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Dielectric Constant Studies. I. An Improved Voltage Tuning Resonance Method and Its Application to Aqueous Potassium Chloride Solutions

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An experimental study of the behavior of various types of apparatus used in the measurement of dielectric constants of aqueous solutions of electrolytes. Although simple theory indicates that the voltage tuning method of detection should give results which are uninfluenced by the conductivity of the solutions and should, hence, be particularly adapted to measurements on electrolytic solu-

tions, it appears, however, that other disturbing factors are present. This is shown by the divergent results obtained when different types of detection are employed and leads to the conclusion that the change in dielectric constant of such solutions as observed by this method depends more or less upon the characteristics of the particular generating and receiving circuits used.

THE experimental evidence for the effect of ions on the dielectric constant of liquids is very conflicting. Debye,¹ after a consideration of the results, obtained prior to 1929, states that, "no definite conclusion with regard to any theory can be drawn from measurements in their present condition." Since 1928, numerous papers have appeared and one might expect considerable improvement; however, the pronounced lack of agreement in published data forces the conclusion that this is not the case. The seriousness of this situation was emphasized to the authors in the course of some work on the dielectric constant of gelatin solutions, the results of which will be reported in a later paper. In connection with that work, it became evident that in some solutions conductivity had an important bearing on the results. These circumstances led the authors to undertake a series of investigations in an attempt to clarify the situation in respect to aqueous solutions of electrolytes. This aim has necessitated the use of several methods of measurement in order to contrast directly their advantages and limitations.

It is the purpose of this paper to discuss the so-called voltage tuning resonance method used in various forms and with varying success by

Jezewski,² Kniepkamp,³ Lattey and co-workers,⁴ and Astin.⁵ Since the presentation of this work in the form of a dissertation, another paper by Jezewski⁶ has appeared which describes work similar in its purpose to that presented here.

Since the theory has been given by Jezewski, and can also be found in the papers of Lattey already referred to, it need be described but briefly here. The voltage tuning principle derives its significance from the fact that analysis of the tunable portion of the circuit of Fig. 1 shows that, if the value of C is adjusted to give a maximum voltage across the condenser, this maximum will be independent of the resistance x in parallel

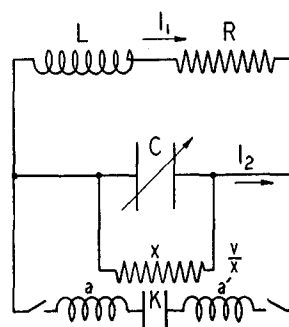


FIG. 1. Diagrammatic resonating circuit.

* This paper constitutes a portion of the dissertation submitted by J. Gilbert Malone to the faculty of the Graduate School, University of Michigan, in partial fulfillment of the requirements for the degree of Sc.D.

¹ Debye, *Polar Molecules*, p. 124, Chem. Cat. Co., N. Y., 1929.

² Jezewski, *Zeits. f. Physik* **48**, 123 (1928).

³ Kniepkamp, *Zeits. f. Physik* **51**, 95 (1928).

⁴ Lattey (*et. al.*), *Phil. Mag.* **7**, 985 (1929); **11**, 997 (1931); **12**, 1111 (1931); **13**, 444 (1932).

⁵ Astin, *Phys. Rev.* **34**, 300 (1929).

⁶ Jezewski, *Phys. Zeits.* **34**, 88 (1933).

with it. This analysis assumes an inductance without capacitance, and a condenser without inductance. Moreover, there must be no reaction of the resonance circuit on the oscillator.

THE OSCILLATOR

The oscillations were produced by the use of a UX210 tube in the circuit shown in Fig. 2.

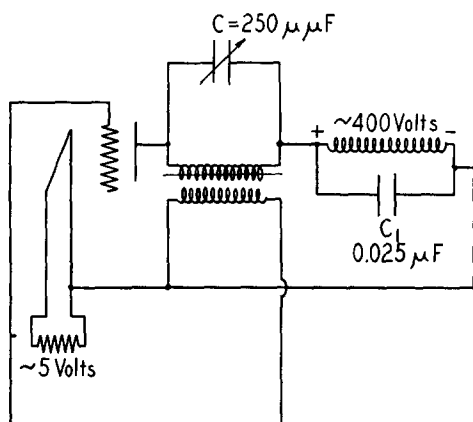


FIG. 2. Oscillator.

The filament was lighted and the plate supplied with the proper voltages by a transformer unit especially designed for this purpose. The inductances of the plate circuit and the grid circuit were wound on the same Bakelite core and fitted with plug connections facilitating their interchange. UX bases are convenient for this purpose as they will not permit the coil so mounted to be placed wrongly in the circuit. This oscillator functioned well for wave-lengths from 20 to 100 meters.

THE RESONATING CIRCUIT

When the voltage tuning resonance method is employed there are several factors to be considered which do not appear from the simple theory. The simple theory takes no account of the inductance of the cell leads. It is obvious, however, from consideration of the circuit shown in Fig. 1 that the inductance will be changed because of the inductance in the leads represented by a and a' if the total capacity is transferred from the cell K to the precision condenser C . It is evident also that some sort of a meter must

be used to indicate the maximum voltage across the condenser C , and whatever sort is used, it presents complications by introducing capacitance, inductance, resistance or some combination of these. Lattey and his co-workers employ a thermocouple galvanometer connected across the condenser terminals through a capacitive impedance. They believe this arrangement to be superior to all others for the purpose.

Two distinct resonating circuits have been used in this work. The first followed that of Lattey and Davies⁷ as closely as possible, and is shown in Fig. 3. This circuit as constructed and

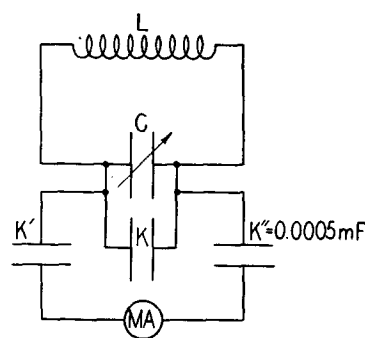


FIG. 3. First receiver.

used by the present authors, gave results in qualitative agreement with those obtained by Lattey and Davies. Since the second circuit is believed to represent an advance, and since it possesses far greater sensitivity and does not sacrifice or compromise any principle embodied in the first, no further discussion of the first circuit is considered necessary.

The second circuit is shown in Fig. 4. In principle it is an alternating voltage indicating device. In this arrangement it is not necessary to balance out an initial plate current as is usually done; the plate current is initially zero because of the d.c. grid bias. When the resonance condition is approached an increase in the plate current of the tube results and can be measured by a milliammeter in the plate circuit. When the voltage across the condenser is a maximum, the plate current is likewise a maximum, and both of these conditions occur, as has been pointed out by Jezewski, when $\omega^2 = 1/LC$.

It is desirable that the parts of the resonator

⁷ Lattey and Davies, *Phil. Mag.* **12**, 1111 (1931).

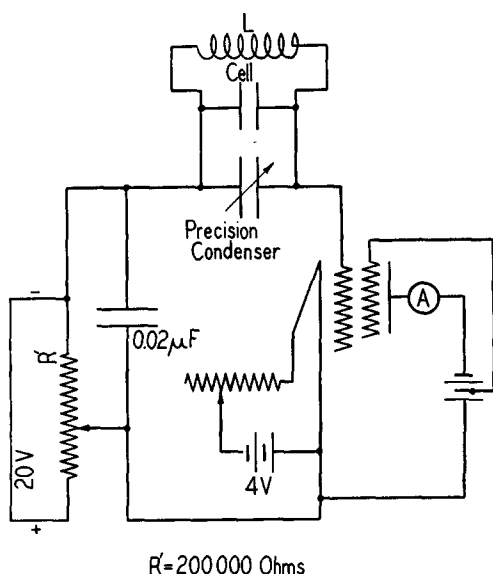


FIG. 4. Second receiver.

be arranged as compactly and as symmetrically as possible. The inductances were made from 8×2 mm copper strip and were mounted on short extensions of the condenser terminals. The tube connections were placed at about the same point, and provision was made to allow the cell to be inserted directly across the terminals of the condenser and the tube connections. It was possible to bring all of these connections together by inclining the condenser to the extent that a radio tube could be hung just below its terminals. The extension of these terminals provided a means for securing the inductance and the cell.

The condenser used was General Radio type 222-L. A UX222 tube was employed. All leads and the tube were shielded and grounded. The dielectric cells used are illustrated by the one shown in Fig. 5. These were made of glass and platinum with very short leads. It has been concluded by Lattey that in such a case the apparent dielectric capacity will not be affected by the conductivity of the solution.

The oscillator was normally kept at a distance of about 90 cm from the resonator. Tests showed that effects of coupling were observable at 30 cm. It has been observed also that unless one works at a considerable distance from conductors such as water pipes, etc., effects due to these may be attributed to coupling. On the basis of such observations the authors believe that the chang-

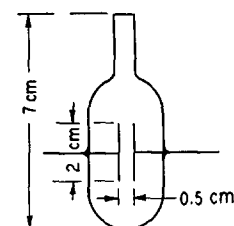


FIG. 5. Dielectric constant cell.

ing of the relative positions of oscillator and resonator is undesirable.

The setting of the condenser, giving maximum current, which is the condition of resonance, is difficult to determine with great precision and is often obtained, in the case of wave meters, by the insertion of a small capacitance in parallel with the variable condenser. Any setting of the condenser such that insertion of this capacitance makes no change in the reading of the indicating device requires that the capacitance has spanned the resonance point to give a corresponding point on the other side. This procedure, while admirable for wave meters, was not very successful here and an alternative was sought.

It is generally known that the curve obtained when current is plotted against condenser readings is symmetrical if the calibration curve of the condenser is linear. To what extent this is true in the present case may be seen from the figures in Table I.

TABLE I. Data on symmetry of resonance curve.

Microamperes	Condenser Values		Mean
	Above	Below	
400	5390	5260	5325
300	5431	5230	5330
200	5470	5172	5329
150	5520	5122	5321
100	5744	4864	5304
Cell filled with solution			
110	5104	5502	5303
140	5278	5322	5300

The first column gives the current as shown by the ammeter *A* in microamperes, the next two columns give the two condenser settings on opposite sides of the resonance point corresponding to the currents in the first column. The last column shows the mean of these condenser values. If the above noted symmetrical relation-

ship holds, the values in the last column should remain constant. The extent of the agreement indicates that the symmetrical relationship is closely approximated until the curve is about 400 condenser divisions in width. The values obtained with an electrolyte show that the curve is flattened as a result of electrolytic conduction. Only a limited range may, therefore, be followed and the accuracy is correspondingly decreased.

If the calibration curve of the condenser were linear, a number of readings might be made at corresponding current values on either side of the resonance point, and the resonance point obtained as above by taking the mean. In practice it was found necessary to use the lower settings of the condenser where the linear relationship does not hold and in such cases three procedures are possible. In the first method, the condenser may be calibrated and the readings converted in terms of the calibration. This method was not employed in the present case, since experience indicated two other methods which were more convenient and of equal accuracy. In both the average of the two condenser readings obtained with the same current but on opposite branches of the resonance curve was plotted against the difference between these readings, i.e., against the width of the resonance curve. The two methods differed, however, in the fact that in method II the plate current was always adjusted to the same value while in method III it was allowed to vary.

The procedure used in taking measurements according to method II was as follows: Two condenser readings were taken, one on each side of the resonance point for the same plate current. The condenser was then set to a new value and, after the plate current had been restored to the original value by suitable variation of the grid bias, another condenser reading was taken on the opposite side of the resonance point. This procedure was then repeated for as many points as desired.

In method III, on the other hand, the plate current was allowed to vary with the closeness of approach to the resonance point, although again for each PAIR of readings the plate current was of course the same.

These two methods gave satisfactory agree-

ment over the node width of 200 to 600 divisions, which range included practically all of the measurements in this work. In practice, however, method III was preferred in that it gave somewhat more consistent results.

In applying the latter method to the measurement of the dielectric constant of an electrolytic solution, curves were determined for water and for the solution in the manner just described and both plotted on the same graph as illustrated in Fig. 6. The curves obtained approximate straight

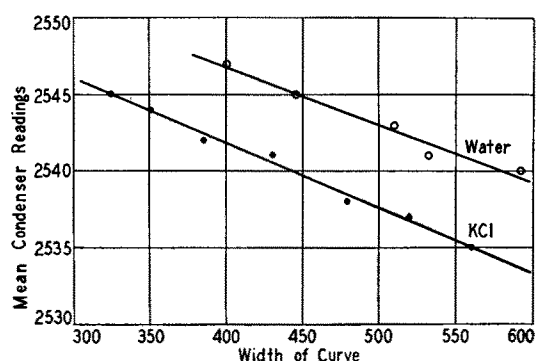


FIG. 6. Plots of typical observational series for the dielectric constant of KCl solutions by the voltage tuning method.

lines and the curve for the solution always falls below the one for water. The mean ordinate distance between these curves is the increase in the capacity of the cell when filled with solution over its capacity when filled with water. The dielectric constant of the solution is calculated from this value. Following this method of procedure, the troublesome conversion of condenser readings into comparable units is avoided and at the same time the effect of an asymmetric wave is minimized.

The apparatus and cells described were designed for the measurement of the dielectric constants of aqueous solutions of electrolytes. It was assumed that the relationship between cell capacity and dielectric constant is linear, and that benzene and water can be employed as calibrating materials to determine this line. Several pure materials, covering a wide range of dielectric constants, were measured. The values obtained agreed well with those recorded in the literature.

THE DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS OF KCl

A review of this subject has been given by Lattey and Davies.⁷ Many observers have measured a large number of solutions.⁸ The conflicting nature of the results obtained emphasizes the futility of making extensive measurements on solutions of a large number of carefully purified inorganic substances at the present time. It has been the purpose of the present authors to confine measurements to a few substances and to study the possibilities of several methods. The Drude method in several modified forms has been used by us, and is the subject of a separate communication.*

Lattey and his co-workers have used the voltage tuning resonance method most extensively. Some of his methods, on first consideration, appear different from and more elegant than those employed by us. Careful analysis, however, reveals that this is probably not the case. Let us consider the problem of finding the true resonance point. The impressed voltage under proper conditions, as has been indicated, gives a potential across the condenser which is symmetrical with respect to capacity and falls off with capacity values either less or greater than this. In order to obtain K_0 , the resonance capacity, Lattey considers that two values for the capacity are obtained, one on either side of the resonance capacity K_0 , which give the corresponding currents I_1 and I_1' and a current I_0 at the resonance point. He is thus enabled to write:

$$(K_0 - K_1)/(I_0^2/I_1^2 - 1)^{\frac{1}{2}} = \phi$$

and

$$(K_1' - K_0)/(I_0^2/I_1'^2 - 1)^{\frac{1}{2}} = \phi.$$

Eliminating K_0 :

$$\phi = (K_1' - K_1)/(I_0^2/I_1^2 - 1)^{\frac{1}{2}} + (I_0^2/I_1'^2 - 1)^{\frac{1}{2}}$$

ϕ is the tuning factor.

Lattey and Davies determine current values with the condenser set at definite values and calculate K_0 by means of the preceding equations. It is obvious from the derivation of the equation

* Compare for instance the results of Milicka and Slama, *Ann. d. Physik* (5) **8**, 663 (1931) with those of Lattey and Davies, *Phil. Mag.* **12**, 1111 (1931); **13**, 444 (1932).

* This communication is really number II in this series and follows the present article.

that, if $I_1' = I_1$, the values of K_0 will be the arithmetical mean of K_1 and K_1' . The method followed in our work consists in reading the values of capacitance, first with the current at a definite value and then after the current has been brought to the same value on the other side of the resonance point by a proper adjustment of the capacity. Such a procedure is more convenient in observation and calculation than that used by Lattey and Davies and is more fundamentally sound in that the accuracy of the indicating device does not introduce a source of error. This is of special significance when a thermionic tube is employed as the voltmeter to measure the potential across the condenser.

The measurements of Lattey and Davies show that the precision was not high. Thus, with a solution of approximately 0.001 N, they show a variation of from 1.5 to 3.0 percent and with a 0.12 N solution the variation is about 10 percent in the extreme cases. Nevertheless, the trend of the values reported by Lattey is definite; and the first consideration in this work is to obtain results which, even though qualitative in nature, are fundamentally sound.

Astin's results⁵ with KCl by the resonance method are represented by three curves, the first showing a decrease to a minimum at a concentration of about 0.001 N followed by a rapid increase to values above that of water, while the other two, with closer coupling, show a continued decrease, more rapid with a cylindrical plate condenser than with a parallel plate condenser.

The data obtained by the present authors do not confirm those of Astin but show instead a continued rise in the dielectric constant with concentration. The observed data are recorded in Table II. These values were taken at 25°C at a wave-length of 31.7 meters. Cell *A* had a capacity of 606 μmf and cell *B* a capacity of 28.2 μmf when filled with water.

The value for pure water has been accepted as the reference value. Only low concentrations could be measured with the larger cell due to conductivity. The apparent dielectric constant change due to solute is small yet definite in direction, fairly reproducible and increases with increasing concentration.

A concentration of 0.0025 N solution gave

TABLE II.* *Summary of dielectric constants (uncorrected) of aqueous KCl solutions.*

Conc.	Cell A		Cell B			
	1	2	1	2	3	4
0.0000	78.58	78.58	78.58	78.58	78.58	78.58
0.0010	78.13	79.13	79.45	79.42	79.42	79.17
0.0020		79.69	79.93	80.95	80.27	80.44
0.0025		81.21	80.27		81.97	81.12
0.0050			81.63			85.71

* *Note:* Each value in each column is the average of series of measurements made by refilling the cell with the same solution. The results in the different columns were made with freshly prepared solutions, at different times and under somewhat different experimental conditions, in order to determine whether there were any uncontrolled factors which might be having an effect.

dielectric constants of 81.57, 81.35 and 81.42 at wave-lengths of 24.5, 46.5 and 82.4 meters, respectively. These values seem to indicate that the results are independent of frequency.

The values here recorded for KCl are in agreement essentially with those obtained by Lattey and Davies. They are in contradiction to the values generally obtained with the Drude method.

It has been pointed out that the theoretical treatment assumes a pure inductance. Every conductor, however, has a certain amount of capacitance associated with it. The authors attempted to change the distributed capacitance effect by immersing the inductance coil of the measuring apparatus in benzene. Results obtained on salt solutions with the coil immersed gave, within the experimental error, no change of dielectric constant with concentration of the salt. The dielectric constant of all solutions,

within the experimental error, under these conditions, was that of pure water. The benzene was not replaced with materials of higher dielectric constant for the reason that conductivity would be a factor in the use of materials such as the alcohols and the amount of material required and the experimental conditions made the use of volatile or expensive materials impractical. Even if the curve of apparent dielectric constants against the dielectric constant of the milieu surrounding the inductance is established the extrapolation to zero dielectric constant, i.e., to zero distributed capacity, is probably not justifiable. It was not practical to surround all of the inductance with benzene, and the problem may be one of reflection effects at the surface of the benzene. This circumstance, while it renders the problem even more complicated, does not change the basic fact that the distributed capacity of the coil is a factor of importance in using the voltage tuning resonance method and, as yet, has not been satisfactorily taken into account.

The results given are consistent with the values obtained by Jezewski as well as qualitatively in agreement with those of Wien.⁹ In contradiction to Jezewski the present authors are convinced, however, that, even though their data recorded in Table II indicate a fairly definite behavior for aqueous KCl solutions, yet, when all things are considered, the voltage tuning resonance method cannot be depended upon to distinguish between the effects of increased conductivity and dielectric constant change in aqueous salt solutions.

⁹ Wien, *Ann. d. Physik* **11**, 429 (1931).