THE ANOMALOUS CONDUCTANCE OF SOLUTIONS COMPOSED OF A LITHIUM HALIDE AND AN ORGANIC ACID IN ANHYDROUS ACETONE

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PREFACE

A host of reactions, both inorganic and organic, are carried out in nonaqueous solvents; still very little is known about the complex species existing in these solutions. If one wishes to judge the likelihood of a reaction in a nonaqueous solvent, then one must know the type of ionic and molecular species which may be formed. This is the first step in solving the thermodynamics and kinetics of such a system. Physical measurements and theory may help clarify the situation by giving clues to the identity of the unknowns.

It is hoped this thesis will shed some light on a few such systems.

I greatly appreciated and acknowledge the help and advice of Dr. C. M. Cunningham and Dr. T. E. Moore.

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CHAPTER I

THE INTRODUCTION

The Problem

Organic acids, both monobasic and dibasic, are usually weak in aqueous solutions. Lithium halides are salts which are completely ionized in the solid state. These halides are strong electrolytes in aqueous solutions. The high dielectric constant of water, 78.6 (1), facilitates the formation of free ions which are capable of conducting current. If a weak monobasic or dibasic organic acid is added to an aqueous solution of one of the lithium halides, the resulting solution will have a conductance only slightly higher than the halide's solution provided that the salt solution is not too dilute.

If the solvent is changed from water to acetone, then the situation is altered quite radically. Acetone has a dielectric constant of 20.47 (2). Acetone is intermediate in behavior between water and organic solvents such as dioxane and cyclohexane, which have dielectric constants of 2.2 and 2.0 respectively. In a solvent of very low dielectric constant, such as dioxane, the plots of log concentration versus the log equivalent conductance for salts usually show minima and maxima which may be explained in terms of the equilibria that exist between ions (which conduct), ion pairs (which are non-conductors) and triple ions (which conduct). The influence of dielectric constant on such curves has been shown graphically by Fuoss and Kraus (3).

Association of strong electrolytes is usually negligible in solvents with dielectric constants above forty-one provided that the solutions are dilute. Ion pair formation may be expected to occur roughly in the dielectric constant range of forty-one to ten. Below a dielectric constant of ten both ion pair and triple ion formation will occur (4). Therefore, a salt dissolved in acetone should possess some ion pairs which will cause a curve of equivalent conductance versus concentration to fall off more rapidly than expected. At high concentrations, tenth-molar and above, this effect may be pronounced and extrapolation of such curve back to zero concentration may lead to erroneously high value of the equivalent conductance at infinite dilution.

Lithium iodide, lithium bromide and lithium chloride are moderately strong electrolytes in acetone. Their solutions probably contain ion pairs and perhaps other associated species. Monoiodosuccinic acid, monobromosuccinic acid and monochlorosuccinic acid are all very weak acids in acetone; in fact nearly all mono- and dibasic organic acids are very weak in acetone. It is extremely difficult to measure the dissociation of organic acids in acetone because of their weakness.

The problem at hand is to explain the change in conductance caused by the addition of monohalosuccinic acids to the corresponding lithium halides in acetone solutions. One would think that the variation in conductance should be slight, for the number of ions should only be increased by negligible amounts by successive increments of acid; provided salt, acid and solvent behave as an ideal solution. Experimental results show that systems involving monohalosuccinic acids and the corresponding lithium halides are far from ideal in reference to the conductance of their solutions. This is graphically shown in Figures 1, 2 and 3.

Figure 1 shows that the specific conductance of a 0.01 molal solution of lithium iodine decreases on additions of monoiodosuccinic acid. An acetone solution which is 0.01 molal in lithium iodide and 0.20 molal in monoiodosuccinic acid shows a specific conductance that is three-quarters of the specific conductance of a 0.01 molal solution of lithium iodide alone.

Figure 2 shows that the specific conductance of a 0.01 molal solution of lithium bromide increases on additions of monobromosuccinic acid. An acetone solution 0.01 molal in lithium bromide and 0.20 molal in monobromosuccinic acid in acetone shows a specific conductance which is one and one-half times the specific conductance of 0.01 molal solution of lithium bromide.

Figure 3 shows that the specific conductance of 0.01 molal solution of lithium chloride in acetone increases greatly on additions of monochlorosuccinic acid. A solution that is 0.01 molal in lithium chloride and 0.20 molal in chlorosuccinic acid shows a specific conductance which is

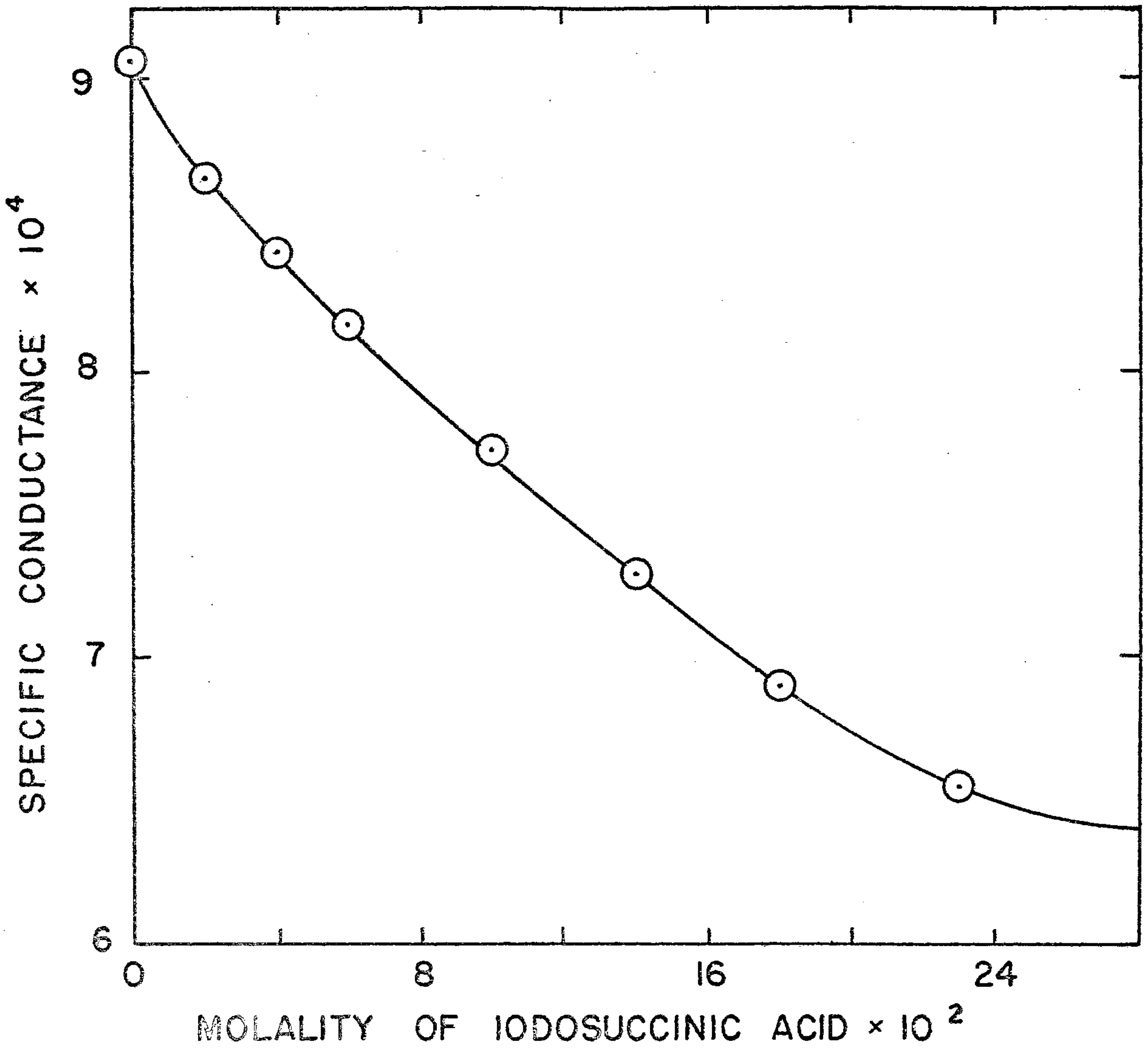


FIG. I THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM IODIDE PLUS VARIOUS AMOUNTS OF IODOSUCCINIC ACID IN ACETONE.

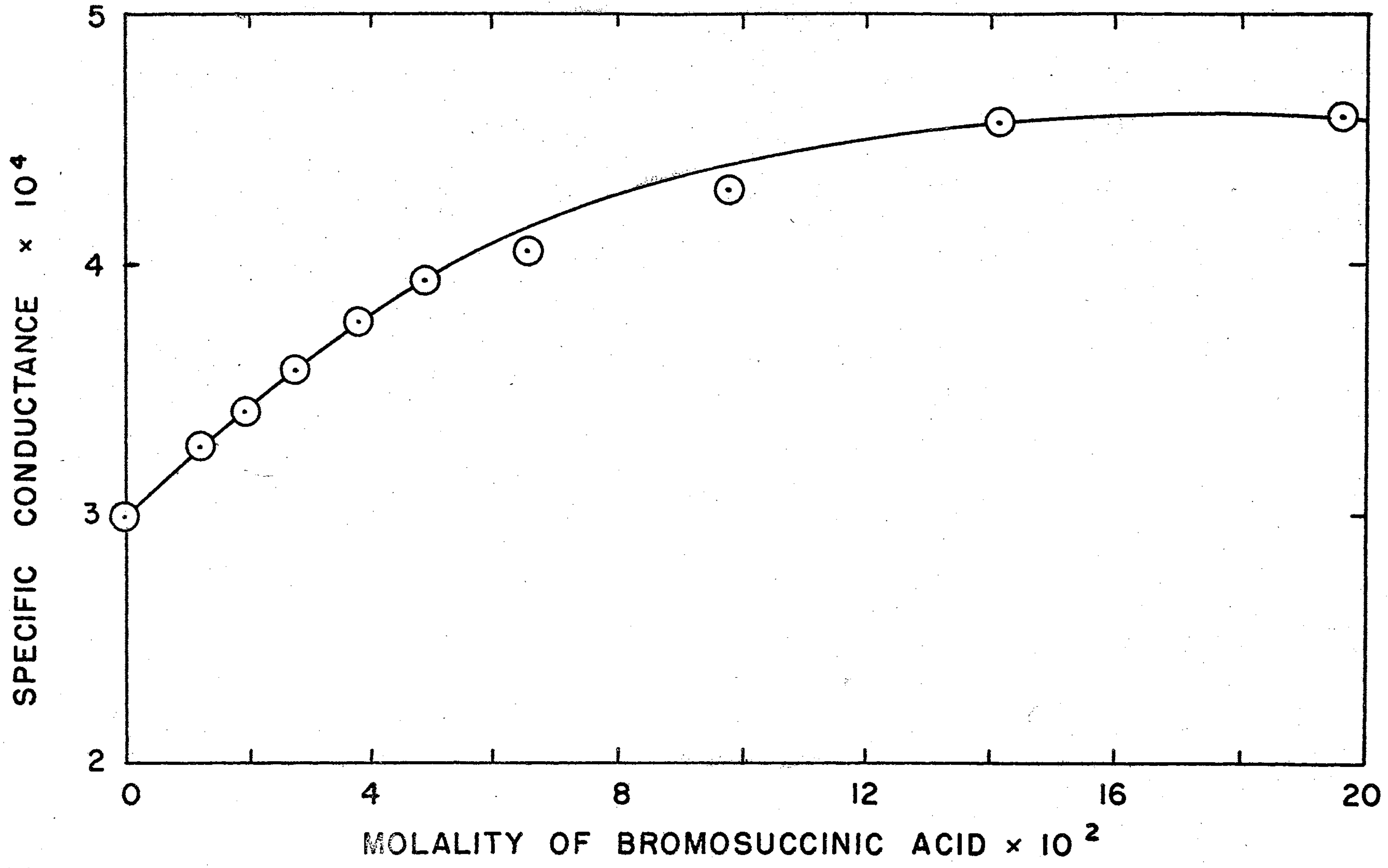


FIG. 2 THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE.

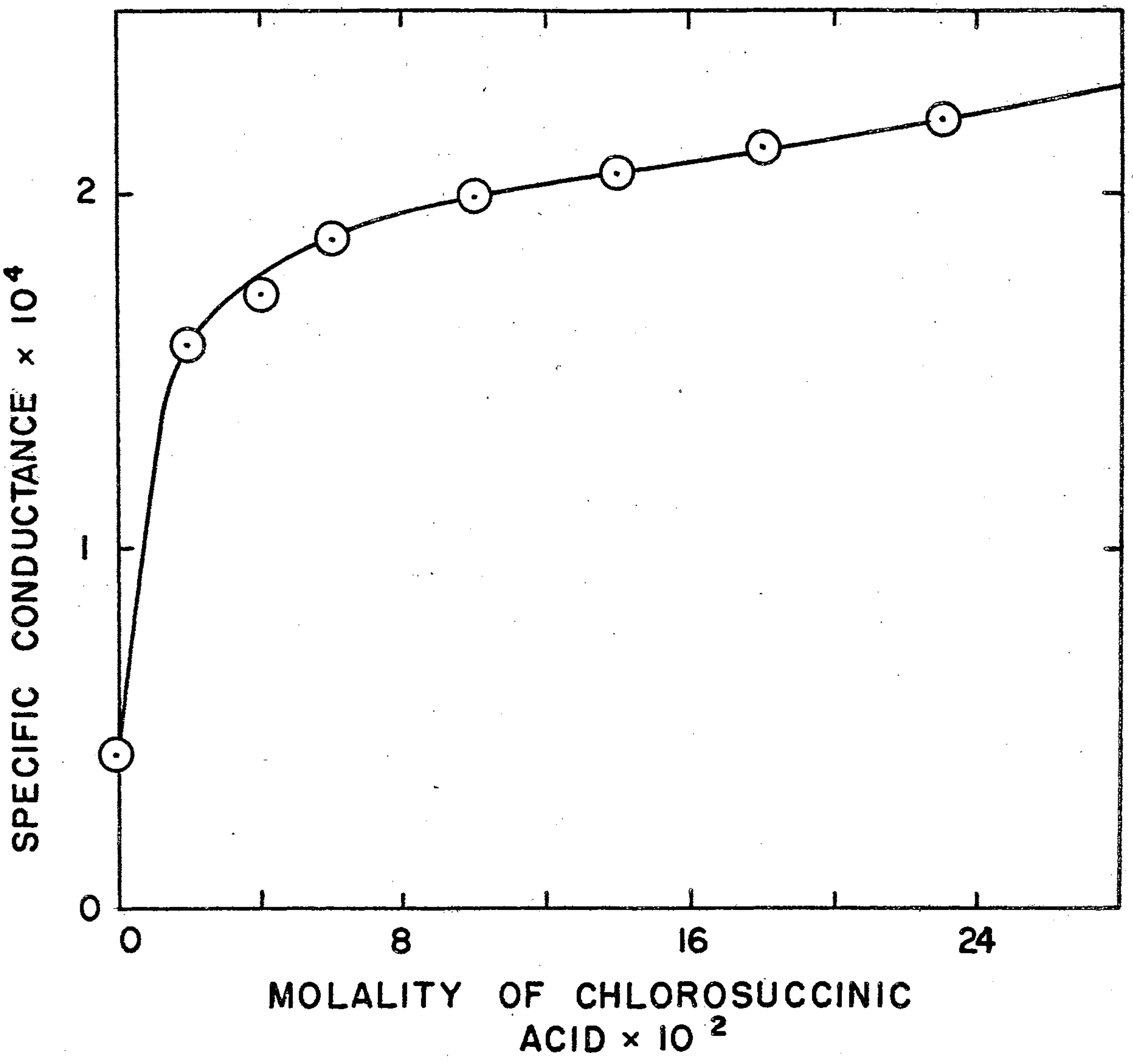


FIG. 3 THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF CHLOROSUCCINIC ACID IN ACETONE.

five times the specific conductance of a 0.01 molal solution of lithium chloride.

This thesis attempts to explain the unexpected electrical conductance of these systems by investigation of similar systems of an inorganic salt and an organic acid in anhydrous acetone. These investigations are accomplished by electrochemical methods.

CHAPTER II

REVIEW OF THE LITERATURE

Literature Concerning the Problem

Olson, Frashier and Spieth (5) have investigated the rate of racemization of l-bromosuccinic acid and dimethyl l-bromosuccinate by lithium bromide in acetone solution. They found that the rate of reaction was first order with respect to the bromide ion concentration, but the specific rate constant decreased on increasing the concentration of acid or ester. Olson and Cunningham (6) found the electrical conductance of 0.01 molal solution of lithium bromide to increase 30% upon making the solution 0.2 molal in bromosuccinic acid. When dimethyl bromosuccinate was substituted for the acid there was a decrease in electrical conductivity of 6%. If lithium perchlorate was substituted for lithium bromide, the electrical conductance fell off linearly as successive amounts of bromosuccinic acid were added. These experiments indicate that there may be some type of association between the bromide ion and the acid or part of the acid that is not favorable for inversion but which does increase the electrical conductivity of the system.

Franklin and Kraus (7) showed that the mass action law can be applied to nonaqueous solutions. They found that salts dissolved in liquid ammonia obey the mass action law fairly well at high dilution. Dutoit and Gyr (8) verified that the mass action law is followed by electrolytes in numerous other solvents.

Kraus and Bray (9) studied electrolytes in liquid ammonia, liquid sulfur dioxide and some organic solvents. In every case the mass action law was obeyed. The mass law for binary electrolytes, disregarding activity coefficients, may be formulated as follows:

$$k = \frac{ca^2}{1-a} \qquad (1)$$

where c is the total salt concentration, a is the degree of dissociation and k is the dissociation constant. If a, the degree of dissociation, is made equal to the conductance ratio (Λ/Λ_0) and this value of a is substituted into the mass action law, then the following equation is obtained:

$$\frac{1}{\Lambda} = \frac{1}{k\Lambda_0^2} \cdot (c\Lambda) + \frac{1}{\Lambda_0} \qquad (2)$$

When (c) is plotted against $1/\Lambda$, the intercept of this linear equation will be $1/\Lambda_0$, while the slope will be equal to $1/k\Lambda_0^2$. Therefore, by use of this type of plot, both the equivalent conductance at infinite dilution and the dissociation constant can be obtained, provided that very dilute solutions are used in obtaining conductance data.

Dutoit and Levrier (10) using the above method computed the equivalent conductances at infinite dilution and the dissociation constants of lithium iodide, lithium bromide and lithium chloride in acetone at 18° C. These values are tabulated below:

TABLE I

OBSERVED VALUES FOR THE DISSOCIATION CONSTANTS AND THE EQUIVALENT CONDUCTANCES AT INFINITE DILUTION OF LITHIUM HALIDES IN ACETONE AT 18° C (10)

Symbols of salts	Λ_0 in mhos/cm^2	K, the dissociation constant
LiI	165	2.7×10^{-3}
LiBr	165	4.9×10^{-4}
LiCl	165	8.2×10^{-5}

The tabulated data indicate that lithium iodide is a stronger electrolyte than lithium bromide, which in turn is stronger than lithium chloride.

Dippy, Jenkins and Page (11) made conductivity measurements on uni-univalent salts in acetone. They found inflections in the plots of equivalent conductance versus square root of concentration at moderate concentrations. Below and above the first inflection point, two fairly straight lines are observed. The line obtained from the points representing more dilute solutions should represent a region where the ions are fairly free of ionic interactions. The slope of this line should be the Onsager tangent. The second line represents a region of ion pair formation and the conductances fall off more rapidly, as shown by the results with potassium and sodium iodide. This second line appears to follow "Kohlrausch's law of independent ion migration", but the value of equivalent conductance at infinite dilution obtained by extrapolating this line to zero concentration is too high.

In the work of Dippy, Jenkins and Page (11) a salt in one sample of acetone gave consistently higher values of the equivalent conductance than the identical salt in another batch of acetone. This observation was explained by solvent conductance, but may have been due to different amounts of water in their acetone samples.

The several experimental values of the equivalent conductances at infinite dilution do not agree very well for the salts sodium iodide, potassium iodide, ammonium iodide and lithium bromide in acetone. (See Table II) One possible cause for this variation is water content, which changes with the experimental acetone.

TABLE II

EQUIVALENT CONDUCTANCES IN mhos/cm^2 AT INFINITE DILUTION OF SODIUM IODIDE, POTASSIUM IODIDE, AMMONIUM IODIDE AND LITHIUM BROMIDE IN ACETONE AT 25° C.

Salt	(11)	(12)	(13)	(14)	(15)	(7)
NaI	182.5	184.6	190			
KI	186.0	185.6	192	174		
NH_4I	162.0		208			
LiBr					206.6	200

Olson and Konecny (15) used the Fuoss-Kraus method to determine how the dissociation constant of lithium bromide varies with the amounts of water present in acetone. The greater the water content of the acetone, the larger becomes the dissociation constant of lithium bromide while the equivalent conductance at infinite dilution decreases. A small part of the drop of the equivalent conductance at infinite dilution may be due to an increase in viscosity caused by the loss of mobility of the lithium ion, which is highly solvated in water. Konecny showed the absence of solvation of lithium ion in dry acetone by calculation of a, the effective mean diameter, (16). Konecny states: "The value a changes gradually from slightly less than the sum of ionic crystal radii (17) to the sum of fully hydrated radii as the water content of the acetone is increased."

Reynolds and Kraus (2) have used the Fuoss-Kraus method to compute the equivalent conductances at infinite dilution and dissociation constants for a number of ionic compounds in acetone. These compounds usually contain one ion which is organic and another ion which is inorganic. These authors have used Fowler's method (18) to calculate the ionic conductances of these compounds. Fowler found that the ionic conductance of tetra-n-butylammonium (67.1 mho/cm^2) equals the ionic conductance of triphenylfluoride (67.1 mho/cm^2) in acetone. If the equivalent conductance at infinite dilution is known for a compound containing one of these ions, then the ionic conductance of the other ion can be computed by subtracting 67.1 mho/cm^2. This procedure can be used to develop a whole series of ionic conductances. The following tabulated ionic conductances were obtained by Reynolds and Kraus:

TABLE III

SOME CATIONIC AND ANIONIC CONDUCTANCES IN mhos/cm^2 AT INFINITE DILUTION IN ACETONE AT 25° C. (2)

Anions	λ_0^-	Cations	λ_0^+
ClO_4^-	115.3	Li^+	72.8
Br^-	115.9	Na^+	78.4
I^-	112.3	K^+	80.5
CNS^-	121.0		

The equivalent conductances at infinite dilution of the salts shown in Table IV were computed by adding the appropriate ionic conductances.

TABLE IV

THE EQUIVALENT CONDUCTANCES IN mhos/cm^2 AT INFINITE DILUTION OF SOME SALTS IN ACETONE AT 25° C.

Salt	Λ_o
LiBr	188.7
LiI	185.1
$LiClO_4$	188.1
$KClO_4$	193.7
$NaClO_4$	195.8

Reynolds and Kraus found the dissociation constants of potassium iodide and potassium thiocyanate to be 8.02×10^{-3} and 3.82×10^{-3} respectively. The acetone used in these experiments was dried in an alumina column, so some water may have been present.

Accascina and Schiavo (19) found the equivalent conductance at infinite dilution for lithium perchlorate to be 187.3. This is good agreement with the calculated units value in Table IV.

CHAPTER III

PROCEDURES USED TO OBTAIN THE EXPERIMENTAL CHEMICALS

The Need for Dry Acetone

Small trace amounts of water in acetone cause a radical change in its properties as a solvent. For instance, the quoted values for the solubility of salts in acetone in "Seidell's Solubilities" (20) are usually too high because wet acetone has been used.

A solution of a salt in acetone is affected by trace amounts of water. The ionic mobility of the ions usually decreases, but the number of free ions and the solubility of the salt increases; thus there is an increase in conductance. The ionization constant is also usually increased.

Therefore, to obtain reproducible experimental results, one must use reproducible acetone. The acetone should be as dry as possible, for the presence of water introduces additional variables such as water-solvated ions, which only make the picture more complex. Later it will be shown that values of the equivalent conductance at infinite dilution for various salts vary over quite a wide range depending on the dryness of the experimental acetone.

There must be some baseline so that one can compare his results with the results of others. Pure solvent is usually this baseline as far as physical constants are concerned. Thus to compare results, the dryness of one's acetone should be determined and results extrapolated back to dry acetone.

Difficulties in Preparing Anhydrous Acetone

Many experimenters have tried to prepare anhydrous acetone. Some claim their acetone is absolutely dry without adequate proof. The real question is how can one tell when the acetone is dry and pure.

Lannung (21) was interested in obtaining the solubility of inorganic salts in acetone. He therefore prepared what he considered to be dry acetone. Lannung saturated this acetone with an inorganic salt at 18° C. and 37° C. and then measured the specific conductance of the resulting solutions. He then added small amounts of water to the acetone and repeated the above procedure.

Mysels (22) has summarized Lannung's work as follows: Cesium iodide and cesium bromide, have high conductance in anhydrous acetone which is affected slightly by additions of small amounts of water. The other salts studied by Lannung -- cesium fluoride, cesium chloride, rubidium chloride, potassium chloride, sodium chloride and potassium fluoride -- have low conductances which are strongly affected by trace amounts of water.

Mysels has taken Lannung's data for salts strongly affected by moisture and plotted specific conductance x 10^6 against trace amounts of water added. These plots give straight lines of various slopes. Mysels has then assumed that the conductance of these salts should be zero in absolutely dry acetone. Extrapolation of these straight lines to zero conductance indicates that Lannung's acetone contained 0.2 to 0.3 weight per cent water.

Since the specific conductance versus weight-per cent water-added curve for cesium fluoride has the steepest slope of all, the conductance of cesium fluoride solutions will change to a greater extent for an identical increment of water than that of any of the other salt solutions in this group. This being the case, Mysels suggested that one could use cesium fluoride for the detection of water in acetone.

Mysels did not consider all the properties of cesium fluoride. The salt is very hydroscopic. It picks up moisture from any available source and must be vacuum-dried before one can obtain reproducible conductance data. The curve produced by plotting per cent by weight of water added to acetone versus the specific conductance of these acetone solutions saturated with cesium fluoride does not give a straight line; instead, it was found by experiment to give a curve which is concave upward (Figure 4).

If a small amount of water is added to an acetone solution saturated with cesium fluoride, more free ions are undoubtedly produced. The increase in the number of free ions in the solution is surely proportional to the amount of water added and to the conductance increase provided the addition is less than 0.1 per cent water by weight, and the acetone is initially very dry.

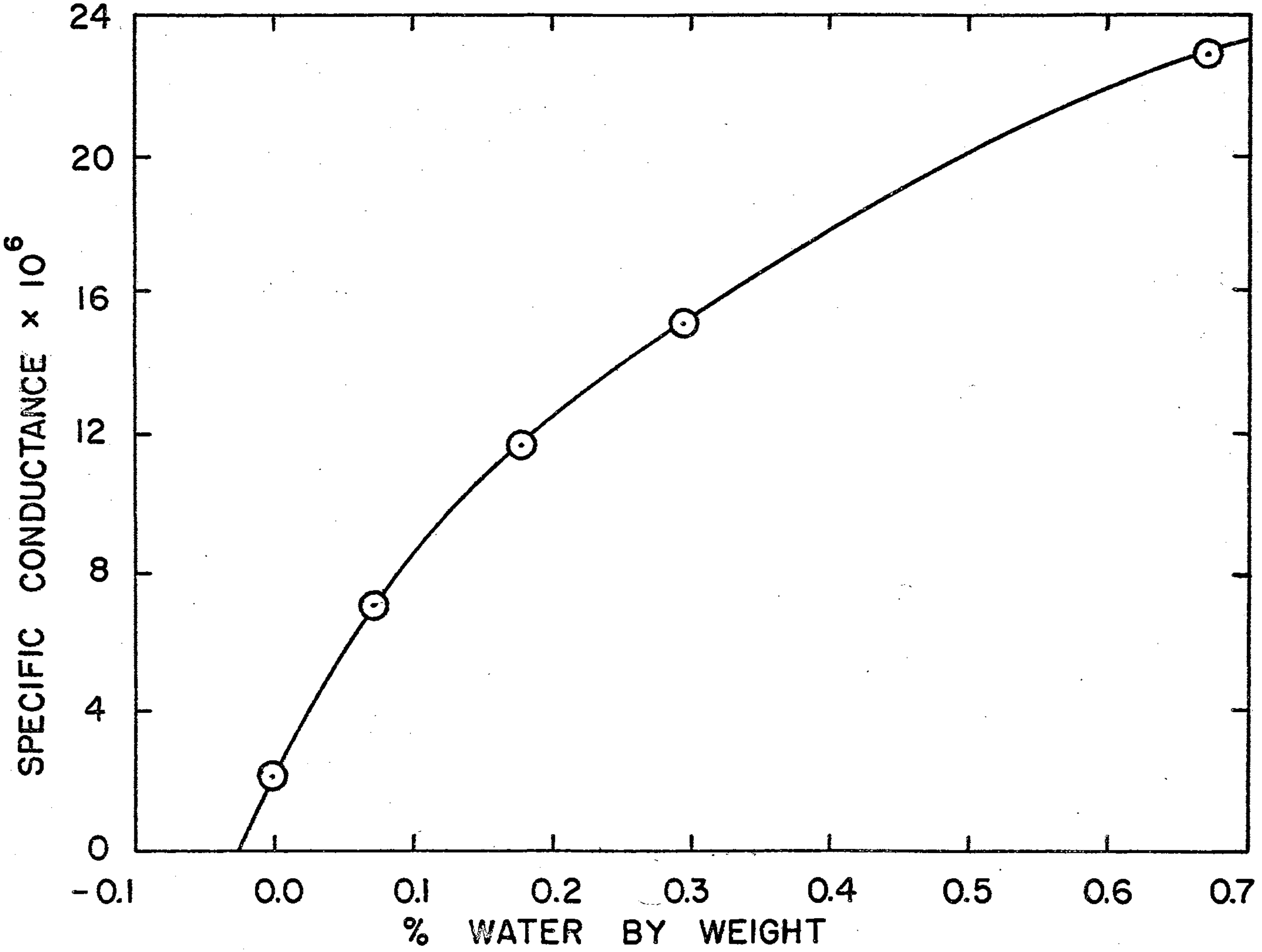


FIG. 4 THE SPECIFIC CONDUCTANCE OF SOLUTIONS SATURATED WITH CESIUM FLUORIDE PLUS VARIOUS AMOUNTS OF ADDED WATER.

It is also probably correct to assume that salts even undissolved in absolute acetone forms some free ions. If this is the case the curve should become asymptotic to the per cent water by weight, the ordinate, as the acetone approaches dryness.

In spite of the above objections, it is still agreed that conductance would be a good method of measuring the water content of acetone. If one could determine the absolute amount of water in one sample of acetone by some other means, then the curve could be standardized. Such a curve would be very useful for water detection.

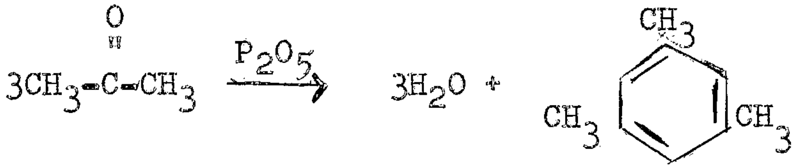
Lucchesi (23) has found a band in the acetone spectrum at 3600_{cm}^{-1} which is strongly affected by trace amounts of water. He thinks the band is due to intermolecular hydrogen bonding between acetone and water. If the concentration of water added is plotted against absorbance at 3600_{cm}^{-1} a Beer's law plot is obtained. If a smooth curve from such a plot is extrapolated to zero absorbance, it should give an estimate of the amount of water in the sample of acetone. The assumption made is that the 3600_{cm}^{-1} band should give 100% absorbance for absolute acetone. The infrared instrument in this laboratory would not measure in the range needed for the determination of water in acetone by this method.

The Karl Fischer reagent can also be used to determine the amount of water in acetone. To do this one must first treat the acetone with a dioxane solution of hydrogen cyanide which converts the acetone to the cyanohydrin and prevents its reaction with the Karl Fischer reagent. The water is then titrated with Karl Fischer reagent. Since the method is only accurate to five parts in a thousand, this test is not suitable for highly dried acetone (24).

The above paragraphs show that it is exceedingly difficult to determine the exact quantity of water in a sample of "dry" acetone. Thus absolute acetone is an intangible goal which one strives for but cannot be certain of reaching because of the uncertainty in the determination of water content.

Timmermans and Gillo (25) discuss the purification of acetone in a comprehensive way. The principal trouble in drying acetone lies in the fact that basic drying agents cause aldol condensation; therefore, some type of acidic drying agent or agents must be used. Calcium sulfate or alumina might be used, but the great affinity of acetone for water at low concentrations renders these reagents useless. Distillation fails for the same reason. Acetone forms an azeotropic mixture with carbon disulfide which might be the basis of a method of purification.

Timmermans and Gillo (25) recommend the use of the acidic drying agent, phosphorus pentoxide, on glass rods or glass wool. If phosphorus pentoxide is added directly to boiling acetone, the following reaction, among others, takes place:



The water in turn reacts with the phosphorus pentoxide to form phosphoric acid. This reaction partially defeats the purpose, i.e., drying, and converts the acetone to mesitylene which in turn must be removed. The rate of this reaction is high at the boiling point of acetone (56.1° C.), but at lower temperatures it is relatively slow (room temperature and below).

To avoid these difficulties, acetone is vacuum-distilled through glass wool or glass rod coated with phosphorus pentoxide. Under these condidtions one should obtain acetone which contains 0.001 weight per cent water.

To sum up one can say that both the preparation of "dry" acetone and the determination of its water content are difficult.

Preparation of Solvent

Baker's reagent grade acetone was first shaken with calcium sulphate for ten minutes; then the bottle containing the acetone and calcium sulphate was stored for forty-eight hours in the dark.

This acetone was then dried by the method of Timmerman and Gillo (23) (apparatus shown in Figure 5, Diagram A). Predried Baker's reagent grade acetone was poured into flask A until it filled the stopcock key. The stopcock A was then closed. The flask A was attached to the system and the system was evacuated for one hour. The stopcock B connecting to the vacuum system was then closed. A two-liter Dewar Flask containing Dry Ice and acetone was arranged so that the Dry Ice-acetone mixture covered flask B. Stopcock A was then opened and the acetone diffused through the drying tube

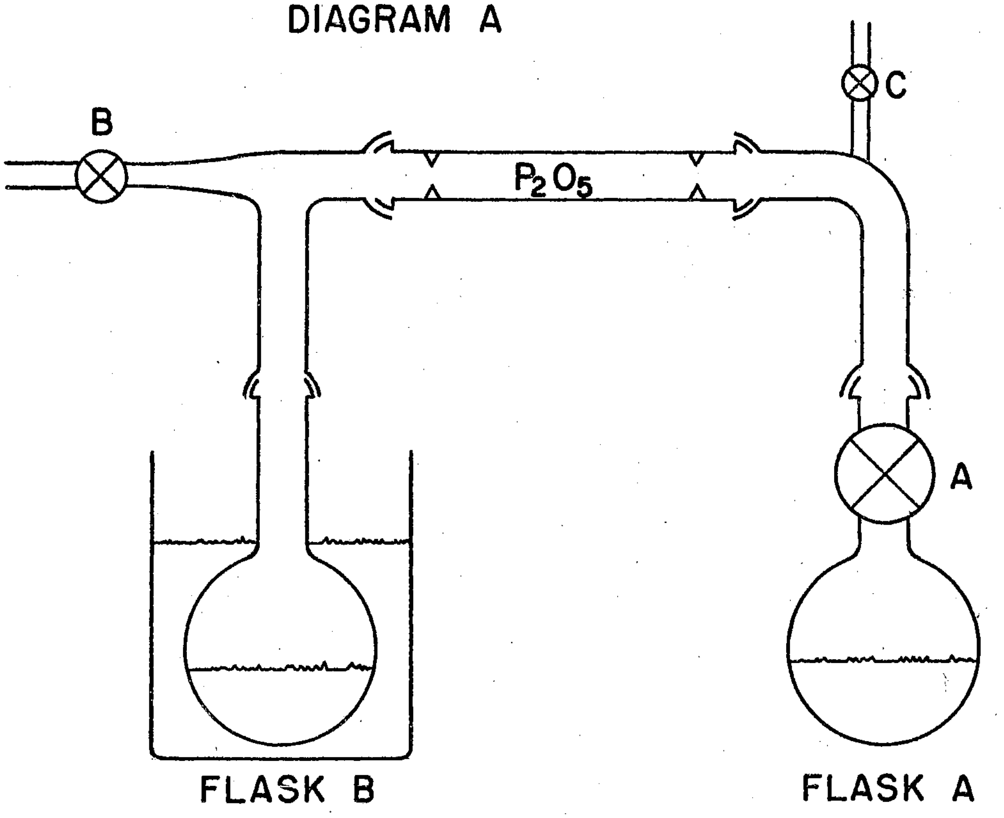


DIAGRAM A

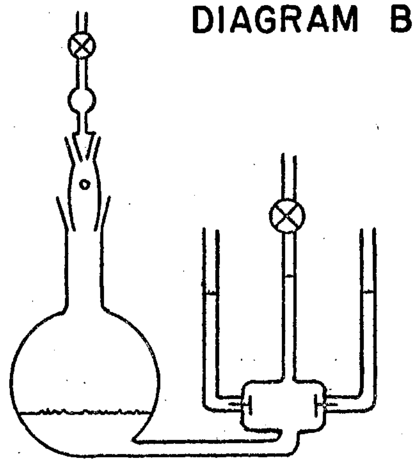


DIAGRAM B

FIG. 5 THE APPARATUS USED IN DRYING ACETONE, DIAGRAM A, AND A MODIFIED SHEDLOVSKY DILUTION FLASK CELL AND WEIGHING PIPETTE, DIAGRAM B.

containing the phosphorus pentoxide on glass wool. The acetone condensed in flask B and was completely distilled into flask B in twelve to twenty-four hours.

Sources of Solutes

Analytical reagent grade lithium bromide and lithium chloride were purchased from the Fisher Chemical Company. Lithium iodide was purchased from the Delta Chemical Company. The salts were dried for forty-eight hours in a vacuum oven at 100° C. and stored in a desiccator. Their acetone solutions were prepared in a dry box.

Racemic bromosuccinic acid was prepared by Holmberg's method (26, 27). The preparation follows in modified form:

To a one-liter round-bottom flask, 35 g. of asparagine and 150 ml. of saturated hydrobromic acid were added. The solution was refluxed for two hours to hydrolyze the amide groups. (When aspartic acid was available, refluxing was omitted.)

The mixture was cooled to 5° C. after adding 93 g. of sodium bromide and 100 ml. of water. Then 35 g. of sodium nitrite was dissolved in 55 ml. of water and added dropwise into the mixture from a separatory funnel. The addition of this solution took one hour. The one-liter beaker containing the mixture was kept in ice and water to hold the temperature below 5° C. An electric stirrer kept the mixture agitated. The evolution of bromine vapors required the use of a hood. Ten minutes after the last nitrite had been added, a cool misture of 15 ml. of concentrated sulfuric acid and 75 ml. of water was added. Ten minutes thereafter the bromosuccinic acid was extracted with ether in a five-liter separatory funnel. One portion of 200 ml. and three portions of 100 ml. each were used. Each extraction mixture was shaken for ten minutes. Each extract was transferred to an evaporating dish. The dish was warmed under a hood by a hot plate turned low, and a blower was directed on the contents. The acid crystallized without difficulty, but it formed a crust over the water which accumulated from the wet ether. As soon as most of the ether had evaporated, the hot plate was turned off, and the crust was scraped to one side. The acid dried to pale yellow crystals.

The acid was dissolved in 125 ml. of acetone, and the solution was filtered through a fine sintered-glass filter. After 150 ml. of thiophene-free benzene was added, the mixture was evaporated to one-tenth volume. The recrystallized acid was recovered by filtration, and washed with 100 ml. of benzene. About 25 g. of snow-white needles with melting point of 159-160° C. were obtained. Beilstein gives a melting point of 160-161° C. (28).

Racemic iodosuccinic acid was prepared from bromosuccinic acid by the method of Westerlund (29), which follows:

Four grams of monobromosuccinic acid was dissolved in ten grams of acetone. Three grams of sodium iodide was also dissolved in ten grams of acetone; then the two solutions were mixed. A clear solution was produced which clouded in a few seconds due to the precipitation of sodium bromide and the mixture became brownish-red from the free iodine produced. The next day the solution was filtered to remove the sodium bromide. The acetone was then allowed to evaporate at room temperature. The residue was dried in a desiccator filled with sulfuric acid. After drying, the yield was about five grams of red-brown crystals. This crude iodosuccinic acid was then dissolved in twenty grams of water. The solution was decolorized with a water solution of sulfurous acid. The product was recovered by three extractions with ether of the same volume as the solution. Colorless crystals with a melting point of 135-140° C. were obtained from these extractions. Westerlund (29) gives a melting point of 138-140° C. for dl-iodosuccinic acid.

The iodosuccinic acid was kept in a brown bottle in the dark; after a month, some decomposition was noted in which free iodine was produced.

Dimethyl dl-bromosuccinate is prepared as follows:

Twenty grams of dl-bromosuccinic acid was dissolved in nine grams of methyl alcohol. Then three grams of concentrated sulfuric acid was added to the solution. This mixture was refluxed for two hours. After refluxing, fifteen cc. of water was added to the mixture. The dimethyl dl-bromosuccinate was extracted from the mixture with three 20 ml. aloquots of ether. The ester was recovered by distilling off the ether and the residual pale yellow liquid was dried over calcium sulfate. The crude dimethyl dl-bromosuccinate was distilled under high vacuum. The resulting distillate was a clear colorless oil with a boiling point of 134° C. at 30 mm. Beilstein (30) gives a boiling point of 132-136° C. at 30 mm. for dimethyl dl-bromosuccinate.

Analytical reagent grade sodium perchlorate, potassium perchlorate and lithium perchlorate were obtained from the Fisher Chemical Company. These salts were vacuum-dried at 50° C. for two days. Their acetone solutions were prepared in a dry box.

Analytical reagent grade succinic acid, α-bromopropionic acid and β-bromopropionic were obtained from the Brothers Chemical Company.

CHAPTER IV

THE APPARATUS USED TO DETERMINE CONDUCTANCES

The Apparatus

A vacuum-tube oscillator supplied a frequency of 1000 cycles per second. The signal was amplified by a three-stage vacuum tube amplifier which was connected to a Wheatstone bridge containing a modified Wager ground. One arm of the bridge was a Jones and Bollinger conductance cell (31). The AC bridge and amplifier used in these experiments has been described by Luder (32).

The cell constants of the three conductance cells used in these experiments were determined by the method of Jones and Bradshaw (33). All the cells were equipped with shiny platinum electrodes.

The temperature of a thermostatic mineral oil bath was maintained at 25 ± .05° C. All resistances were measured at this temperature.

A modified Shedlovsky flask cell (34) with a weighing pipette (shown by Fig. 5, Diagram B, Page 21) was used to determine the conductances of a series of dilute solutions of lithium halide and alkali metal perchlorates.

CHAPTER V

EXPERIMENTAL RESULTS

Figures 6 and 7 show Fuoss-Kraus plot (35, 36, 37) of lithium chloride and lithium bromide, respectively, in acetone. Figure 8 shows Fuoss-Kraus plots of lithium perchlorate, sodium perchlorate and potassium perchlorate in acetone. All experimental data were obtained at 25° C.

Experimental data for lithium iodide were obtained but were quite erratic-probably due to the air oxidation of the iodide. Solutions of lithium iodide and sodium iodide were clear when made but became pale yellow on standing.

If the ionic conductance of the perchlorate ion at infinite dilution in acetone is taken as 115.3 (2, 19), then the ionic conductance at infinite dilution for the other experimental ion can be computed and tabulated (Table V). Table V also gives the dissociation constants and the equivalent conductances at infinite dilution of the experimental salts.

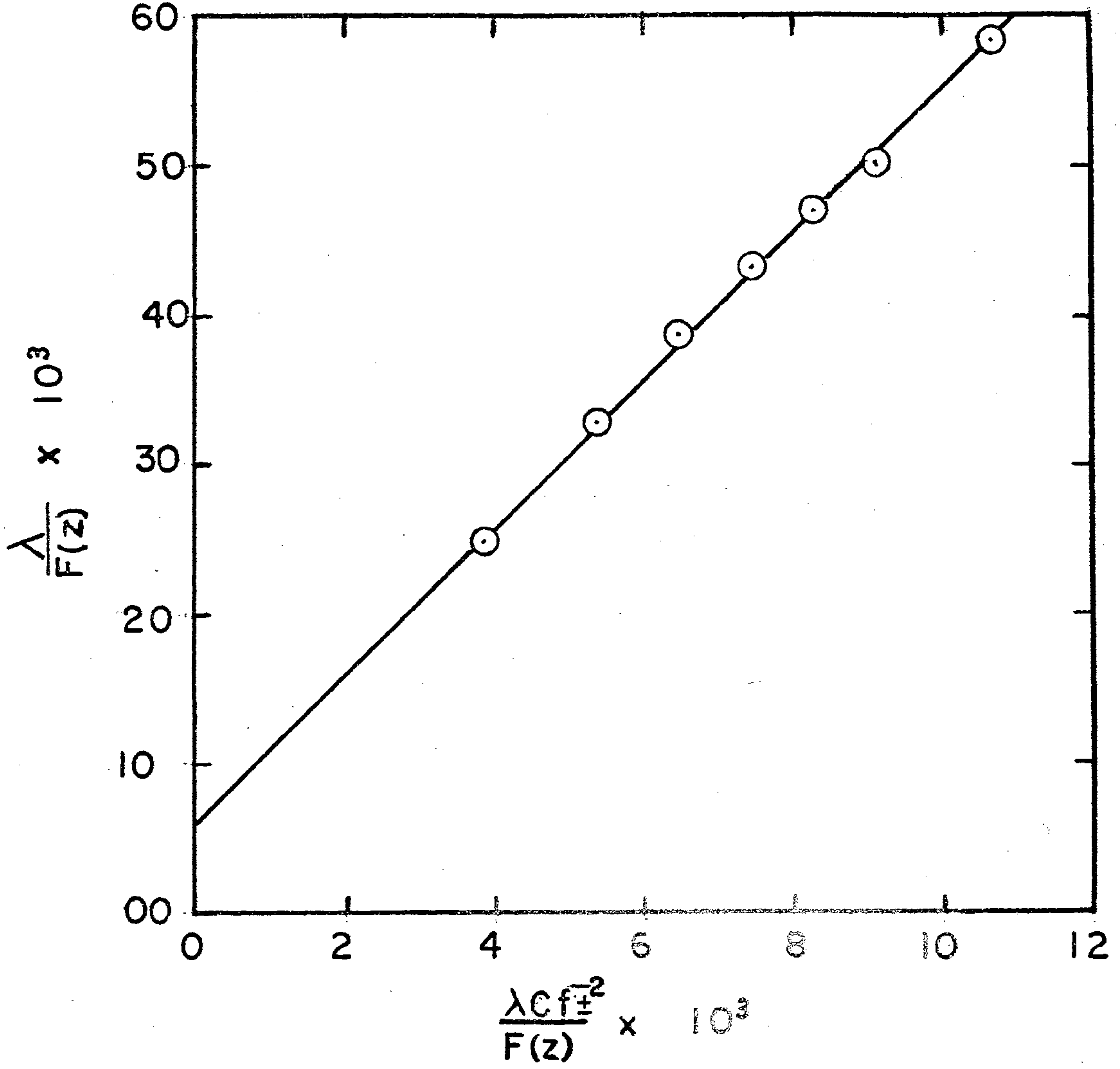


FIG. 6 FUOSS AND KRAUS PLOT, LITHIUM CHLORIDE IN ACETONE

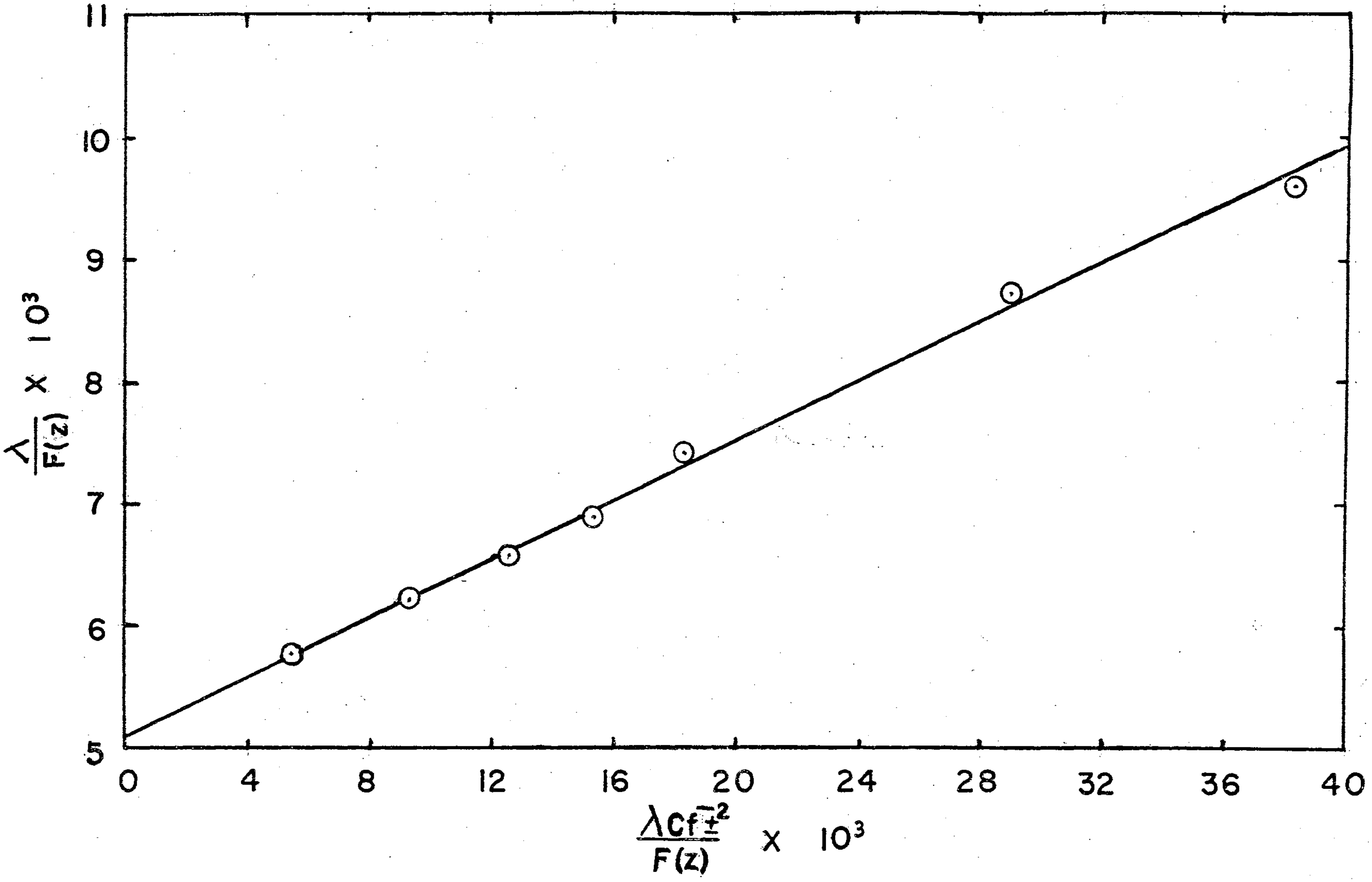


FIG. 7 FUOSS AND KRAUS PLOT OF LITHIUM BROMIDE IN ACETONE

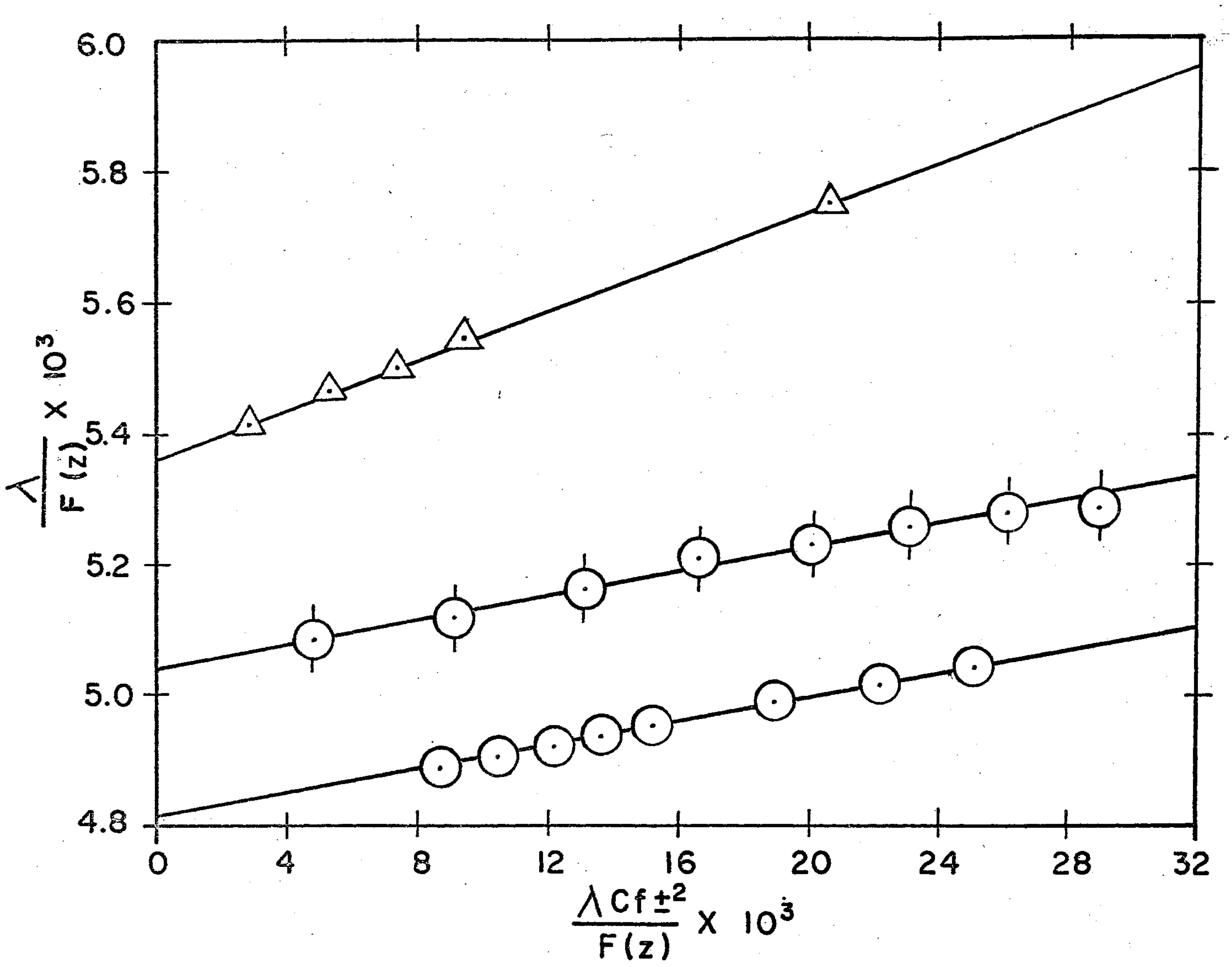


FIG. 8 FUOSS AND KRAUS PLOT OF LITHIUM PERCHLORATE, SODIUM PERCHLORATE AND POTASSIUM PERCHLORATE.

△ $LiClO_4$ ⨀ $NaClO_4$ ⊙ $KClO_4$

TABLE V

THE DISSOCIATION CONSTANTS, THE EQUIVALENT CONDUCTANCES IN mhos/cm^2 AT INFINITE DILUTION AND THE CATIONIC AND ANIONIC CONDUCTANCES IN mhos/cm^2 OF ALKALI METAL HALIDES AND ALKALI METAL PERCHLORATES DETERMINED FROM EXPERIMENTAL CONDUCTANCE DATA

Salt	$K \times 10^3$	Λ_0	Cation (λ_0^+)	Anion (λ_0^-)
$LiClO_4$	1.33	186.7	71.4	115.3
$NaClO_4$	2.59	198.6	83.3	115.3
$KClO_4$	2.66	207.1	91.8	115.3
LiCl	0.00767	162.9	71.4	91.5
LiBr	0.213	196.0	71.4	124.6
LiI (9)*	2.70	171.3	71.4	100.9
NaI (11)*	8.91	184.2	83.3	100.9
KI (2)*	8.02	192.7	91.8	100.9
KCNS (2)*	3.83	201.6	91.8	109.8

* The data for the last four salts were obtained from the indicated references and are included for comparison.

The dissociation constants of the perchlorates increase as the metal becomes more electropositive.

The dissociation constants of the lithium halides show a sharp decrease as the attached non-metals become more electronegative. This simply shows the existence of more ion pairs in a lithium chloride solution than in a lithium bromide solution which in turn has more ion pairs than lithium iodide solution. The lithium-halide bond is still ionic, but lithium halides, as solutes, apparently go into acetone in the form of ion pairs. The solubilities of the iodide and the bromide increase with temperature while the solubility of the chloride decreases; thus iodide and bromide have a negative heat of solution while the chloride has a positive heat of solution. One can facilitate the solution of lithium chloride in acetone by cooling the system. The fluoride is almost insoluble in acetone. The mechanism of solution must gradually change from ionic to ion-pair. Apparently, ion pairs do not have as much tendency to solvate as do ions.

The cationic conductance at infinite dilution increases as one goes from lithium to sodium to potassium; therefore, one would predict the corresponding conductance of rubidium would be about 100 mhos/cm^2.

The anionic conductances at infinite dilution increase in the following order: Chloride, iodide, thiocyanate, perchlorate and bromide.

Figure 9 shows that the specific conductance of chlorosuccinic acid is negligible compared to the specific conductance of any of the salts studied while Figure 10 shows the same is true for bromosuccinic acid.

Figure 11 presents the affect of trace amounts of water in acetone. The two specific conductance curves have identical shapes, but the curve showing higher specific conductances was obtained with the acetone containing more water. The water causes the lithium bromide ion pair-ion equilibrium to shift toward the ionic side. The increased ionic concentration causes the increase in specific conductance. The water content only shifts the curve up and down; therefore, small amounts of water apparently have no bearing on the anomalous jump in conductance of this system.

Figure 12 shows that successive additions of iodosuccinic acid to a 0.01 molal solution of sodium iodide cause a decrease in the specific conductance curve. If the same measurements are repeated on the same solutions twenty-four hours later, the curve sinks in the middle showing that some type of chemical changes are taking place in the solutions. The iodide solutions may first react with atmospheric oxygen. Iodide ions may then form a series of complex ions as in aqueous solutions. The iodine-containing solutions investigated in this research are a problem in themselves and present another facet more complex than the general problem at hand.

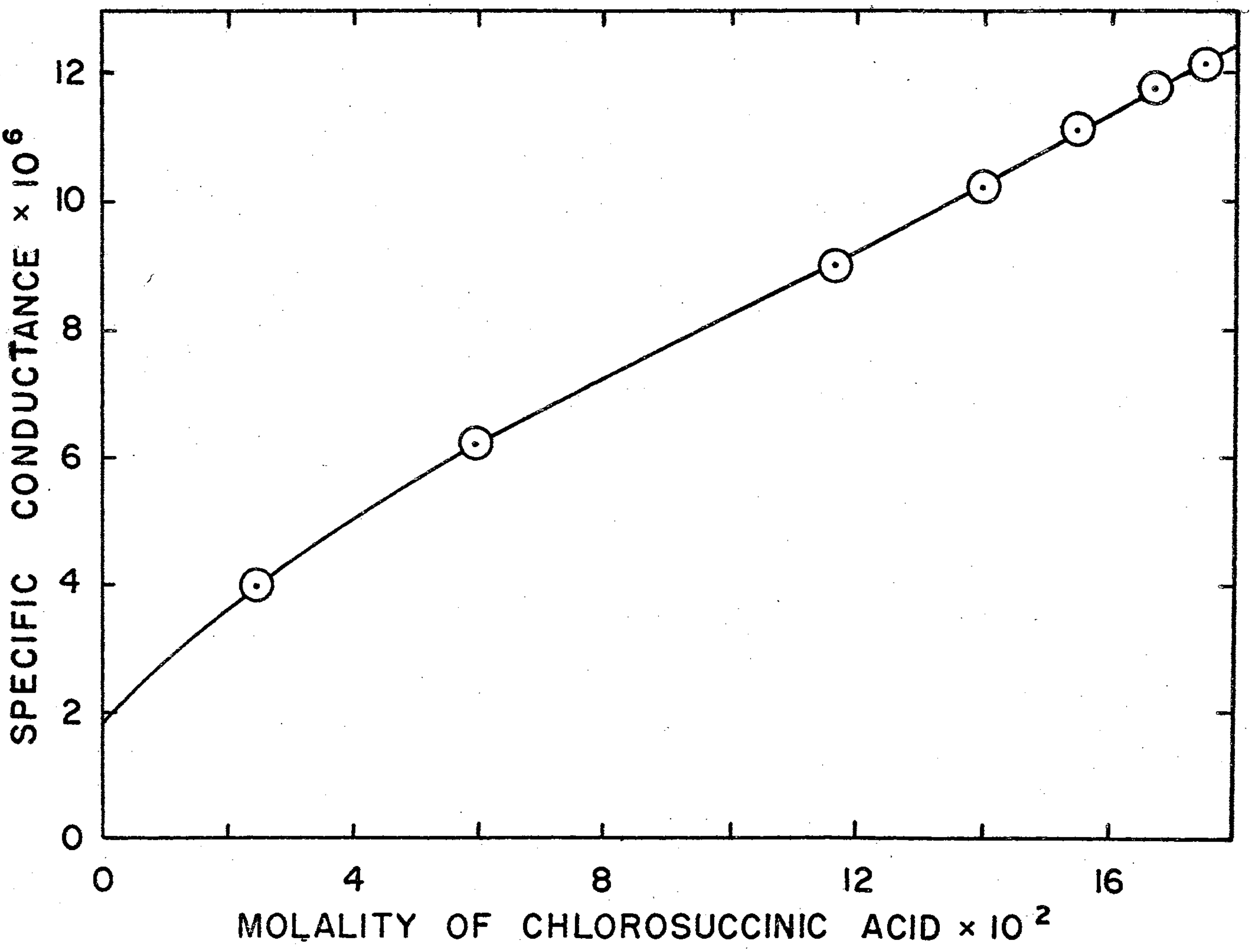


FIG. 9 THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF VARIOUS AMOUNTS OF CHLOROSUCCINIC ACID IN ACETONE.

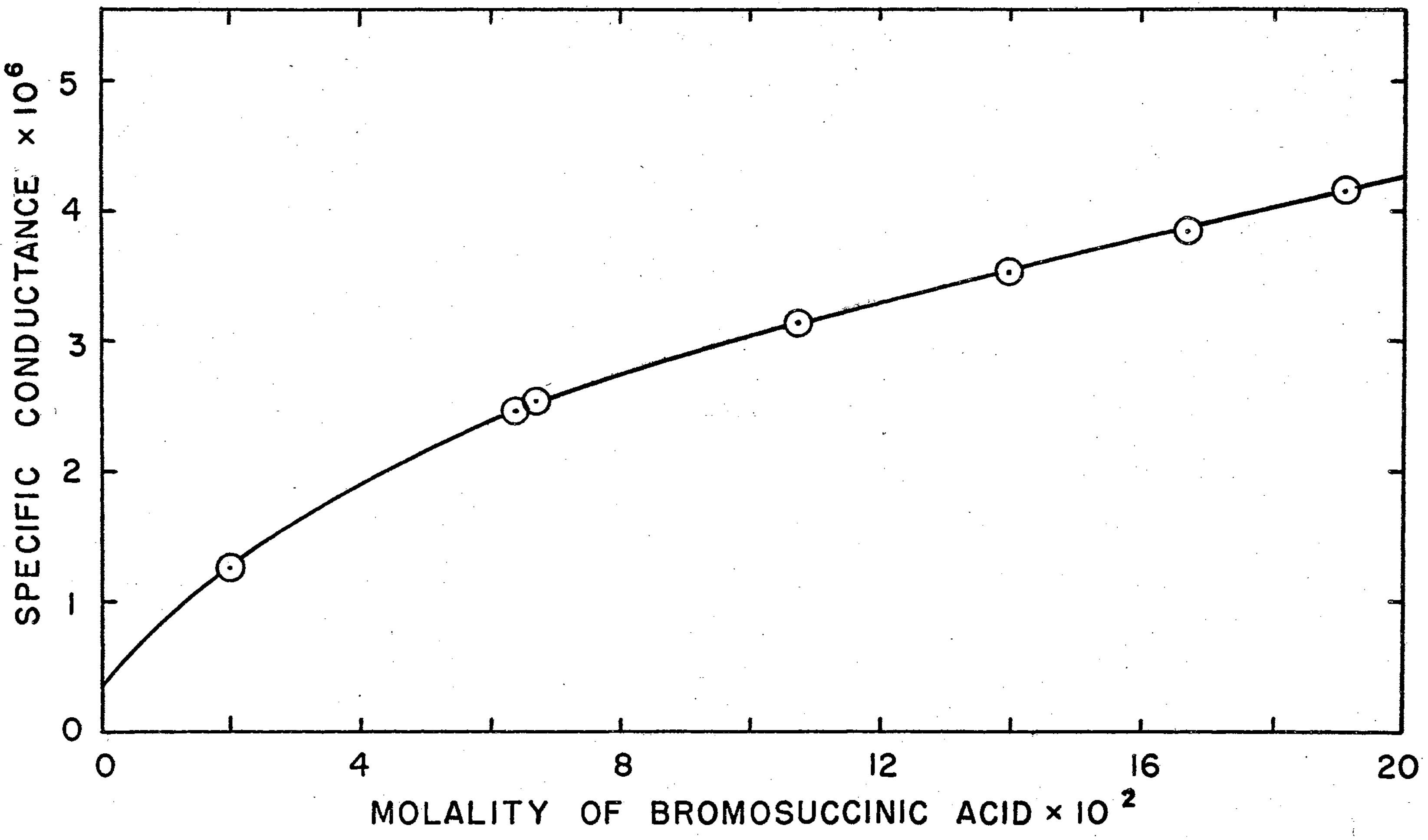


FIG. 10 THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE.

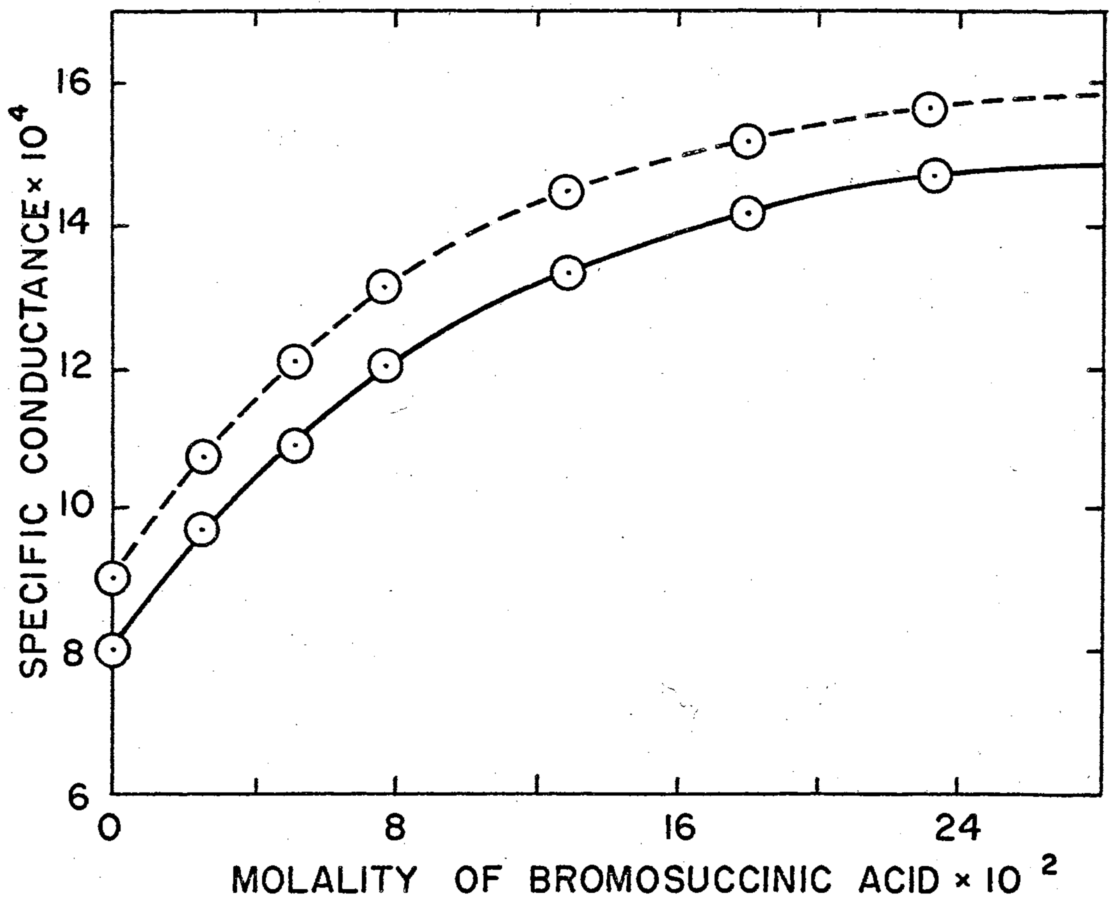


FIG. 11 THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF 0.0642 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE. THE UNBROKEN LINE (——) REPRESENTS ACETONE CONTAINING 0.11% WATER BY WEIGHT. THE BROKEN LINE (---) REPRESENTS ACETONE CONTAINING 0.27% WATER BY WEIGHT.

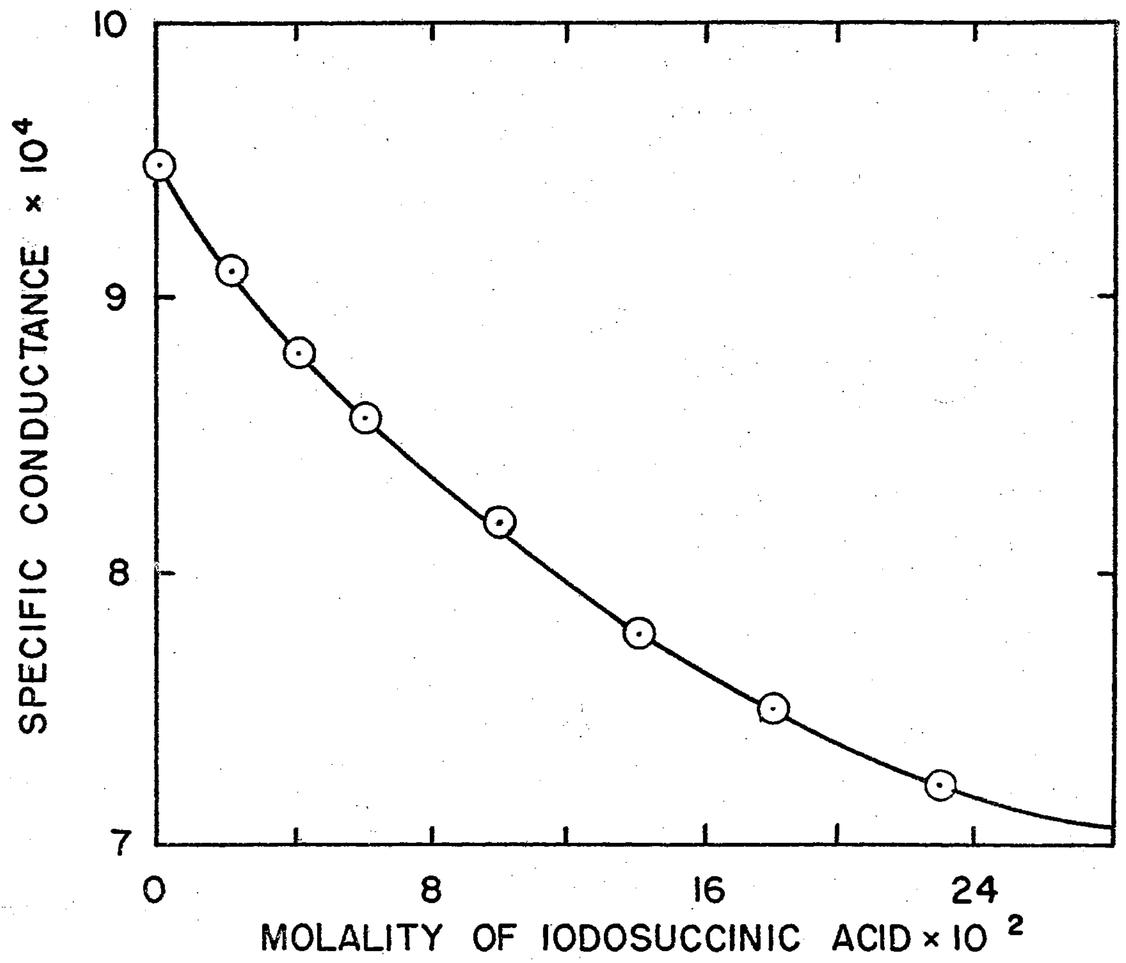


FIG. 12 THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL SODIUM IODIDE PLUS VARIOUS AMOUNTS OF IODOSUCCINIC ACID IN ACETONE.

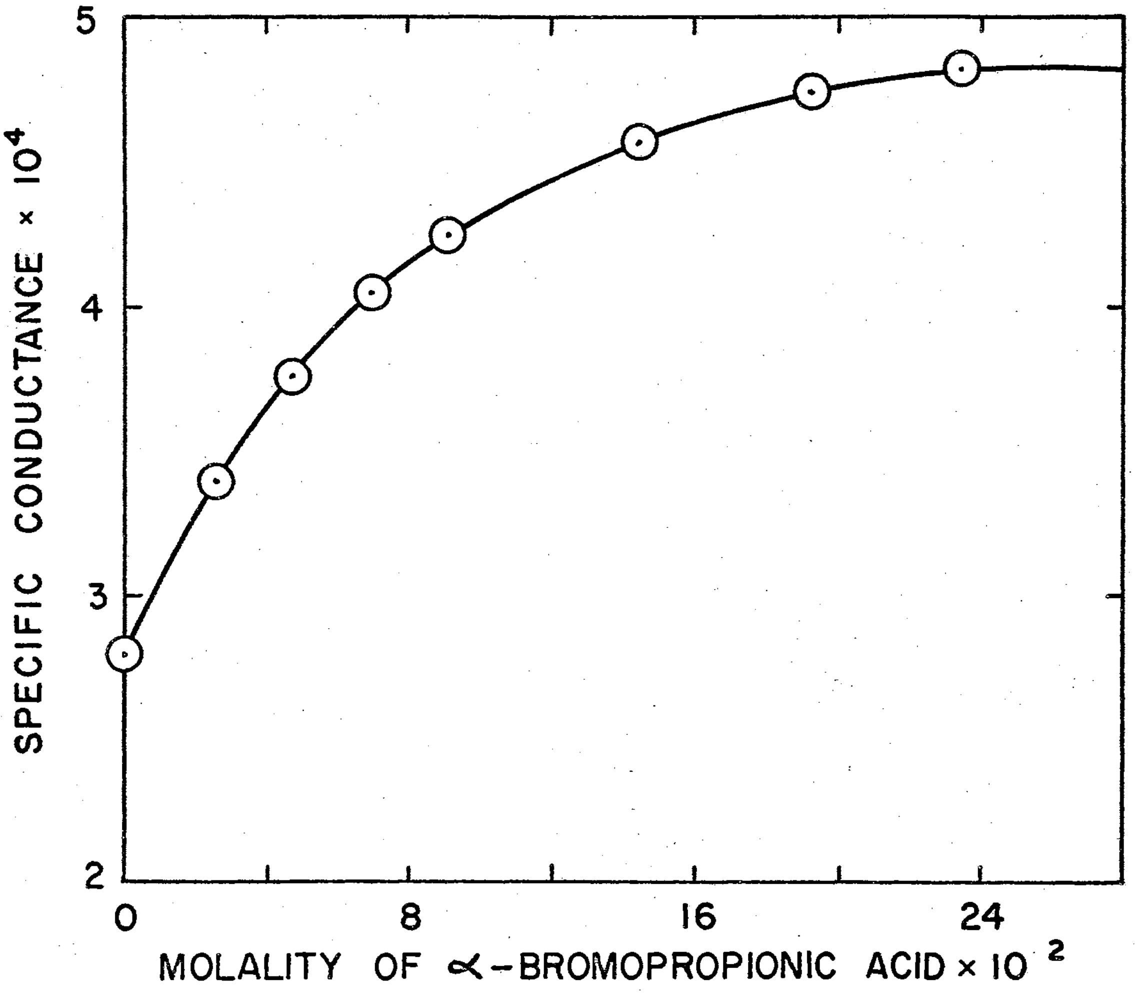


FIG. 13 THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF α-BROMOPROPIONIC ACID IN ACETONE.

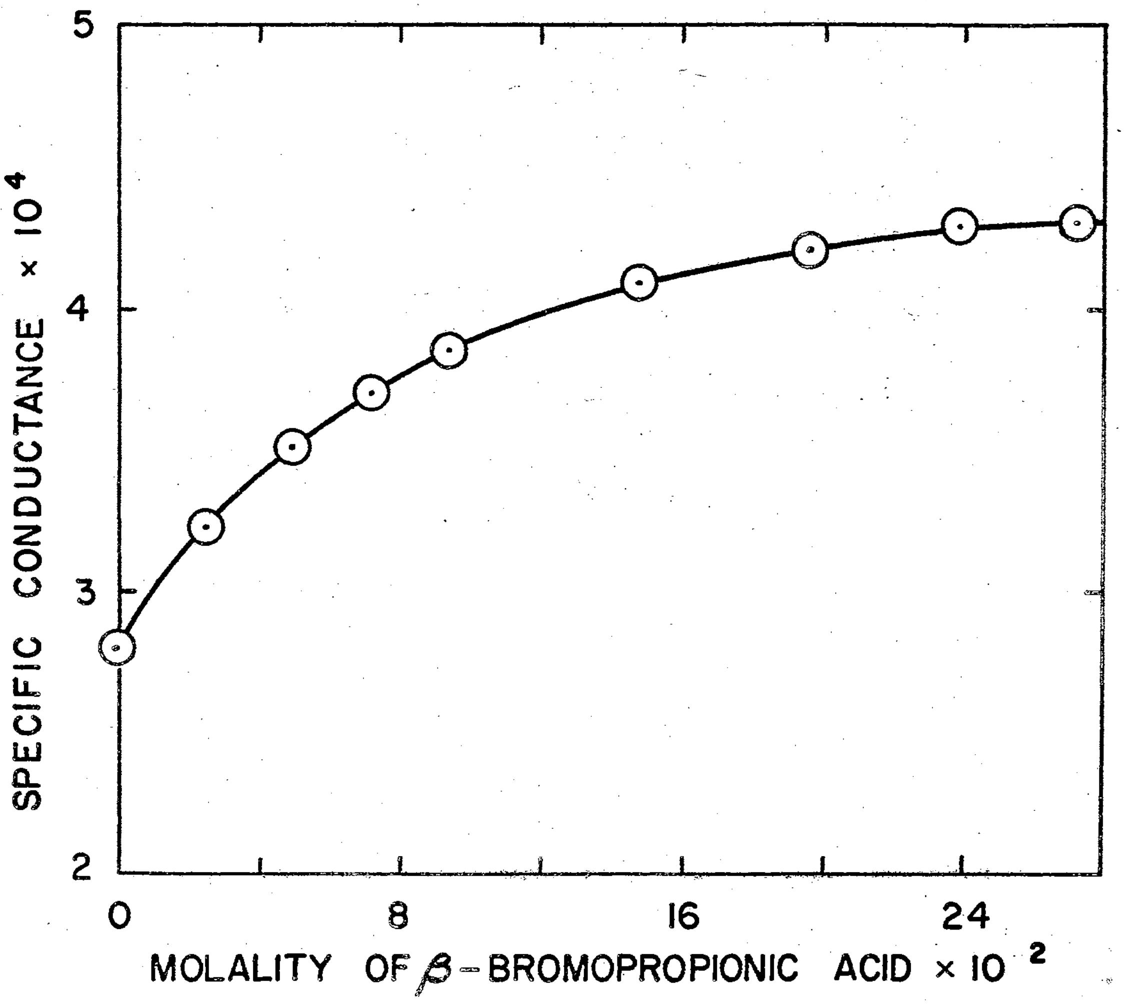


FIG. 14 THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF β — BROMOPROPIONIC ACID IN ACETONE.

When successive increments of α-bromopropionic (Figure 13) or β-bromopropionic acid (Figure 14) are added to 0.01 molal solution of lithium bromide, there is a general increase in the conductance curves. The slightly stronger α-bromopropionic acid gives a marked increase in specific conductance when compared to β-bromopropionic acid. Both acids are extremely weak in acetone. This indicates that inherent acid strength is in some way associated with the mechanism of the increase in conductance observed in these systems.

Figure 15 shows that successive additions of dimethyl dl-bromosuccinate to a 0.01 molal solution of lithium bromide causes a slight linear decrease in the specific conductance curve. This decrease is probably due to an increase in the viscosity of the solution caused by the dimethyl dl-bromosuccinate.

Figure 16 shows that when successive amounts of bromosuccinic acid are added to 0.01 molal solution of lithium perchlorate, there is a slight linear decline in the specific conductance curve. The ions formed by lithium perchlorate apparently do not participate in the type of association that exists in lithium bromide -bromosuccinic acid system. It appears that the lithium ion itself is not an intrinsic part of the mechanism which causes increased specific conductance in the lithium bromide-bromosuccinic acid system.

If increments of bromosuccinic acid are added to 0.01 molal lithium iodide, a decreasing specific conductance

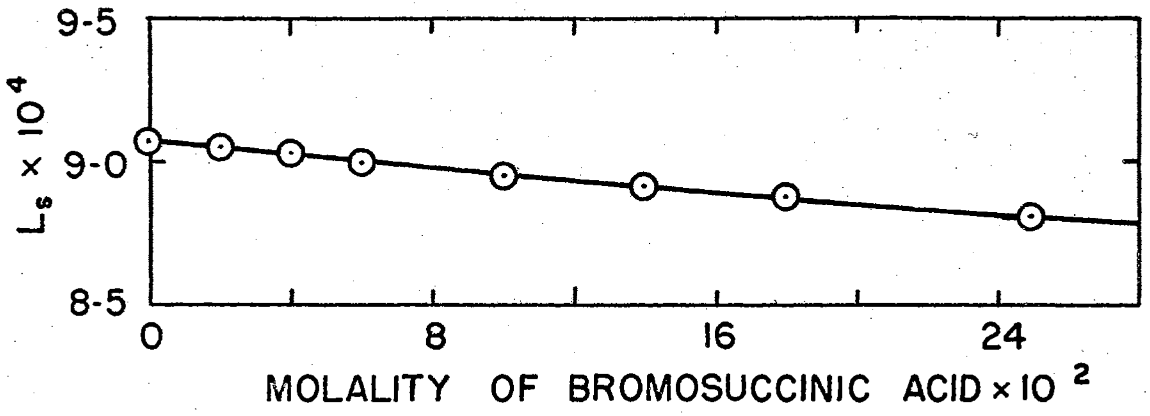


FIG. 16 THE SPECIFIC CONDUCTANCE (L_S) OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM PERCHLORATE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE.

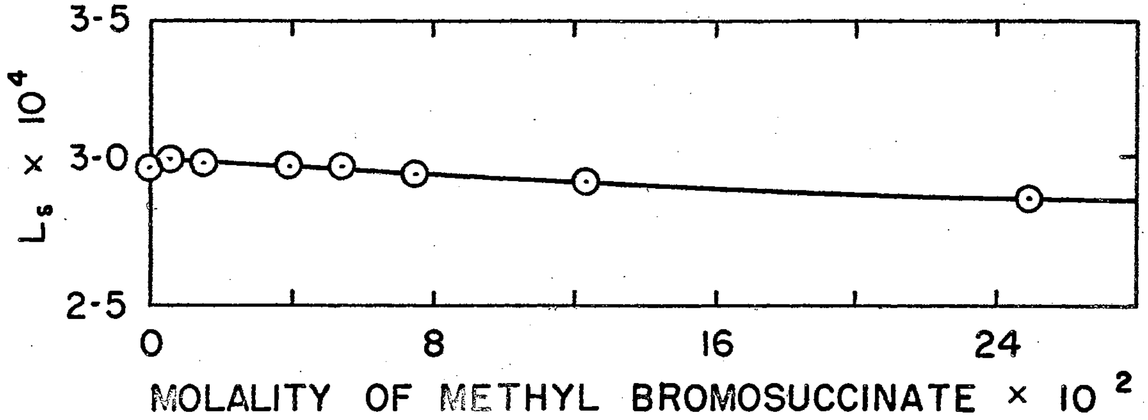


FIG. 15 THE SPECIFIC CONDUCTANCE (L_S) OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF DIMETHYL BROMOSUCCINATE IN ACETONE.

curve (Figure 17) is obtained. The curve decreases in the middle when the conductance measurements are repeated twenty-four hours later on the same solutions. This seems to again indicate that the iodide ion is complexing to produce larger ions, inactive molecules, or is chemically reacting with atmospheric oxygen.

When successive increments of bromosuccinic acid are added to 0.01 molal solutions of lithium chloride, one obtains an increase in the specific conductance curve (Figure 18). When measurements are repeated on the same solutions twenty-four hours later, one obtains a further increase in the specific conductance curve. This curve is like the curve produced in the lithium chloride-chlorosuccinic acid system which may indicate that bromine of the acid is exchanging with the chloride ion of the salt.

If 0.05 molal lithium chloride is used instead of 0.01 molal, then a larger increase in the specific conductance curve is obtained, but the curves have essentially the same shapes.

The method of continuous variation is often used to determine the combining weights of the components of a complex. The concentration of the two components which make up the complex are varied so their combined concentration is equal to a constant and a physical property which is proportional to the complex concentration is measured for the series of combinations to determine a maximum or minimu. The concentration of one component divided by the concentration of the other at the maximum or minimum should give the combining weights, provided that only one complex is formed.

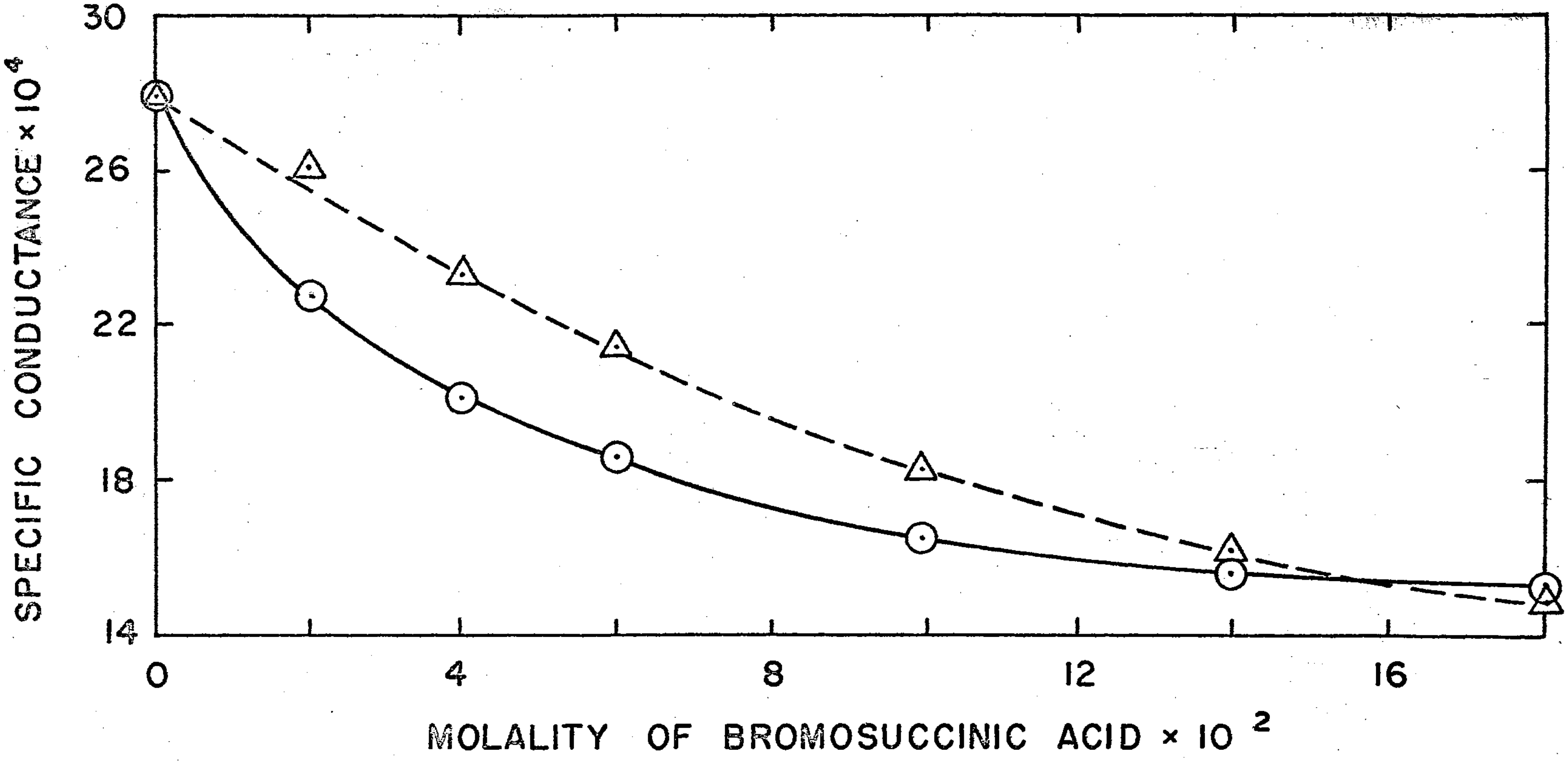


FIG. 17 THE BROKEN LINE (– – –) REPRESENTS THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.05 MOLAL LITHIUM IODIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE. THE UNBROKEN LINE (——) REPRESENTS THE SAME SOLUTIONS BUT THE CONDUCTANCE MEASUREMENTS WERE TAKEN 24 HOURS AFTER THE SOLUTIONS WERE MADE UP.

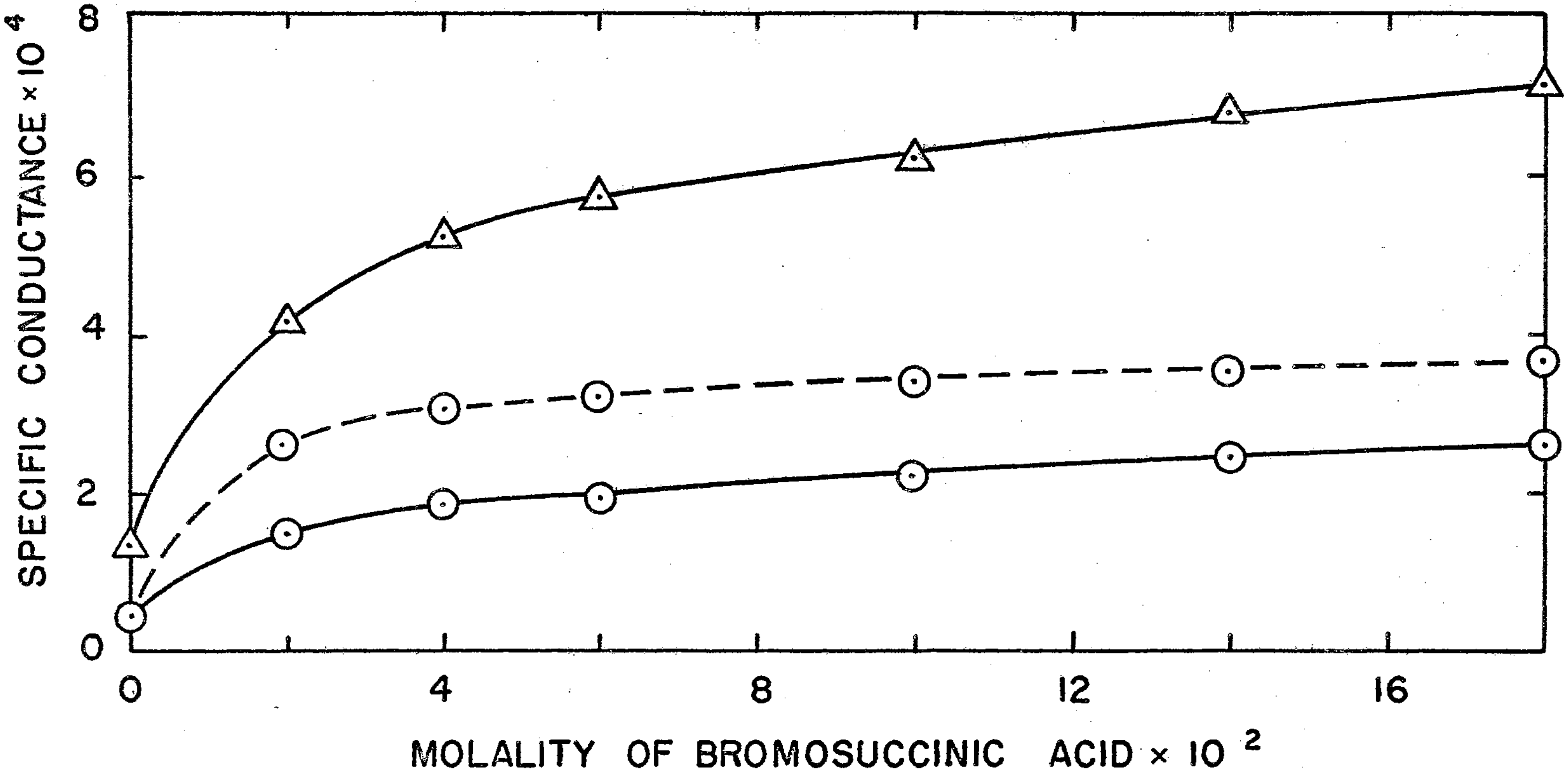


FIG. 18 THE UNBROKEN LINE (——) REPRESENTS THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF 0.01 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE. THE BROKEN LINE (– – –) REPRESENTS THE SPECIFIC CONDUCTANCE OF THE ABOVE SOLUTIONS WITH THE DIFFERENCE THAT CONDUCTANCE MEASUREMENTS WERE TAKEN 24 HOURS AFTER THE SOLUTIONS WERE MADE UP. THE TRIANGLES (△) REPRESENT THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF 0.05 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE.

If concentrations of a lithium halide and an organic acid are varied so that their combined concentrations equal a constant while the specific conductances for the series of solutions are measured, a maximum is observed at a concentration of two lithium halides to one organic acid. (Data shown in Tables VI, VII, VIII and IX). However, when the concentrations of lithium bromide and bromosuccinic acid were held at the constant low value of 0.03 molal, no maximum was observed. (Table X).

Since the specific conductance is approximately proportional to the total number of ions in solution when their mobilities are nearly equal, the maxima should be a function of total ionic concentration. The maxima may then be explained in each case by an association of a halide ion with the organic acid, if the following assumptions are made: the ionization constant of the lithium halide remains unchanged, the mobility of the ions remains unchanged, the change in viscosity has no appreciable effect and the activity coefficients are neglected. The specific conductance then becomes proportional to twice the lithium ion concentration.

TABLE VI

THE SPECIFIC CONDUCTANCES OF SOLUTIONS CONTAINING LITHIUM BROMIDE AND BROMOSUCCINIC ACID VARIED SO THEIR COMBINED MOLALITIES GIVE A 0.30 MOLAL SOLUTION

Molality of Lithium Bromide	Molality of Bromosuccinic Acid	Specific Conductance in mhos/cm^2 x 10^3
0.30	0.00	2.41
0.25	0.05	2.62
0.20	0.10	2.67
0.15	0.15	2.49
0.10	0.20	2.03
0.05	0.25	1.37
0.00	0.30	0.0267

TABLE VII

THE SPECIFIC CONDUCTANCES OF SOLUTIONS CONTAINING LITHIUM BROMIDE AND α-BROMOPROPIONIC ACID VARIED SO THEIR COMBINED MOLALITIES GIVE A 0.30 MOLAL SOLUTION

Molality of Lithium Bromide	Molality of α-Bromopropionic Acid	Specific Conductance in mhos/cm^2 x 10^3
0.30	0.00	2.41
0.25	0.05	2.67
0.20	0.10	2.78
0.15	0.15	2.68
0.10	0.20	2.27
0.05	0.25	1.54
0.00	0.30	0.00824

TABLE VIII

THE SPECIFIC CONDUCTANCES OF SOLUTIONS CONTAINING LITHIUM BROMIDE AND β-BROMOPROPIONIC ACID VARIED SO THEIR COMBINED MOLALITIES GIVE A 0.30 MOLAL SOLUTION

Molality of Lithium Bromide	Molality of β-Bromopropionic Acid	Specific Conductance in mhos/cm^2 x 10^3
0.30	0.00	2.41
0.25	0.05	2.50
0.20	0.10	2.48
0.15	0.15	2.31
0.10	0.20	1.87
0.05	0.25	1.31
0.00	0.30	0.0103

TABLE IX

THE SPECIFIC CONDUCTANCES OF SOLUTIONS CONTAINING LITHIUM CHLORIDE AND CHLOROSUCCINIC ACID VARIED SO THEIR COMBINED MOLALITIES GIVE A 0.060 MOLAL SOLUTION

Molality of Lithium Chloride	Molality of Chlorosuccinic Acid	Specific Conductance in mhos/cm^2 x 10^4
0.06	0.00	0.95
0.05	0.01	2.84
0.04	0.02	3.55
0.03	0.03	3.44
0.02	0.04	2.79
0.01	0.05	1.60
0.00	0.06	0.07

TABLE X

THE SPECIFIC CONDUCTANCES OF SOLUTIONS CONTAINING LITHIUM BROMIDE AND BROMOSUCCINIC ACID VARIED SO THEIR COMBINED MOLALITIES GIVE A 0.030 MOLAL SOLUTION

Molality of Lithium Bromide	Molality of Bromosuccinic Acid	Specific Conductance in mhos/cm^2 x 10^4
0.030	0.000	5.82
0.025	0.005	5.45
0.020	0.010	4.96
0.015	0.015	4.31
0.010	0.020	3.47
0.005	0.025	2.32
0.000	0.030	0.06

CHAPTER IV

DISCUSSION OF RESULTS AND CONCLUSIONS

When an organic acid is added to a lithium halide in dry acetone, the specific conductance of the resulting solution is higher than the sum of the specific conductance of the acid and the specific conductance of the lithium halide at the same concentrations as long as no chemical reaction is taking place.

Some type of chemical reaction is evidently taking place in the alkali iodide systems. The iodide ions can react with atmospheric oxygen to form free iodine and oxygen ions. The free iodine may form higher polymer ions. The free iodine may also react with acetone to form iodoacetone. If atmospheric oxygen was excluded from the alkali iodide systems then perhaps no free iodine would form and the distorting chemical reaction would not take place.

When lithium perchlorate is substituted for lithium bromide, there is slight linear decrease in the specific conductance on addition of bromosuccinic acid. This decrease is probably caused by the increase in viscosity. This experimental evidence indicates that the lithium ion is not involved in the mechanism which causes the anomalous rise in specific conductance of the lithium bromide-bromosuccinic acid system.

When dimethyl dl-bromosuccinate is added to lithium bromide in acetone, there is a slight linear decrease in the specific conductance, this is probably due to the increase in viscosity. This suggests that the free acid may be involved in the mechanism which causes the increase in the specific conductance of the lithium bromide-bromosuccinic acid system.

The acids used with 0.01-molal lithium bromide may be rated as to acid strength by use of Pauling's electronegativity scale (38). The acids in order of highest acid strength follow: bromosuccinic, α-bromopropionic, β-bromopionic, succinic (data for succinic acid given in Table XXI, Appendix) and dimethyl dl-bromosuccinate. The conductance curves for bromosuccinic acid (Figure 2) and α-bromopropionic acid (Figure 13) are nearly alike; the rise in specific conductance is about the same for all the points on each curve.

The curve for β-bromopropionic (Figure 14) has the general shape of the above mentioned curves but the whole curve is proportionally lowered, while succinic acid (Table XXI) shows a still lower, almost linear rise. Dimethyl dl-bromosuccinate (Figure 15) shows a linear decrease. The above statements indicate a correlation between acid strength and the anomalous rise in conductance. The stronger the acid, the greater the rise. The electronegative properties of the acid probably facilitate the formation of the associated groups which causes the rise in specific conductance.

The abnormally high ionic conductances of the hydrogen ion, 349 mhos/cm^2, and the hydroxyl ion, 198 mhos/cm^2, in water (39) can perhaps be explained by a Grotthuss-type proton or hydroxyl ion transfer followed by rotation of the water molecule, but in acetone the average ion conductance-viscosity product is about 0.29, which gives an average ion conductance of 92 mhos/cm^2 and the range of ion conductances is only 70 to 120 mhos/cm^2, (40); therefore the mobility of different ions in acetone is nearly the same. For instance, the mobilities of the hydrogen ion and the sodium ion are nearly the same in acetone, since their respective ionic conductances are 87.7 mhos/cm^2 (41) and 83.3 mhos/cm^2. (Table V, page 31).

All that the above paragraph shows is that if the number of ions in an acetone system remains constant, then changes of the <u>kinds</u> of ions will produce no large change in conductance. Increased conductance should be nearly proportional to the increase in ionic concentration.

The number of ions in the lithium bromide-bromosuccinic acid and lithium chloride-chlorosuccinic acid systems can be increased if the halide ions of the lithium halide associate with the hydrogen ions of the halosuccinic acid to form undissociated molecules of hydrogen halide and allow more lithium halide and halosuccinic acid to dissociate. The proposed association will occur if the hydrogen halide is a weaker acid than the halosuccinic acid in acetone. The number of hydrogen halide molecules produced would be greater for the stronger organic acids. The stronger acids would cause a larger rise in conductance since the number of lithium and organic acid ions would be proportionally increased. The flattened portion of the curve at higher acid concentration indicates that a large portion of the halide ion is tied up in undissociated hydrogen halide molecules, thus; further acid additions cause smaller and smaller increases in ionic concentration.

The addition of acid may slightly increase the dielectric constants of the media but their increase in viscosity more than offsets the number of ions so produced. The increased viscosity slows the progress of the ions through the solution. This effect also tends to flatten the curves at higher acid concentrations.

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APPENDIX

TABLE XI

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM IODIDE PLUS VARIOUS AMOUNTS OF IODOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 1)

Molality of Lithium Iodide	Molality of Iodosuccinic Acid	Specific Conductance mhos/cm^2 x 10^4	Specific Conductance 24 Hours Later, mhos/cm^2 x 10^4
0.01	0.00	9.07	9.07
0.01	0.02	8.67	8.14
0.01	0.04	8.40	7.55
0.01	0.06	8.16	7.12
0.01	0.10	7.72	6.62
0.01	0.14	7.28	6.34
0.01	0.18	6.90	6.24
0.01	0.23	6.55	6.20

TABLE XII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 2)

Molality of Lithium Bromide	Molality of Bromosuccinic Acid	Specific Conductance mhos/cm^2 x 10^4	Specific Conductance, 24 Hours Later, mhos/cm^2 x 10^4	Specific Conductance of Bromosuccinic Acid, mhos/cm^2 x 10^4
0.01	0.0000	2.981	2.990	0.000
0.01	0.0120	3.268	3.289	0.009
0.01	0.0191	3.429	3.449	0.012
0.01	0.0274	3.592	3.568	0.015
0.01	0.0387	3.777	3.756	0.019
0.01	0.0485	3.911	3.910	0.021
0.01	0.0647	4.079	4.068	0.025
0.01	0.0972	4.326	4.313	0.030
0.01	0.1411	4.602	4.604	0.035
0.01	0.1958	4.636	4.616	0.042

TABLE XIII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF CHLOROSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 3)

Molality of Lithium Chloride	Molality of Chlorosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^4	Specific Conductance, 24 Hours Later, mhos/cm^2 x 10^4	Specific Conductance of Chlorosuccinic Acid, mhos/cm^2 x 10^4
0.01	0.00	0.431	0.452	0.000
0.01	0.02	1.622	1.659	0.036
0.01	0.04	1.777	1.779	0.056
0.01	0.06	1.936	1.976	0.063
0.01	0.10	2.058	2.056	0.082
0.01	0.14	2.160	2.150	0.102
0.01	0.18	2.253	2.249	0.119
0.01	0.23	2.350	2.328	0.147

TABLE XIV

THE SPECIFIC CONDUCTANCE OF ACETONE SATURATED WITH CESIUM FLUORIDE PLUS VARIOUS AMOUNTS OF ADDED WATER (Figure 4)

Amount of Water Added to the Dry Acetone, % by Weight	Specific Conductance, mhos/cm^2 x 10^6
0.000	2.18
0.075	7.14
0.179	11.72
0.295	15.21
0.676	23.08

TABLE XV

DATA FOR A FUOSS AND KRAUS PLOT (35, 36, 37) OF LITHIUM CHLORIDE IN ACETONE AT 25° C.

(Figure 7)

$C \times 10^5$	Λ	R	$\frac{1}{2}\log R$	$\sqrt{R}$	Z	F(Z)	Λ/Λ_0
10.581	39.1237	120,956	2.541316	347.79	.020143	.97965	.24061
19.640	29.7712	85,636	2.466323	292.63	.023940	.97575	.18309
28.220	25.1419	70,573	2.424318	265.65	.026372	.97327	.15462
36.609	22.4996	60,657	2.391440	246.29	.028445	.97114	.13837
44.559	20.6362	54,454	2.368010	233.35	.030022	.96951	.12691
52.340	19.4013	49,304	2.346441	222.05	.031550	.96793	.11932
72.745	16.5171	41,673	2.309927	204.14	.034318	.96507	.10158
92.417	13.7228	39,482	2.298201	198.70	.035258	.96410	.08439

$\gamma = \frac{\Lambda}{\Lambda_0 F(Z)}$	$C\gamma \times 10^5$	$\frac{1}{2}\log C\gamma$	$\sqrt{C\gamma \times 10^3}$	$-\log f_{\pm}^2$	$f_{\pm}^2$	$\frac{F(Z)}{\Lambda} \times 10^3$	$\frac{\Lambda C f_{\pm}^2}{F(Z)} \times 10^3$
.24561	2.5988	.707388	5.0979	.038319	.91554	25.0398	3.8688
.18764	3.6852	.783231	6.0706	.946433	.89859	32.7750	5.3847
.15887	4.4833	.825800	6.6957	.051216	.88876	38.7111	6.4789
.14248	5.2161	.858674	7.2222	.055242	.88055	43.1625	7.4685
.13090	5.8328	.882913	7.6367	.058412	.87416	46.9810	8.2909
.12327	6.4519	.904842	8.0324	.061439	.86808	49,8899	9.1071
.10526	7.6571	.942033	8.7505	.066932	.85717	58.4285	10.6720
.08753	8.0893	.953454	9.1927	.070314	.85045	70.2553	11.1873

TABLE XVI

DATA FOR A FUOSS AND KRAUS PLOT (35, 36, 37) OF LITHIUM BROMIDE IN ACETONE AT 25° C.

(Figure 8)

$C \times 10^5$	Λ	R	$\frac{1}{2} \log R$	$\sqrt{R}$	Z	$F(Z)$	$1/\Lambda_0$
3.4740	169.6706	84,949	2.464578	291.46	.019208	.98061	.86549
6.6601	156.3679	48,081	2.340985	219.27	.025532	.97414	.79763
9.6639	147.4657	35,136	2.272876	187.45	.029866	.96967	.75222
12.5450	140.6264	28,383	2.226529	168.48	.033228	.96620	.71734
16.5104	128.9329	23,522	2.185738	153.37	.036502	.96281	.65769
32.3707	108.8893	14,204	2.076165	119.19	.046969	.95187	.55545
47.7730	97.4842	10,731	2.015320	103.59	.054043	.94439	.49727
62.5406	89.8315	8,912	1.975002	94.41	.058298	.93880	.45823

$\gamma = \frac{\Lambda}{\Lambda_0 F(Z)}$	$C\gamma \times 10^5$	$\frac{1}{2} \log C\gamma$	$\sqrt{C\gamma} \times 10^3$	$-\log f_{\pm}^2$	$f_{\pm}^2$	$\frac{F(Z)}{\Lambda} \times 10^3$	$\frac{\Lambda C f_{\pm}^2}{F(Z)} \times 10^3$
.88260	3.06615	.743325	5.5377	.042357	.90707	5.7794	5.4523
.81880	5.45329	.868330	7.3847	.056485	.87805	6.2298	9.3870
.77575	7.49677	.937439	8.6583	.066226	.85856	6.5756	12.6180
.74243	9.31378	.984547	9.6504	.073815	.84369	6.8707	15.4047
.68309	11.27809	1.026116	10.6198	.081230	.82942	7.4675	18.3381
.58354	18.88959	1.138103	13.7441	.105127	.78501	8.7416	29.0695
.43125	20.60211	1.156955	14.3535	.109788	.77662	9.6876	38.2978
.48810	30.52607	1.242335	17.4718	.133640	.73512	10.4507	43.9922

TABLE XVII

DATA FOR A FUOSS AND KRAUS PLOT (35, 36, 37) OF LITHIUM PERCHLORATE IN ACETONE AT 25° C.

(Figure 9)

$C \times 10^5$	Λ	R	$\frac{1}{2}\log R$	$\sqrt{R}$	Z	$F(Z)$	Λ/Λ_0
1.6590	182.0059	165,850	2.609831	407.22	.014401	.98549	.97481
3.2001	179.1128	87,358	2.470650	295.56	.019842	.96996	.95931
4.6141	176.9929	61,313	2,393776	247.62	.023684	.97602	.94796
6.0028	175.1963	47,612	2.338859	218.21	.026876	.97275	.93833
14.6860	166.4716	20,481	2.155676	143.11	.040979	.95813	.89161
28.3040	161.9075	10,926.5	2.019240	104.53	.056104	.94221	.86716
41.8380	158.5872	7,546.7	1.938877	86.87	.067510	.92998	.84938
54.4160	156.7665	5,869.7	1.884320	76.62	.076541	.92020	.83963

$\gamma = \frac{\Lambda}{\Lambda_0 F(Z)}$	$C\gamma \times 10^3$	$\frac{1}{2}\log C\gamma$	$\sqrt{C\gamma \times 10^3}$	$-\log f_{\pm}^{2}$	$f_{\pm}^{2}$	$\frac{F(Z)}{\Lambda} \times 10^3$	$\frac{\Lambda C f_{\pm}^{2}}{F(Z)} \times 10^3$
.98916	1.64102	.607556	4.0509	.030985	.93114	5.4146	2.8529
.97893	3.13267	.747959	5.5969	.042810	.90613	5.4712	5.2999
.97125	4.48144	.825707	6.6945	.051204	.88879	5.5145	7.4368
.96462	5.79042	.881355	7.6095	.058204	.87457	5.5523	9.4552
.93057	13.66635	1.067827	11.6904	.089419	.81392	5.7555	20.7683
.92035	26.04958	1.207902	16.5158	.126328	.74761	5.8194	36.3615
.91333	38.2119	1.291101	19.5479	.149520	.70874	5.8642	50.5653
.91244	49.6513	1.347983	22.2833	.170443	.67539	5.8699	62.6112

TABLE XVIII

DATA FOR A FUOSS AND KRAUS PLOT (35, 36, 37) OF SODIUM PERCHLORATE IN ACETONE AT 25° C.

(Figure 9)

$C \times 10^5$	Λ	R	$\frac{1}{2} \log R$	$\sqrt{R}$	Z	$F(Z)$	Λ/Λ_0
2.7041	193.1395	95.872	2.490845	309.63	.017797	.98204	.97265
5.3793	189.6242	49,088	2.345482	221.56	.024871	.97480	.95495
7.9330	187.6578	33,635	2.263398	183.40	.030046	.96948	.94479
10.435	184.9976	23,938	2.206968	161.05	.034216	.96518	.93165
12.791	183.7943	21,299	2.164185	145.93	.037761	.96150	.92559
15.080	182.1018	18,228	2.130371	134.02	.041117	.95800	.91707
17.297	181.0086	15,992	2.101952	126.46	.043575	.95543	.91156
19.378	180.3442	14,328	2.078094	119.70	.046036	.95285	.90821

$\gamma = \frac{\Lambda}{\Lambda_0 F(Z)}$	$C\gamma \times 10^5$	$\frac{1}{2} \log C\gamma$	$\sqrt{C\gamma} \times 10^3$	$-\log f_{\pm}^2$	$f_{\pm}^2$	$\frac{F(Z)}{\Lambda} \times 10^3$	$\frac{\Lambda C f_{\pm}^2}{F(Z)} \times 10^3$
.99044	2.67824	.713906	5.1749	.039582	.91289	5.0846	4.8549
.97964	5.26978	.860868	7.2588	.055218	.88061	5.1407	9.2148
.97453	7.73095	.944092	8.7921	.067249	.85854	5.1662	13.1833
.96230	10.04169	1.000900	10.0207	.076647	.83821	5.2173	16.7649
.96265	12.31325	1.045685	11.1094	.084975	.82229	5.2314	20.1054
.95728	14.43578	1.079672	12.0137	.091892	.80928	5.2608	23.1979
.95408	16.50272	1.108777	12.8463	.098260	.79756	5.2784	26.1357
.95315	18.47014	1.133237	13.5905	.103952	.78713	5.2835	28.8691

TABLE XIX

DATA FOR A FUOSS AND KRAUS PLOT (35, 36, 37) OF POTASSIUM PERCHLORATE IN ACETONE AT 25° C.

(Figure 9)

$C \times 10^5$	Λ	R	$\frac{1}{2} \log R$	$\sqrt{R}$	Z	$F(Z)$	Λ/Λ_o
4.8146	199.6372	52,095	2.358398	228.24	.023599	.97610	.96443
5.8894	198.4505	42,842	2.315935	206.98	.026023	.97363	.95869
6.9192	197.3825	36,663	2.282113	191.48	.027608	.97200	.95354
7.9153	196.4918	32,195	2.253895	179.43	.029462	.97008	.94924
8.8633	195.3724	28,916	2.230567	170.05	.031087	.96841	.94378
11.3793	193.0673	22,791	2.176670	150.20	.035196	.96417	.93752
13.6738	191.1510	19,157	2.141160	138.41	.038194	.96105	.92343
15.6996	190.0121	16,785	2.112410	129.54	.040809	.95831	.91793

$\gamma = \frac{\Lambda}{\Lambda_o F(Z)}$	$C\gamma \times 10^5$	$\frac{1}{2} \log C\gamma$	$\sqrt{C\gamma} \times 10^3$	$-\log f_{\pm}^2$	$f_{\pm}^2$	$\frac{F(Z)}{\Lambda} \times 10^3$	$\frac{\Lambda C f_{\pm}^2}{F(Z)} \times 10^3$
.98804	4.75702	.838669	6.8971	.052755	.88561	4.8894	8.7207
.98466	5.79906	.881679	7.6151	.058247	.87488	4.9062	10.4973
.98101	6.78780	.915873	8.2391	.063020	.86491	4.9244	12.1526
.97852	7.74528	.944511	8.8006	.067315	.85641	4.9370	13.7305
.97456	8.63791	.968182	9.2935	.071085	.84901	4.9567	15.1814
.97236	11.06478	1.021974	10.5189	.080458	.83088	4.9940	18.9325
.96086	13.13861	1.059276	11.4625	.087676	.81719	5.0277	22.2077
.95786	15.03801	1.088592	12.2629	.093797	.80575	5.0437	25.0807

TABLE XX

THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF VARIOUS AMOUNTS OF CHLOROSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 10)

Molality of Chlorosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^6
0.0252	4.03
0.0600	6.25
0.1165	8.99
0.1399	10.25
0.1549	11.20
0.1670	11.81
0.1750	12.06

TABLE XXI

THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 11)

Molality of Bromosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^6
0.0200	1.24
0.0640	2.45
0.0670	2.53
0.1078	3.14
0.1397	3.51
0.1673	3.83
0.1912	4.12
0.2122	4.32

TABLE XXII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS COMPOSED OF 0.0642 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 12)

Molality of the Lithium Bromide	Molality of the Bromosuccinic Acid	Specific Conductance with Acetone Containing 0.27% Water (Figure 4) mhos/cm^2 x 10^4	Specific Conductance with Acetone Containing 0.11% Water (Figure 4) mhos/cm^2 x 10^4
0.0642	0.0000	9.03	8.03
0.0642	0.0257	10.77	9.72
0.0642	0.0514	12.10	10.90
0.0642	0.0771	13.12	12.00
0.0642	0.1285	14.42	13.30
0.0642	0.1799	15.18	14.20
0.0642	0.2313	15.68	14.70

TABLE XXIII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL SODIUM IODIDE PLUS VARIOUS AMOUNTS OF IODOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 13)

Molality of Sodium Iodide	Molality of Iodosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^4	Specific Conductance 24 Hours Later, mhos/cm^2 x 10^4
0.01	0.00	9.48	9.50
0.01	0.02	9.11	8.38
0.01	0.04	8.81	7.96
0.01	0.06	8.56	7.75
0.01	0.10	8.18	7.55
0.01	0.14	7.78	7.39
0.01	0.18	7.51	7.29
0.01	0.23	7.24	7.24

TABLE XXIV

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF α-BROMOPROPIONIC ACID IN ACETONE

(Figure 14)

Molality of Lithium Bromide	Molality of α-Bromopropionic Acid	Specific Conductance, mhos/cm^2 x 10^4
0.01	0.0000	2.88
0.01	0.0251	3.40
0.01	0.0478	3.79
0.01	0.0700	4.06
0.01	0.0909	4.26
0.01	0.1451	4.59
0.01	0.1923	4.76
0.01	0.2345	4.86

TABLE XXV

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF β-BROMOPROPIONIC ACID IN ACETONE

(Figure 15)

Molality of Lithium Bromide	Molality of β-Bromopropionic Acid	Specific Conductance, mhos/cm^2 x 10^4
0.01	0.0000	2.91
0.01	0.0255	3.23
0.01	0.0498	3.51
0.01	0.0721	3.70
0.01	0.0939	3.85
0.01	0.1484	4.09
0.01	0.1967	4.21
0.01	0.2400	4.28
0.01	0.2727	4.31

TABLE XXVI

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF DIMETHYL BROMOSUCCINATE IN ACETONE AT 25° C.

(Figure 16)

Molality of Lithium Bromide	Molality of Dimethyl Bromosuccinate	Specific Conductance, mhos/cm^2 x 10^4
0.01	0.0000	2.98
0.01	0.0056	3.02
0.01	0.0151	3.00
0.01	0.0388	2.98
0.01	0.0469	2.96
0.01	0.0744	2.93
0.01	0.1243	2.86
0.01	0.2488	2.74

TABLE XXVII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM PERCHLORATE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 17)

Molality of Lithium Perchlorate	Molality of Bromosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^4
0.01	0.00	9.18
0.01	0.02	9.12
0.01	0.04	9.08
0.01	0.06	9.02
0.01	0.10	8.92
0.01	0.14	8.84
0.01	0.18	8.76
0.01	0.25	8.61

TABLE XXVIII

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.05 MOLAL LITHIUM IODIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 18)

Molality of Lithium Iodide	Molality of Bromosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^3	Specific Conductance, 24 Hours Later, mhos/cm^2 x 10^3
0.01	0.00	2.81	2.80
0.01	0.02	2.63	2.28
0.01	0.04	2.33	2.01
0.01	0.06	2.14	1.86
0.01	0.10	1.83	1.66
0.01	0.14	1.63	1.57
0.01	0.18	1.49	1.53

TABLE XXIX

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 19)

Molality of Lithium Chloride	Molality of Bromosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^4	Specific Conductance, 24 Hours Later, mhos/cm^2 x 10^4
0.01	0.00	0.424	0.426
0.01	0.02	1.506	2.615
0.01	0.04	1.849	3.025
0.01	0.06	1.962	3.215
0.01	0.10	2.220	3.398
0.01	0.14	2.425	3.535
0.01	0.18	2.580	3.617

TABLE XXX

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.05 MOLAL LITHIUM CHLORIDE PLUS VARIOUS AMOUNTS OF BROMOSUCCINIC ACID IN ACETONE AT 25° C.

(Figure 19)

Molality of Lithium Chloride	Molality of Bromosuccinic Acid	Specific Conductance, mhos/cm^2 x 10^4
0.05	0.00	1.135
0.05	0.02	4.150
0.05	0.04	5.235
0.05	0.06	5.740
0.05	0.10	6.215
0.05	0.14	6.775
0.05	0.18	7.100

TABLE XXXI

THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING SUCCINIC ACID AND THE SPECIFIC CONDUCTANCE OF SOLUTIONS CONTAINING 0.01 MOLAL LITHIUM BROMIDE PLUS VARIOUS AMOUNTS OF SUCCINIC ACID IN ACETONE AT 25° C.

Molality of Lithium Bromide	Molality of Succinic Acid	Specific Conductance, mhos/cm^2 x 10^4
0.00	0.02	0.00390
0.00	0.04	0.00416
0.00	0.06	0.00410
0.00	0.10	0.00414
0.01	0.00	2.96
0.01	0.02	3.07
0.01	0.04	3.13
0.01	0.06	3.20

VITA

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