

THE CONDUCTIVITY OF DILUTE SOLUTIONS OF
HYDROGEN BROMIDE IN ACETONE

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PREFACE

Because of the apparently complex nature of solutions of the hydrogen halides in acetone, little reliable information is available on such solutions. Solutions of hydrogen chloride in acetone have been investigated somewhat more than those of the other hydrogen halides (although the results of such investigations are hardly conclusive), but almost no information is available for the remaining hydrogen halide solutions. Hydrogen bromide was chosen for the work reported in this thesis because its solutions in acetone appear to decompose more slowly than those of hydrogen iodide and it is more easily handled than hydrogen fluoride. The purpose of this study was to investigate the conductivity of solutions of hydrogen bromide in acetone and to obtain values for the limiting conductance and the dissociation constant of hydrogen bromide in acetone solutions by the method of Fuoss and Kraus.

I am indebted to my advisor, Dr. Clarence Cunningham, and to Drs. Tom Moore and Paul Arthur for their assistance in experimental procedures and in the interpretation of results. Gratitude is extended to Robert Goodrich, C. W. Jones, and Dr. Darvin Keck for personal advice and encouragement during the preparation and writing of this thesis. I wish also to acknowledge Mrs. Margaret Edmister of the Department of English and Foreign Languages, who rendered great assistance by translating an article from Russian. Gratitude is further extended to the Department of Chemistry for supplying the necessary chemicals and apparatus to conduct this study.

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CHAPTER I

INTRODUCTION

Conductivity measurements provide an accurate and easily effected means of studying the dissociation of electrolytes in solution. In the case of a strong electrolyte, the theoretical conductance at infinite dilution, the "limiting conductance," or Λ_0 , can be obtained directly from conductivity measurements at various concentrations. In the case of weak electrolytes more elaborate considerations are necessary since the limiting conductance is not obtained directly. Particularly in aqueous solutions the limiting conductance is usually found from the limiting ionic conductance of the individual ions in solution, which are obtained from conductance data of strong electrolytes. (1).

In non-aqueous solutions, however, particularly in solvents of low dielectric constant, all electrolytes may be considered weak electrolytes, so that the limiting ionic conductances cannot be obtained. (1, 2, 3, 4). In cases of this type it is necessary to examine the electrolyte under investigation directly. A theoretical treatment for electrolytes in solvents of low dielectric constant has been proposed by Fuoss and Kraus (5, 6, 7). This method has been used on many solutions of salts in various solvents of low dielectric constant as well as for some weak electrolytes in aqueous solutions.

Acetone is a solvent with a relatively low dielectric constant of 20.47. (8). A number of conductivity studies of salts in acetone have been reported. (9, 10, 11, 12). The results of such studies, however,

are often lacking in reproducibility, primarily because of the difficulty encountered in obtaining pure acetone. Water is the chief impurity in acetone and is the most difficult impurity to remove. The presence of even trace amounts of water can alter appreciably the specific conductance of a salt-acetone solution, and varying amounts of water produce corresponding variations of specific conductance for the same salt dissolved in acetone. (13). Thus it becomes apparent that reproducibly pure acetone is necessary for reproducible conductance data.

One of the important difficulties encountered in conductivity studies of hydrogen halide-acetone solutions is that acetone has basic properties and is able to react with or form complexes with the hydrogen halides, and compounds of acetone and hydrogen halides have actually been reported. (14, 15, 16). Such reactions definitely take place at higher concentrations, making conductance data at best difficult to interpret; but information is lacking on the extent of this reaction in very dilute solutions.

In this thesis a conductivity study of hydrogen bromide-acetone solutions at low concentrations is presented. Dilute solutions of hydrogen bromide in acetone were prepared, and conductivity data were obtained from them. Finally the method of Fuoss and Kraus was applied to the data in order to obtain a value for the limiting conductance of hydrogen bromide in acetone and a value of the dissociation constant.

CHAPTER II

REVIEW OF LITERATURE

Purification of Acetone

Several methods for the desiccation of acetone have been used. Most of them include distillation from some drying agent. Reynolds and Kraus (8) used first calcium chloride followed by two distillations from activated alumina. Acetone prepared in this manner was reported to have a specific conductance of $1-2 \times 10^{-9}$ mho cm^{-1} , but Dippy and Hughes (13) were unable to reproduce this low specific conductance using the same method. Le Roux and Swart (17) used distillation from anhydrous magnesium perchlorate. Howard and Pike (18) reported a method which is said to give reproducibly very pure acetone. Synthetic zeolite type 5A Molecular Sieve (Lind Air Products) was used as the desiccant followed by distillation through a Vigreux column. Subsequent treatment and distillation did not effect a change in the density of the distillate, indicating that one treatment was sufficient for maximum purification. The density at 25° of acetone prepared in this manner was 0.7842 g/cm^3 . Dorofeeva and Kudra (19) first treated acetone with potassium permanganate for oxidizing possible admixtures, then dried it over anhydrous calcium chloride and finally with freshly fused potassium hydroxide. The acetone was then distilled, the fraction boiling at $56.3-57.1^{\circ}$ being collected. Acetone prepared in this manner had a density at 20° of 0.783 g/cm^3 .

A method of a different type was used by Bjornson (20). Acetone treated with anhydrous calcium sulfate was distilled at room temperature under vacuum through a column of phosphorus pentoxide and was collected in a flask immersed in a dry ice-acetone bath. This method suffers the disadvantage of reaction of the acetone with the drying agent, producing condensation compounds.

Hydrogen Halide-Acetone Solutions

There is a singular lack of information regarding solutions of hydrogen halides in acetone, as pointed out in a review article by Janz and Danyluk (21). Apparently no value for the limiting conductance of any of the hydrogen halides in acetone and no conclusive value of the dissociation constant in dilute solutions have been reported.

Dorofeeva and Kudra (19) investigated the conductivity of hydrogen chloride in acetone and found an anomalous behavior with a maximum and a minimum occurring in the conductance curve over a range of concentrations of 4.6 to 4.5×10^{-3} molar. They did not attempt to obtain the limiting conductance of hydrogen chloride in acetone, discussing rather the formation of complexes at various concentrations and changes in the conductivity of the solution effected by this complexing.

Everett and Rasmussen (22) cite some work done by Kane in which he reported a dissociation constant for hydrogen chloride in acetone to be about 10^{-8} . Kane did his work in 1929, about five years before Fuoss and Kraus (7) proposed a method of treating electrolytes dissolved in solvents of low dielectric constant. Everett and Rasmussen also studied the solution of hydrogen chloride in acetone, but they used EMF methods. In the treatment of their data they found that the order

of magnitude of the dissociation constant of hydrogen chloride in acetone appeared to be 10^{-7} - 10^{-8} .

No information regarding hydrogen bromide in acetone was found, although Janz and Danyluk (21) indicated that work was in progress at the time of their writing (1960).

For purposes of comparison, some work with hydrogen halides in alcohols is cited. The work of Shedlovsky and Kay (23) revealed the dissociation constant for hydrogen chloride in methanol (dielectric constant 32.63) to be 5.9×10^{-2} . Bezman and Verhoek (24) found a value of 84.25 for the limiting conductance of hydrogen chloride in ethanol (dielectric constant 24.30) and a dissociation constant of 1.13×10^{-2} ; the method of Fuoss and Kraus was used in the treatment of the data. El-Aggan, Bradley, and Wardlaw (25) obtained values of 82.46 and 8.23×10^{-3} for the limiting conductance and the dissociation constant, respectively, of hydrogen chloride in ethanol. Using the method of Fuoss and Kraus, Nunez and Day (26) found a dissociation constant of hydrogen bromide in ethanol to be 1.87×10^{-2} .

Janz and Danyluk (21) give a review of other conductance work done on solutions of hydrogen halides and some organic solvents.

CHAPTER III

EXPERIMENTAL METHODS

Preparation of Chemicals

Acetone was purified by the method used by Howard and Pike (18). Reagent grade acetone was placed over type 5A Molecular Sieve that had been dried at 340° C. for three hours. The acetone and desiccant were placed into the flask from which the acetone would be distilled later and were stored in the dark for about 24 hours with occasional shaking. The flask containing the acetone and desiccant was attached to a vacuum-jacketed column about four feet long packed with glass helices. The column, condenser, and collecting flask had been purged previously with air passed through a tube containing dry silica gel. The first 100 ml of the distillate collected were discarded, and the rest was collected until the level of acetone in the distilling flask had reached the level of the desiccant pellets. Distillation was stopped at this point. The acetone was transferred in the dry box to brown bottles and stored there ready for use.

The purity of the acetone was checked against data obtained by Bjornson (20). Samples of the dried acetone were saturated with cesium fluoride which had been dried in a vacuum oven for several hours at 120° C., and the specific conductance of the solution for each sample was obtained. According to the curve prepared by Bjornson from conductance data obtained from acetone solutions saturated with cesium fluoride with various trace amounts of water added, the acetone

prepared in this manner was essentially dry, being more nearly dry than that prepared by Bjornson. On a similar graph prepared by Mysels (27) the acetone appeared to be very nearly anhydrous.

The density at 25° was obtained using a 50 ml pycnometer.

Hydrogen bromide gas was obtained in a cylinder from the Matheson Company. This gas was supposed to have a minimum purity of 99.8% and was labeled "anhydrous." Gas from the cylinder was passed through a cold trap packed with Pyrex glass wool (approximate temperature -20° C.) and into a flask containing the dried acetone.

The Apparatus

Resistances were measured with a high precision Jones bridge built by Leeds and Northrup. A vacuum-tube oscillator supplied a thousand-cycle alternating current across the bridge. The detector circuit consisted of a high gain, low noise amplifier connected to the vertical input of an oscilloscope, whose horizontal input was supplied from the oscillator. This arrangement indicated a balanced bridge by a horizontal straight line on the screen of the oscilloscope.

The constant temperature bath consisted of an insulated drum containing mineral oil. Refrigerated water at 17° C. was circulated very slowly through a copper coil immersed in the oil, and direct current was supplied to a heater in the bath by a rectifier supplied with 230 VAC, 3-phase. The temperature was regulated to $25.00 \pm .01^\circ \text{C.}$ by a thermistor regulator.

Two cells were used. One had a cell constant of 0.0826 cm^{-1} and the other 0.6597 cm^{-1} . The cell with the smaller constant was used only for measuring specific conductances of pure solvent and solvent saturated with cesium fluoride. The cell with the larger constant was

of the dilution type, having a 500 ml Florence flask with a ground glass stopper attached to it; the cell is shown in Fig. 1. Dilutions can be made quite readily in this type of cell.

The cells were cleaned initially with chromic-nitric acid mixture, rinsed with conductivity water, steamed for two hours with steam generated from conductivity water, dried at 110° C., and stored in the dry box ready for use. (25). They were cleaned only by steaming with conductivity water after the initial cleaning.

Analytical Method

Dilute solutions containing hydrogen bromide can be analyzed by titration of the hydrogen ions with standard base or by titration of the bromide ions by standard silver nitrate. (At the concentrations and sample sizes deemed expedient for the experiment, gravimetric methods could not give the desired accuracy.) Since the solutions to be analyzed were about 0.01-0.05 normal and since carbon dioxide could not be easily expelled from the acetone solutions if any was dissolved, and also because of the difficulty in preparation, storage, and use of dilute standard base, the use of acid-base titration was decided against.

Titration with standard silver nitrate solution using eosin indicator (Fajan's method) proved to be particularly suited to the analysis of hydrogen bromide dissolved in acetone. (28, 29, 30, 31). Eosin indicator is usable at low pH and is highly sensitive to the endpoint, even at concentrations as low as 5×10^{-4} normal. The only modification of the Fajan's method was that dextrin solution was not added to the solutions being titrated, since this seemed to make the

end-point less distinct. To one part acetone solution about 1.3 parts of distilled water were added in order to make the acetone solutions behave like aqueous solutions.

Standard silver nitrate solution was prepared according to Kolthoff and Sandell (31). Fused reagent grade silver nitrate was used as a primary standard.

Procedure

When necessary all work was carried out either in the dry box or else with some other adequate protection from atmospheric moisture.

Acetone was dried by the method already described. About 50 ml of dried acetone were placed into a 250 ml Erlenmeyer flask. The flask was then stoppered with a device shown in Figure 2, the stopcock being completely closed. The flask containing the acetone was then removed to the hood.

The apparatus for passing hydrogen bromide over the acetone was set up in the following manner: The cylinder containing anhydrous hydrogen bromide was attached with Tygon tubing to a U-tube filled with Pyrex glass wool and placed into a salt-ice-water mixture in a Dewar flask. A piece of Tygon tubing with a pinch clamp at the far end was attached to the outlet of the U-tube. Before use the U-tube and glass wool were dried in a drying oven, then attached to the apparatus. The tubing and U-tube were then purged with hydrogen bromide gas for a few minutes, and then the pinch clamp was secured.

In the hood the tubing from the U-tube was attached to tube 2 of the 3-way stopcock (Fig. 2) and the pinch clamp opened. The stopcock was then turned to connect 2 and 3. The valve on the hydrogen bromide

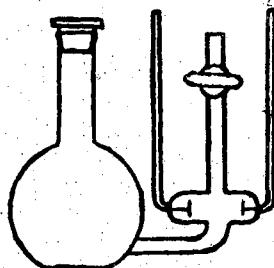


Fig. 1. Dilution cell.

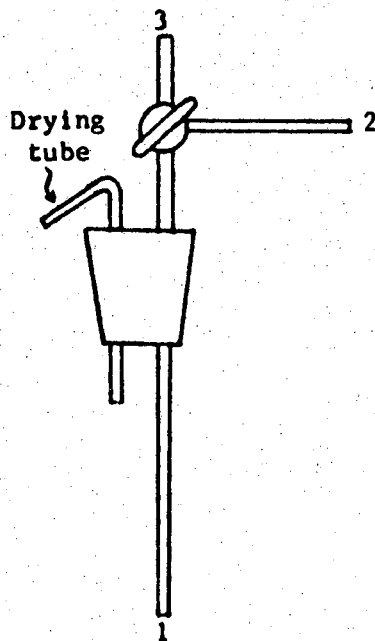


Fig. 2. Stopper equipped with drying tube connection and 3-way stopcock.

cylinder was opened, and the stopcock tubes that had been exposed to atmospheric moisture were purged with hydrogen bromide. After about a minute the stopcock was turned, connecting 1 and 2. This allowed the gas to pass into the flask and over the acetone. Exposure of the acetone to the gas for 1-2 minutes was sufficient to make 0.01-0.05 normal solution. Then the valve on the cylinder was closed, the stopcock fully closed, the pinch clamp secured, and the flask returned to the dry box.

Three samples of the solution of about 15 ml each were weighed out using a Bailey weighing burette. These were analyzed by the Fajan's method already described.

From the remaining solution a solution of about 2×10^{-3} normal was prepared by dilution in the dilution cell in which the resistances were to be measured. All dilutions were done by weight, using the weighing burette. The cell containing the solution whose resistance was to be measured was placed into the constant temperature bath, a stopwatch started, and the resistance read at time intervals of about two minutes for 20-30 minutes. Successive dilutions and readings were taken until sufficient data were collected.

The entire procedure was repeated three times in order to check for reproducibility.

CHAPTER IV

RESULTS

It was found that the resistance of the acetone solutions did not reach a constant value, but constantly changed with time. This was to be expected as discussed by Janz and Danyluk (21) because of the release of H_3O^+ ions from acid catalyzed condensations of the solvent. In order to have some basis for reading a specific value of the resistance of each solution, plots of resistance vs. time were prepared. Usually the resistance-time curves were essentially straight lines after thermal equilibrium had been reached. When this was the case, the straight line was simply extrapolated to zero time. For some solutions, however, the resistance-time curves were smooth curves. When this was the case, a tangent to that part of the curve from about 8 minutes to about 15 minutes was drawn and extended to zero time. The resistance at zero time was called " R_0 " and was used as the value of the resistance for each respective solution.

Two separate batches of acetone were prepared. The first batch had a density of 0.7839 g/cm^3 and a specific conductance of $1.08 \times 10^{-7} \text{ mho cm}^{-1}$, both at 25° . The second batch had a density of 0.7838 g/cm^3 and a specific conductance of $6.9 \times 10^{-8} \text{ mho cm}^{-1}$. Conway (32) gives $5.5 \times 10^{-8} \text{ mho cm}^{-1}$ for the specific conductance of acetone. Howard and Pike (18) reported a density of 0.7842 g/cm^3 for acetone, using the same method of purification used in this experiment.

The specific conductances of the solutions were of the order of

10^{-6} mho cm^{-1} . Since the specific conductance of the solvent was appreciable, a solvent correction was necessary, producing some uncertainty in obtaining the actual specific conductance of the solute.

Figure 3 shows a plot of equivalent conductance vs. the square root of concentration. From the graph it can be seen that the data gave a curve typical of that for a weak electrolyte. This was to be expected since strong electrolytes become weaker as the dielectric constant of the solvent decreases. (4). The reproducibility of the four separate runs was good as shown by Figure 3.

The data were treated by the method of Fuoss and Kraus, using the procedure given by Glasstone (2). The Onsager constants were calculated using equations from Glasstone (33), and the constant for the Debye-Huckel limiting law was calculated using an equation from Robinson and Stokes (34). A great deal of difficulty was encountered in estimating a trial value of the limiting conductance, Λ_0 , and several series of calculations were necessary before the value of Λ_0 was approximated. The final plot of the data is shown in Figure 4. The method of least squares was used for determining the best line for the data. (35).

Examination of the plot shows greater scattering of the points as the concentration is decreased. This is to be expected since the solvent correction becomes relatively larger at increased dilutions and because experimental error in the dilutions and in reading the resistances is increased for very low concentrations.

The Fuoss and Kraus plot has a large slope, being about 77, and a small intercept, being about 0.01. (The intercept is the reciprocal

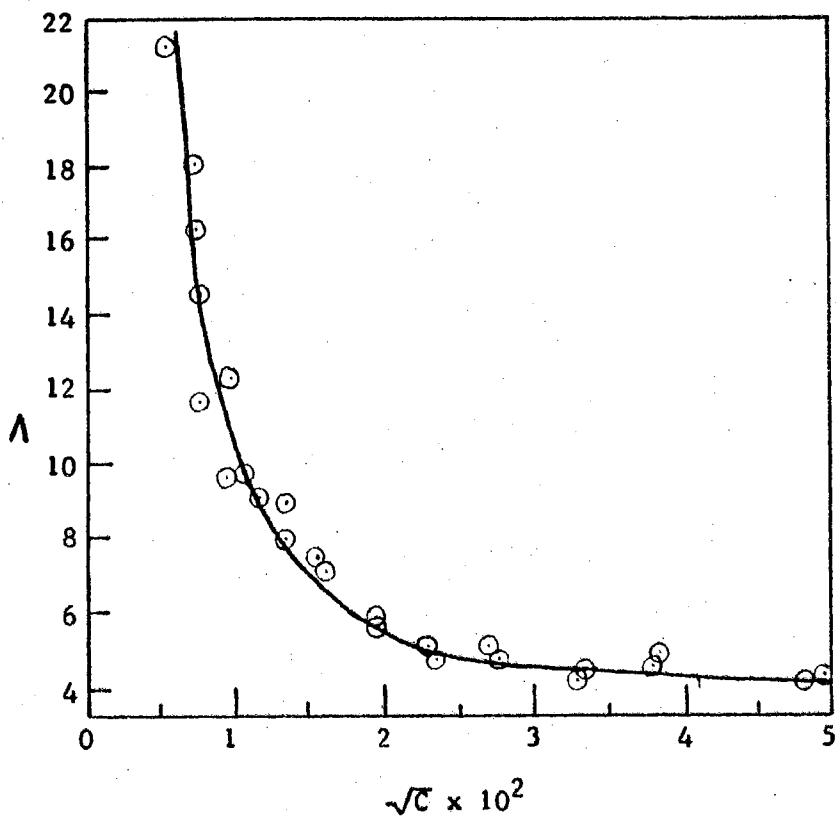


Fig. 3. Plot of λ vs. $-\sqrt{C}$

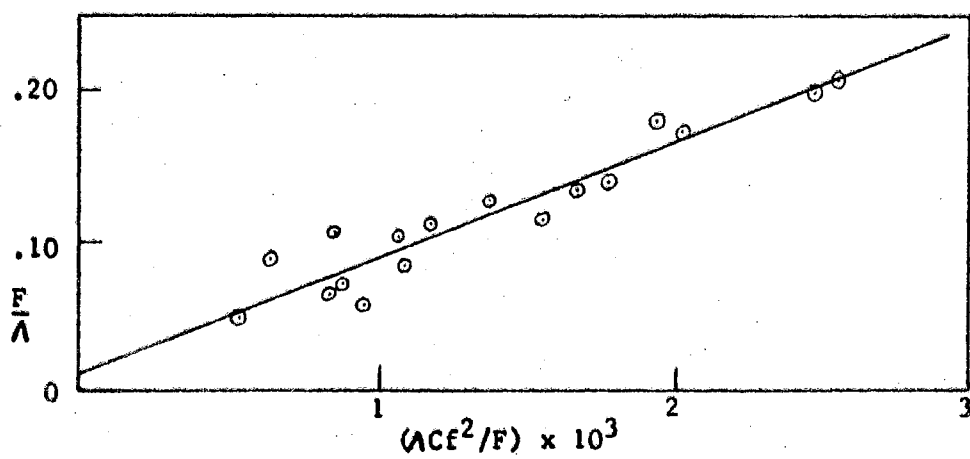


Fig. 4. Fuoss and Kraus plot.

of λ_0 .) Because of the large slope, a small chance in λ_0 chosen for the calculation can produce a relatively large change in the intercept, since it is so small. Since the data are accurate only to four significant figures in most cases and in a few cases only to three significant figures, the value of the intercept can have no more than two significant figures after the calculations are carried through, with some uncertainty in the second figure. The only way that this can be avoided is to collect data accurate to more significant figures. This was for all practical purposes impossible in the experiments reported herein.

Table I shows the change in the calculated value of λ_0 by the method of least squares and the estimated value used for the calculation.

TABLE I
COMPARISON OF ESTIMATED AND
CALCULATED VALUES OF λ_0

<u>Estimated</u>	<u>Calculated</u>
91	120
120	110
110	100
100	120
120	120

Examination of the table shows that the calculated value is oscillating within a certain range. It must be remembered, however, that only two figures are significant with some uncertainty in the second figure. Thus within the accuracy of the experiment the value probably lies within the range 110-120, or $1.1 \times 10^2 \leq \lambda_0 \leq 1.2 \times 10^2$.

Using a value for the slope of the line in the Fuoss and Kraus plot of 77, the dissociation constant then falls within a range of $0.90 \times 10^{-6} \leq K \leq 1.1 \times 10^{-6}$, or is about 1×10^{-6} .

CHAPTER V

INTERPRETATION OF RESULTS

Implications of the Study

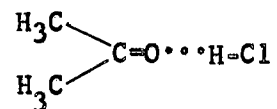
Table II is taken from a review article by Janz and Danyluk (21). On the basis of dielectric constant alone, one might expect that the limiting conductance of hydrogen bromide in acetone would be about 50. This is not the case, however. Hydrogen bromide appears to be a stronger electrolyte in acetone than consideration of the dielectric constant alone would permit. Since Λ_0 is a function of the mobilities of the respective ions in solution, it is possible to interpret the high value of Λ_0 as a manifestation of high mobility of one or more ions in the solution. In water the hydrogen ion has been shown to have an extremely high mobility, which is explained in terms of a "proton jump" mechanism, in which a proton may be transferred from one water molecule to a neighboring molecule, provided that both are favorably oriented. (36). An analogous "proton jump" mechanism in acetone would produce the effect of increased mobility of the hydrogen ion, and a corresponding increase in the value of Λ_0 of hydrogen bromide.

TABLE II

Λ_0 FOR HBr IN SOME ALCOHOLS AT 25°

Solvent	Dielectric constant	Λ_0
Methanol	32.63	212.3
Ethanol	24.30	88.9
1-Propanol	20.1	47.2

Dorofeeva and Kudra (19) suggested a possible complex of the following type for acetone and hydrogen chloride:



As a result of this complexing, they indicate that the hydrogen-halogen bond is weakened, allowing for greater dissociation of the hydrogen halide molecule. It is not unreasonable to postulate a similar complexing between hydrogen bromide and acetone. As was pointed out earlier, 1:1 compounds of acetone and hydrogen bromide have been reported at low temperatures. In dilute solutions this complexing may still be taking place. The sort of complex suggested by Dorofeeva and Kudra would allow for the possibility of increased conductivity of hydrogen bromide in acetone over hydrogen bromide dissolved in a solvent of similar dielectric constant with which it does not react or form complexes.

Hydrogen bromide gas is not a simple ionic compound; and in acetone, for which the dielectric constant is low, it is not unlikely that the hydrogen bromide molecule tends to remain associated. The hydrogen bonding between the hydrogen of the molecule and the oxygen of the acetone, however, could effect sufficient weakening of the hydrogen-bromine bond to allow increased dissociation. In this case the conducting species would be the bromide ion and the acetone-hydrogen ion complex, and the dissociation constant would be for the dissociation of those two ions. This situation is analogous to the formation of hydronium ions and bromide ions in hydrobromic acid. It is also similar to a complex proposed by Kearns (37) for chloroform and acetone, $(\text{CH}_3)_2\text{C}=\text{O} \cdots \text{H}-\text{CCl}_3$, for which the heat of association was

found to be -2.4 kcal/mole. Hydrogen bonding between hydrogen chloride molecules and molecules of other organic solvents has been reported from infra-red studies by Gordy and Martin (38).

It is important to point out that the experiments reported in this thesis do not necessarily suggest an acetone-hydrogen bromide complex, but merely confirm the possibility that such a complex may exist in the light of other work.

Mead, Fuoss, and Kraus (39) reported that the critical concentration - that concentration above which the Fuoss and Kraus equation was no longer applicable - could be calculated at 25° from the equation

$$c = 3.2 \times 10^{-7} D^3,$$

where D is the dielectric constant of the solvent. For acetone the critical concentration becomes 2.8×10^{-3} molar. For the hydrogen bromide solutions, however, it was found experimentally that the critical concentration was actually about 6×10^{-4} molar. Figure 5 illustrates the behavior of the Fuoss and Kraus plot over the experimental range of concentration from 2.5×10^{-3} molar to 2.7×10^{-5} molar. This may indicate that the solution is more complex at the higher concentrations. At any rate, the theory of Fuoss and Kraus does

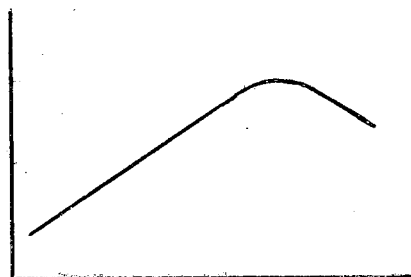


Fig. 5. An Example of a Fuoss and Kraus Plot for HBr Concentration Less Than 2.8×10^{-3} M.

not apply for this particular system except at very low concentrations. Below about 6×10^{-4} molar the solution appears to follow the theory correctly.

The order of magnitude of the dissociation constant for hydrogen chloride in acetone was reported by Everett and Rasmussen (22) to be 10^{-7} - 10^{-8} . Since hydrogen bromide is a stronger acid usually than hydrogen chloride, the value of the dissociation constant of hydrogen bromide in acetone reported in this thesis (1×10^{-6}) is reasonably close to and larger than the value reported for hydrogen chloride.

Summary and Conclusions

The limiting conductance of hydrogen bromide in acetone was found to be 1.2×10^2 , and the dissociation constant, 1×10^{-6} . In the interpretation of these results and their reliability it must be remembered that the resistance decreased with time in the solutions studied, probably because of the release of H_3O^+ ions from the acid catalyzed condensation reactions of the solvent. Since the technique used in obtaining the resistance measurements did not include any correction for this change in resistance with time, it is expected that some error is present in the resistance measurements as each solution was diluted. The production of H_3O^+ ions, however, should take place at successively slower rates as the solutions are diluted; and the water produced may have little effect in the very dilute solutions in dry acetone. On the basis of these statements, it is possible that the conductance measurements corresponding to the higher concentrations are larger than they would be if correction could be made for the amount of water present. This effect would become less as large amounts of dry acetone are added.

In Fig. 4 (page 14), if the conductance is decreased slightly at higher concentrations and no change is made at lower concentrations, the slope of the line would be increased slightly with a corresponding decrease in the value of the intercept. If the intercept is decreased, Λ_0 increases. Thus the value of Λ_0 reported in this thesis may be less than the actual value.

A refinement of the procedure used in the experimental work perhaps would produce more reliable data. If a known amount of hydrogen bromide gas at 25° C. could be introduced directly into the conductivity cell containing a known amount of acetone at 25°, the conductivity of the solution could be measured from the time of mixing for every solution at the various concentrations. This would help to overcome the difficulty involved in making accurate measurements caused by the reaction of the hydrogen bromide and the acetone.

In order to elucidate the nature of the solutions and the conducting species, a study of infra-red spectra of the solutions at various concentrations is needed. The spectra should reveal information regarding the extent of complexing at various concentrations and something of the nature of the conducting species. In order to determine the mobility of the conducting species, an investigation of transference numbers is suggested.

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APPENDIX

TABLE III

DATA FOR GRAPH OF Λ VS. \sqrt{C} AND
FUOSS AND KRAUS PLOT

C x 10 ⁴	\sqrt{C} x 10 ²	R _o kohms	Λ	x	F	α	f	X*	Y**
22.98	4.794	70.36	4.033						
11.07	3.328	140.5	4.142						
5.691	2.386	235.5	4.732	.0237	.9760	.04408	.9568	2.526	.2063
2.697	1.642	328.8	7.038	.0199	.9799	.06529	.9637	1.799	.1392
1.393	1.180	484.5	9.004	.0161	.9838	.08320	.9705	1.201	.1093
.5583	.7472	594.5	17.95	.0144	.9855	.1656	.9736	.965	.0549
24.81	4.981	62.20	4.233						
11.36	3.371	130.5	4.355						
5.360	2.315	240.2	4.922	.0234	.9763	.04583	.9573	2.477	.1984
2.413	1.553	350.7	7.348	.0192	.9806	.06812	.9649	1.683	.1335
1.158	1.076	534.4	9.724	.0153	.9846	.08978	.9720	1.081	.1013
.5525	.7433	658.2	16.18	.0136	.9863	.1491	.9750	.862	.0610
.2660	.5158	983.2	21.16	.0108	.9891	.1945	.9802	.547	.0467
14.62	3.823	99.90	4.471						
7.708	2.776	179.4	4.681						
3.779	1.944	296.3	5.707	.0212	.9786	.05302	.9613	2.037	.1715
1.870	1.367	382.6	8.851	.0185	.9813	.08200	.9661	1.574	.1109
.9485	.9739	538.2	12.20	.0155	.9844	.1127	.9716	1.110	.0807
.6389	.7993	662.7	14.49	.0139	.9860	.1336	.9746	.892	.0680
14.92	3.863	91.20	4.801						
7.450	2.730	178.6	4.866						
3.770	1.942	310.1	5.459	.0207	.9791	.05069	.9622	1.794	.1794
1.868	1.367	430.8	7.826	.0174	.9824	.07242	.9678	1.394	.1255
.9415	.9703	678.0	9.60	.0137	.9862	.08849	.9749	.871	.1027
.5859	.7654	878.9	11.6	.0119	.9880	.1067	.9782	.658	.0852

*X = $(\Lambda C f^2 / F) \times 10^3$

**Y = F/ Λ

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