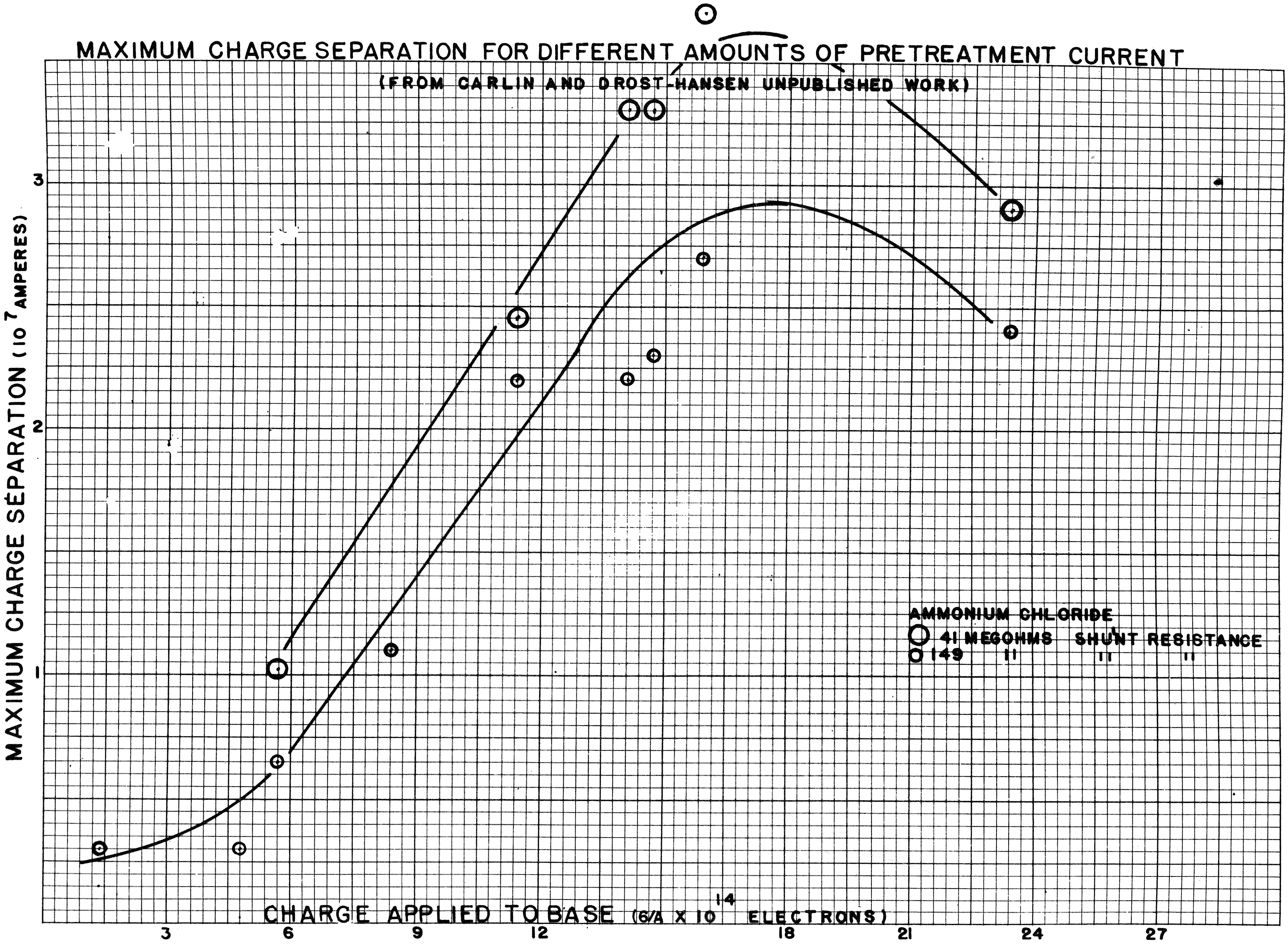

AMOUNT OF SOLUTION FROZEN FOR DIFFERENT FREEZING RATES
MILLILITERS OF SOLUTION FROZEN
60
40
20
TIME SOLUTION FROZEN (MINUTES)
20
40
60
80
10^{-4} POTASSIUM CHLORIDE
FREEZING BLOCK -65 C
○ FREEZING BLOCK -20 C
LARGE TEFLON CUP
1000 MEGOHMS

FIGURE 7

Effect of Electrolytic Treatment of the Freezing Base.

When a solution of ammonium chloride is frozen on a nickel base, a measured charge separation is observed such that the liquid phase is negative with respect to the solid phase. If before freezing, however, a current is passed through the solution using the freezing base as the negative electrode, the measured charge separation increases up to forty times the measured charge separation when the base was not subjected to electrolytic pretreatment. This effect has been noticed by Reynolds, Brook and Gourley[5] and Drost-Hansen[6] and has led to an investigation of this effect by the author. The earliest studies of a more quantitative nature of this phenomena were those of Carlin and Drost-Hansen[4], where the behavior of ammonium chloride solutions were observed when frozen on a nickel base.

> "Using a solution of 10^{-4} M ammonium chloride, current was passed through the solution before freezing. The time and current was measured and the number of coulombs calculated. Immediately after this treatment, freezing was allowed to take place and the amount of charge separation was measured. A plot of charge separation versus coulombs passed through the cup in the pretreatment is shown in graph below (Figure 8 in this paper). A maximum, or leveling off, is observed for approximately 150 x 10^{-5} coulombs. This number may be converted into the number of ions per cm^2 freezing base."



MAXIMUM CHARGE SEPARATION FOR DIFFERENT AMOUNTS OF PRETREATMENT CURRENT

(FROM CARLIN AND DROST-HANSEN UNPUBLISHED WORK)

FIGURE 8

Using the method described above, a solution of 3 x 10^{-4} M potassium chloride was pretreated in cups with different freezing base materials, such as gold, aluminum, etc. Measurement was made of the current applied during pretreatment and also of the measured charge separated during freezing. The results of these measurements are shown in Figure 9. The untreated bases invariably yield the largest measured charge separation. The measured charge separation decreases to a lower, relatively constant value irrespective of the direction of the current applied during pretreatment. The high value for an aluminum base pretreated with an oxygen layer may be that the oxygen combines with the aluminum to form alumina (Al_2O_3) which would have a conductance between that of pure aluminum and a layer of oxygen. Thus, the effects of a pretreated base, when using potassium chloride solution, do not parallel the effects observed when freezing an ammonium chloride solution.

When the base is pretreated, a gaseous layer is deposited on the freezing base and the measured charge separation is quite different from that measured for an untreated base. Thus, it is of importance to find the most efficient method of removing the gaseous electrolytic layer. The following methods were studied to determine how effectively this layer could be removed.

Dissolution and Diffusion.

If there is a delay between pretreatment and freezing, the gaseous layer should dissolve and diffuse into the solution. Many runs were made to see if a relationship could be found between such a delay time and the measured charge separation. Many factors, such as absorption of gases from the atmosphere, make it difficult to get a quantitative relationship but, qualitatively, it appears that increasing the time between pretreatment and freezing decreases the effect of pretreatment so that the resulting charge separation tends toward the value measured for charge separation when using an untreated base.

Stirring.

The solution was stirred after pretreatment with a glass spatula at 300 revolutions per minute. The results were similar to those described above.

Ultrasonic Vibrations.

A solution of ammonium chloride was first frozen on an untreated base and the measured charge separation recorded. The base was next pretreated (base both negative and positive) and the measured charge separation again noted.

The bases were again pretreated but this time subjected to ultrasonic vibrations and the measured charge separation recorded. Ultrasonic waves with a frequency of 22 KC were applied to the base from a Mullard ultrasonic transducer. The results (tabulated in Table II) of these runs are of a qualitative nature rather than quantitative, since no absolute measure can be assigned to the efficiency with which the vibrations can be applied to the base. In every case where the base was treated with ultrasonic vibrations after pretreatment, the value of the measured charge separation returned to a value near that found for an untreated base. This shows that the gaseous electrolytic layer is largely removed.

Table II- Results of Ultrasonic Vibrations on a Pretreated Base Using an Ammonium Carbonate Solution.

Charge on Base	Vibration Time (minutes)	Potential Across 1000 megohms (volts)
None	0	20
Negative	0	100
Negative	1	18
Positive	0	2
Positive	1	16

Approximately same amount of pretreatment current was passed through all the samples. Charge separation measured across 1000 megohms.

CHARGE SEPARATION FOR DIFFERENT AMOUNTS OF PRETREATMENT ON DIFFERENT FREEZING BASES

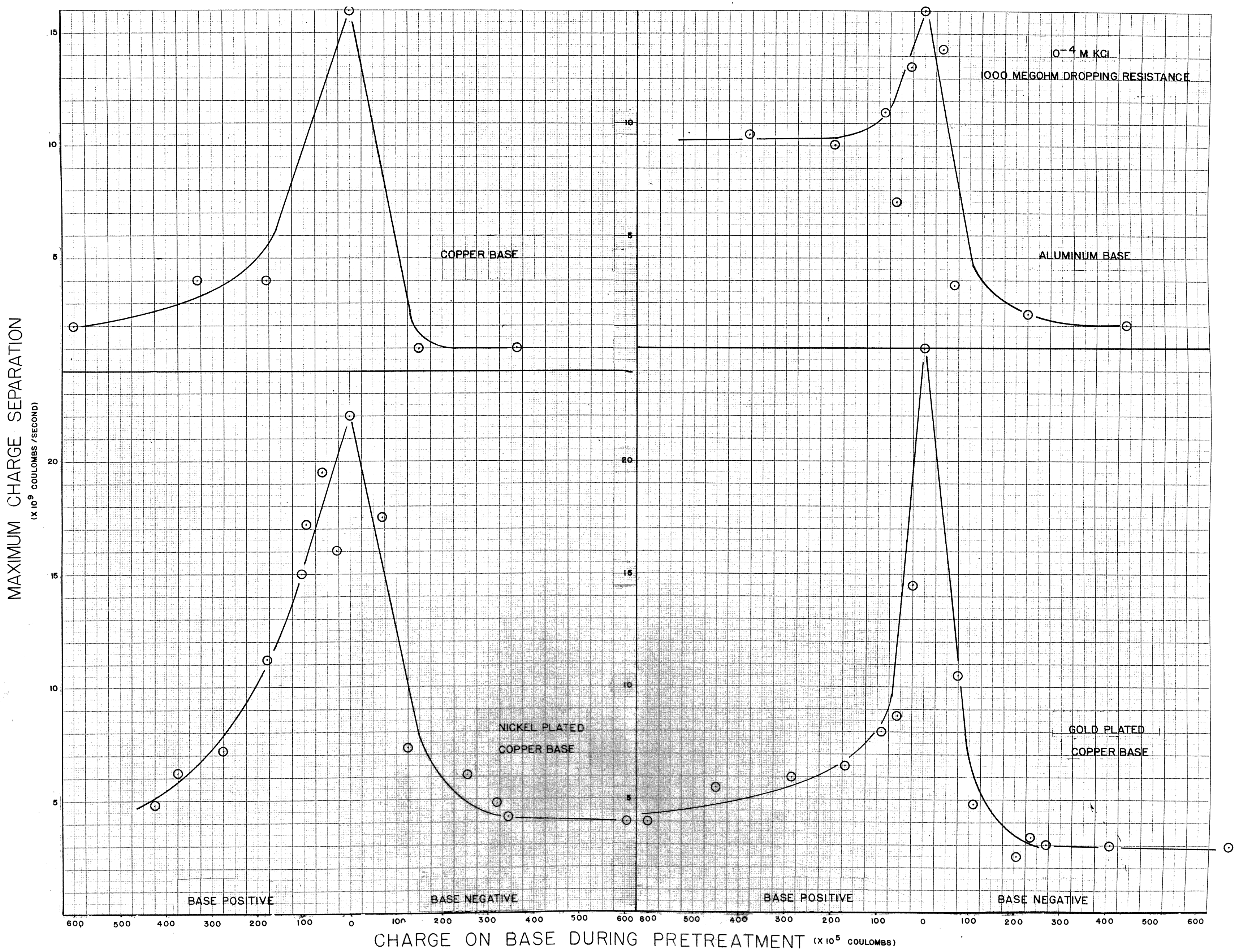


FIGURE 9

CHAPTER IV

DISCUSSION

The investigations described in this thesis are concerned, principally, with two problems. The first problem is to determine the effect of different freezing bases on the efficiency of measured charge separation; the second is to determine the effects produced when the base has been pretreated before freezing.

Effect of Different Freezing Bases on the Measured Charge Separation.

The bases used in these experiments have different thermal conductivities; thus different freezing rates will result when using the same freezing block. The difference in the freezing rate has been shown to affect the amount of ions incorporated into the ice. Furthermore, variations in the maximum measured charge separation have also been noted. These variations are evident from the graphs in Figure 3, which show the maximum measured charge separation and optimum concentration for solutions of potassium chloride frozen on several different bases. Additional factors which may affect the measurement of measured charge separation are: 1) supercooling of the solution; 2) mechanical lag in the recording instrument; 3) absorption of gases from the atmosphere; 4) changes in the resistance of the bulk ice and interface as a function of temperature. The data reported in this thesis indicate that the freezing rate is the most important of these factors.

Runs were made to note the effect of the freezing rate on the incorporation of ions into the ice. Figure 4 shows that an increase in freezing rate changes the optimum concentration to a lower value and increases the measured charge separation. This behavior raises the question as to whether this results from increased incorporation of chloride ions alone or from incorporation of additional potassium as well as chloride ions.

Using the flame spectrophotometer to determine the concentration of potassium ion, it was noted that an increase in freezing rate from 0.11 to 0.167 gmols of ice per minute resulted in a tenfold increase in concentration of potassium ion in the ice (see Figure 5). As freezing continues and the ice thickens, fewer and fewer potassium ions are incorporated into the ice. This behavior is to be expected since the freezing rate decreases as the ice thickens.

It may be seen in Figure 6 that the total amount of measured charge separation is directly proportional to the amount of solution frozen; the proportionality constant depends on the freezing rate. It was shown that the concentration of potassium ions in the ice increases with an increased freezing rate as long as the ice forms in an orderly manner and is accompanied by an increased measured charge separation. Therefore, the concentration of chloride ions in the ice must also increase but by a greater proportion.

It is important to note that addition of ammonium ion to potassium chloride solution does not materially affect incorporation of potassium ion into ice. The measured potential changes sign however, indicating that ammonium ion is incorporated. Since the concentration of potassium ion in ice is unaffected by the presence of other ions in solution and is also independent of the electrical behavior of the solution during freezing, incorporation of potassium ion must be a property of ice and the ion and be independent of the freezing base.

Carlin and Drost-Hansen[4] have shown that a measure of incorporability of ions in relation to incorporability of ammonium ions can be obtained in the following manner. Ammonium ions are added in increasing amounts to a solution whose liquid phase freezing potential is positive relative to its solid phase, until such potential difference decreases to zero. At this point, the same total amount of negative and positive ions are incorporated. The amount of ions in solution are known; therefore, relative incorporabilities can be calculated if an arbitrary value of incorporability is assigned to the ammonium ion. The incorporabilities of ions relative to the ammonium ion show a definite relationship to their ionic radii.

From the above information, it has been established that 1) cation and anion are both incorporated into ice but in different amounts; 2) incorporability of potassium ion increases with increasing freezing rate; 3) total charge separation increases with increasing freezing rate; 4) addition of ammonium ion does not affect the amount of potassium ions incorporated into ice, but changes the measured charge separation showing that ammonium ions are also incorporated. There also exists a relationship between the incorporability of the ions and their ionic radii as shown by Carlin and Drost-Hansen[4].

The incorporability of ions in ice depends upon the properties of the ions and the ice and on the freezing rate, but not directly on the type of material on which the ice was formed. The relationship between the incorporability and the freezing rate established an indirect relationship between incorporability and type of material used for the base since the freezing rate depends in part on the thermal conductivity of this material.

It has been found that small changes in the freezing rate have little or no effect on the optimum concentration. This is seen in Figure 3, which shows the optimum concentration for different freezing bases. Though the thermal conductivities of the bases differ, the optimum concentration in all cases is approximately 1.5×10^{-4} M KCl.

The measured charge separation, however, is strongly dependent on the freezing rate. This dependence is particularly notable when the solution supercools; there results a large initial measured charge separation, which subsequently returns to the normal value as the freezing progresses. In Table 1, a noticeable change in maximum measured charge separation is recorded for KCl when frozen on different bases.

When a dilute solution freezes, the amount of ions incorporated into the ice is independent of the base, but the measured charge separation may differ because the resistance of the base-ice interface varies due to adsorbed gases, surface oxidation and other surface phenomena.

Effect of Electrolytic Treatment of the Freezing Base.

Carlin and Drost-Hansen[4] have shown that when a nickel freezing base is made the cathode in an electrolytic pretreatment, the effect of freezing an ammonium compound is to increase the measured charge separation.

> "One possible way of interpreting the increased charge separation is by assuming that the current passed through the electrolyte in the pre-treatment has converted the base to a more or less reversible hydrogen electrode by the deposition of free hydrogen (Base negative during pre-treatment). Assume therefore that the most efficient charge separation corresponds to (at least) a monomolecular layer of hydrogen on the base. We can then calculate the diameter of the deposited hydrogen from the optimum number deposited. In this manner the radius of the hydrogen molecules is found to be 1 angstrom. This is in excellent agreement with what one would expect. Thus, it seems established that the effect of pretreatment in this case is to allow the electrode process to take place with greatest ease by conditioning the electrode as a hydrogen-electrode. When the base was treated with a layer of oxygen (base positive during pretreatment) the charge separation decreased considerably."

When potassium chloride is frozen on a pretreated base (base either positive or negative during pretreatment), the measured charge separation always decreases. This is quite different from ammonium chloride, which had an increased measured charge separation for a hydrogen layer on the base and a decreased measured charge separation for an oxygen layer.

This phenomenon can possibly be explained by considering the work function of the metal base. The work function is the energy required to transfer an electron from the metal to a vacuum. Baker and Baltz[7] have shown that the energy required to transfer an electron from a metal to a dielectric liquid is less than that needed to remove an electron from a metal to a vacuum. They have also shown that a layer of hydrogen on a metal surface will decrease the work function while a layer of oxygen on a metal surface increases the work function, thus changing the energy necessary for removing an electron from the metal. This would in effect change the conductivity of the base-ice interface.

Applying the theory of increase or decrease of the work function by a gaseous layer on the freezing base to our problem, we see that, when ammonium chloride was frozen, ammonium ion was selectively incorporated into the ice, the ice would have a positive charge and, for current to flow, electrons would have to transfer from the base to the ice. A layer of hydrogen would facilitate flow of current through the base-ice interface by decreasing the work function of the metal base and increasing the ability of electrons to transfer.

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[7] Edward B. Baker and Howard A. Baltz, "Thermionic Emmission into Dielectric Liquids", Phys. Rev., 51, 274 (1937). I am indebted to Dr. Marks Brook for calling my attention to this article.

Figure 8 shows how the measured charge separation increases to a maximum value as current is applied during pretreatment and then decreases. Garlin and Drost-Hansen[4] have shown that maximum measured charge separation for ammonium chloride solution on a pretreated base is obtained when a monomolecular layer of hydrogen has been deposited on the freezing base. Any additional current applied during pretreatment would start a second layer of hydrogen depositing on the freezing base. A second layer of hydrogen increases the thickness of the gaseous layer which, in turn, increases the distance the electron travels through the interface into the ice, thereby decreasing the measured charge separation.

When the base is positive during pretreatment, a layer of oxygen is deposited on the base. This layer of oxygen increases the work function which decreases the ability for electrons to transfer; therefore, the measured charge separation decreases.

When freezing a solution of potassium chloride, chloride ion is selectively incorporated into the ice. The ice acquires a negative charge and, for current to flow, electrons have to move from the ice, through the gas at the interface, to the base. The gas decreases the conductivity of the base-ice interface and lowers the measured charge separation. In this case, a layer of either hydrogen or oxygen reduces the measured charge separation.

Workman and Truby[8] have shown that samples of ice frozen from cesium fluoride solutions may act as a rectifier. They studied the rectification phenomenon in much detail and summarized the characteristic behavior for a rectifying system as follows:

> "1. If oxygen is already present at an electrode-ice interface (deposited by electrolysis immediately before the freezing of the sample), polarization generally will not occur when this electrode acts as the anode.
>
> "2. If hydrogen is already present at an electrode-ice interface (deposited by electrolysis immediately before the freezing of the sample), polarization will occur when this electrode acts as the anode.
>
> "3. When a platinum electrode is frozen onto the ice sample (in this case with no appreciable amount of gas present at the electrode-ice interface), it is found that polarization occurs immediately when the potential is applied in such a direction as to make this electrode the anode."

They also have shown that initial electrical treatment of a cesium fluoride contaminated ice sample may affect the rectification characteristics and have presented the following example.

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[8] E. J. Workman and F. K. Truby, "The Electrical Properties of Pure and Fluoride-Contaminated Ice", Unpublished paper (1955).

> "A fluoride-contaminated ice sample, is removed from the Teflon cup of Fig. 1, and "clean" platinum electrodes frozen onto both ends. An external emf is applied to the electrodes, and O_2 is thus electrolyzed to the one electrode, and H_2 to the other. The current through the sample, for the given applied voltage, will increase initially with time as the layers of gas at the electrodes become more prominent. When the steady state has been reached, the external emf can now be reversed, causing polarization to occur at the electrode which was originally the cathode. A rectifier has thus been formed in which the direction of easiest current flow has been established by the initial electrical treatment of the sample."

It is suggested that the mechanism for rectification of the ice is the same as previously described, i.e., a hydrogen layer on a metal lowers the work function of the metal, thus the energy needed to transfer electrons from the metal to the semi-conductor (the ice) via the gaseous layer is reduced; a layer of oxygen increases the energy required for this process. It has been shown, in this paper, from measured charge separation measurements of ammonium chloride frozen on a pretreated base that a layer of hydrogen on the base allows the measurement of a large measured charge separation, while a layer of oxygen decreases the measured charge separation to practically zero.

Thus this mechanism will account for the large values of rectification found by Workman and Truby[8].

Reynolds, Brook and Gourley[5] have found that a base may retain some products of electrolysis for at least one hour after pretreatment. The length of time the hydrogen layer is retained depends upon the affinity of the metal for hydrogen. A platinum or nickel base retains a pretreated hydrogen layer longer than a copper base under the same conditions.

The adsorbed gas at the interface may be removed by several methods. It may be removed by allowing the pretreated base and solution to stand without agitation. Many tests indicate that the measured charge separation returns to normal after the gas dissolves and diffuses into the solution. This is a very inefficient method for removing a gaseous layer. The rate of dissolution depends on the amount of agitation and, in this case, with practically no agitation it would take a long time; also the solution absorbs gases from the atmosphere, such as carbon dioxide, which affect the measured charge separation.

The most efficient way for removing the products of electrolysis from the interface is by ultrasonic vibrations. Richards[9] has shown that acoustical energy can produce

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[9] William T. Richards, "The Chemical Effects of High Frequency Sound Waves", II "A Study of Emulsifying Action", Jour. of Amer. Chem. Soc., 51, 1724 (1929).

violent agitation at an interface. At the electrode surface, therefore, concentration differences between interface layers and bulk solution are reduced and the products of electrolysis are largely removed. Barnartt[10] has shown that, when the products of electrolysis exist as a coating over the surface of the electrode, ultrasonic agitation gives rise to considerable depolarization by removing this layer.

On applying ultrasonic vibrations to the base, even for only a short period following pretreatment, the base performed similarly to an untreated base. This result indicates that the products of electrolysis are largely removed.

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[10] S. Barnartt, "The effects of Ultrasonic Waves on Electrolytes and Electrode Processes", Quarterly Reviews, Chem. Soc. of London, VII, (1953).

CHAPTER V

SUMMARY

The amounts of ions incorporated for a given rate of freezing depend on various properties of the ice and the ions, and are independent of the material on which the ice forms. The amount of ions incorporated is very dependent upon freezing rate. A change in freezing rate changes the incorporation of both positive and negative ions. The effect of various freezing bases primarily changes the freezing rate because of differences in thermal conductances.

Pretreating bases before freezing results in the deposition of a gaseous layer which changes the work function of the base and may cause a change in the measured charge separation. This mechanism is also suggested to explain the rectification of ice described by Workman and Truby[8]. Electrolytic products deposited on the base influence the measured charge separations; it is of interest therefore to study processes by which such layers may be removed. An efficient method applies ultrasonic vibrations to produce maximum agitation at the liquid-solid interface.

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