

A NEW METHOD FOR MEASURING THE DIELECTRIC CONSTANTS OF CONDUCTING LIQUIDS

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ABSTRACT

A modified resonance method for determining the dielectric constants of conducting liquids is described in which no correction is necessary for the conductivity of the dielectric. The circuit contains an inductance in parallel with two series condensers, one of which is either shunted by a resistance or contains the conducting liquid as its dielectric. The vacuum tube voltmeter is found a more sensitive resonance indicator than a thermocouple and is connected to measure the p. d. across the shunted condenser. It is shown theoretically and experimentally, that the capacity of the condenser for maximum p. d. across it is independent of the parallel resistance. A preliminary curve is given showing the variation of the dielectric constants of weak KCl solutions with concentration. The dielectric constant decreases, reaching a minimum at a concentration of 0.0005 mols per liter. The average activity coefficient of the ions calculated by means of Hückel's equation is 1900. This result is checked by using two condensers of different size and shape. Readings from the two condensers agree only when the coupling with the oscillator is extremely loose. The lowering obtained is much greater than that reported by any other observers. However, results very similar to those of other experimenters are obtained when the coupling is increased slightly, but then readings from the two condensers do not check. The frequency employed is 3×10^6 , the highest value at which lead wire effects are negligible. No change of the dielectric constant with different applied fields is found for a 0.0005 normal KCl solution. This investigation was prompted by earlier results of Furth. Previous values for sugar solutions are checked. Standardization of the condensers is with benzene. The dielectric constant of benzene is determined by a method devised for non-conducting liquids which gives directly absolute values. The dielectric constant for benzene is 2.239 ± 0.005 at 25°C. The dielectric constant of water obtained from a comparison with benzene is 79.5 ± 0.5 at 25°C.

INTRODUCTION

RESEARCHES on the dielectric constants of conducting liquids have increased greatly in number since the appearance of the Debye-Hückel theory of solutions. There is, however, almost no agreement in the results of the investigators, especially from those employing resonance methods. For example, determinations of the average activity coefficients for KCl ions by use of Hückel's equation¹ give results varying from 810 as reported by Walden, Ulich and Werner,² to 0 as reported by Voight,³ and for NaCl from 600 as reported by Sommer⁴ to 30 as reported by Hellman and Zahn.⁵

¹ E. Hückel, *Phys. Zeits.* **26**, 93 (1925).

² Walden, Ulich and Werner, *Zeits. f. Phys. Chem.* **115**, 177; **116**, 261 (1927).

³ B. Voight, *Zeits. f. Physik* **44**, 70 (1927).

⁴ S. Sommer, Berlin Dissertation, 1923 data from Bluh *Phys. Zeits.* **27**, 226 (1926).

⁵ H. Hellman, and H. Zahn, *Ann. d. Physik* **81**, 711 (1926).

Values falling almost anywhere between these limits are obtained from the data of other observers. Perhaps the best agreement between two experimenters is in the works of Pechold⁶ and Carman and Schmidt.⁷ The results in each case were obtained by a force method.

The purpose of the investigation discussed in this paper was to determine the factors which might account for the discrepancies in results of resonance methods and to eliminate as many of them as possible. The undesirable factors can be readily summarized.

A condenser containing a conducting dielectric may be considered as a pure capacity in parallel with a resistance. In order to investigate the capacitive properties of the dielectric, the impedance of the pure capacity to an alternating current should be at least of the same order of magnitude as that of the resistance. This can be accomplished only by increasing the frequency of the current employed. The frequency has been increased to the limit; modern vacuum tube technique, making it possible to exceed 10^8 cycles per second. At such high frequencies however, complications are introduced which more than neutralize the advantage of decreased capacitive impedance. First, is the effect of lead wires because at very high frequencies they constitute the major part of the inductance of the circuit. Accurate determinations of the capacity changes involved in dielectric constant measurements require the evaluation of the lead effects. Some observers such as Walden, Ulich and Werner have used an arrangement, at frequencies around 10^8 , in which a standard condenser is placed in parallel with the one containing the liquid under investigation and in their calculation have neglected the inductance of the leads between the two condensers. From the dimensions of the apparatus a consideration of this would certainly alter the results. Furthermore, if the leads are considered the evaluation process is difficult and uncertain, especially since the change which they introduce is not a constant change but one which varies as the capacity ratio varies. This has been mentioned by Lattey.⁸ To eliminate the lead correction, the frequency in the present research was kept below 3×10^6 where the leads, by actual test, had a negligible effect.

The maintenance of constant frequency presents another problem when working in the radio range. The variations of frequency of the oscillator were found much less in simple resonance circuits than in bridge circuits so that the former type was considered preferable and has been used in this work. Detection of resonance with a thermocouple circuit, the method used by most investigators in this field, was not satisfactory because the reaction of the thermocouple circuit on the secondary, at such coupling as gave measurable deflections, could not be accurately interpreted. Likewise, resonance indicated by a dip in the grid current of the oscillator was sufficiently sensitive only when the coupling was too close to be sure of no frequency variation at resonance. A vacuum tube used as an electrostatic

⁶ R. Pechold, *Ann. d. Physik* **83**, 427 (1927).

⁷ A. P. Carman, and C. C. Schmidt, *Phys. Rev.* **30**, 925 (1927).

⁸ R. T. Lattey, *Phil. Mag.* **41**, 829 (1921).

voltmeter was found to be the most sensitive resonance indicator. Furthermore, its effect on the circuit can be made capacitive only, the magnitude of which can be determined if necessary.

The simplest resonance circuit which has been used in this type of work is shown in Fig. 1, where x represents the resistance of the dielectric in the condenser C . The value of C for maximum current in the circuit under an induced emf of constant frequency is

$$C = (C_0/2)(1 + (1 + 4L/C_0x^2)^{1/2})$$

where C_0 is the value of C at resonance when x is infinite. It should be observed that this equation involves a correction for the conductivity of the liquid which increases as the conductivity increases. The conductivities of liquids at high radio frequencies are not accurately known so that definite limitations are placed on the method. Lattey has devised a circuit of greater possibilities by placing an air condenser in series with the conducting condenser. He has shown that by a proper choice of circuit constants the resistance correction can be made more accurately than in the other circuit. It was found, however, that by adapting the vacuum tube voltmeter to the type of circuit used by Lattey an arrangement could be found in which the resistance correction could be entirely eliminated.

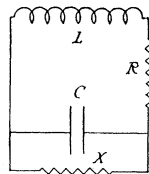


Fig. 1. Simple resonance circuit containing conducting dielectric.

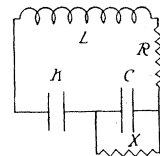


Fig. 2. Resonance circuit with conducting condenser in series with non-conducting condenser.

DESCRIPTION OF THE CIRCUIT

The series circuit is shown in Fig. 2. The tube voltmeter is connected to indicate the maximum potential drop across C rather than across L . The conditions for this maximum p. d. when an emf E_0 of constant frequency is induced in the circuit are obtained as follows. The impedance Z of the the circuit to an alternating current of angular frequency ω is

$$Z = j\omega L + R - \frac{j}{\omega k} + \frac{1}{j\omega C + 1/x} \quad [j = (-1)^{1/2}]$$

or

$$\frac{|E_0|^2}{|I|^2} = |Z|^2 = \left(R + \frac{x}{1 + x^2\omega^2 C^2} \right)^2 + \left(\omega L - \frac{1}{\omega k} - \frac{x^2\omega c}{1 + x^2\omega^2 C^2} \right)^2$$

If E_c is the p.d. across C , then

$$\frac{|E_c|^2}{|I|^2} = \frac{x^2}{1+x^2\omega^2C^2}$$

Eliminating I^2 and replacing $(1+x^2\omega^2C^2)$ by B

$$|E_c|^2 = |E_0|^2 \left(\frac{x^2\omega^2k^2B}{(BRk\omega + kx\omega)^2 + (B\omega^2Lk - B - x^2\omega^2kC)^2} \right).$$

The maximum value of E_c obtained by varying C corresponds to the minimum value of the denominator providing it does not become zero. The value of C corresponding to the maximum value of E_c is

$$C = k \frac{(\omega^2Lk - 1)}{R^2k^2\omega^2 + (\omega^2Lk - 1)^2}$$

If $(\omega^2Lk - 1)$ is positive, C corresponds to a finite maximum of E_c .

Since x is missing from this last equation it means that the resistance of the electrolyte will have no effect on the value of C for the maximum deflection of the voltmeter. Furthermore C is a function of terms which can be kept constant so that changes in C can be measured directly by the change in a standard condenser placed in parallel with C .⁹

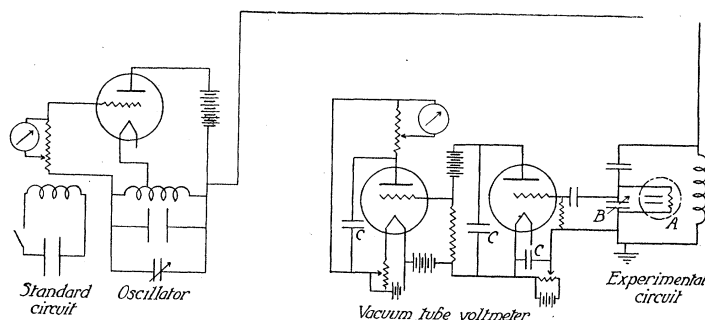


Fig. 3. Diagram of the experimental circuits. A is the test condenser containing conducting liquid, B is the standard variable condenser, CCC low impedance by-pass condensers.

The experimental arrangement used to obtain preliminary data as test of the circuit is shown in Fig. 3. The oscillator was a simple Hartley circuit adjusted to a frequency 2.7×10^6 . The frequency was regulated by closing the switch in the standard circuit and varying a vernier condenser on the oscillator for minimum deflection of the grid galvanometer. The vernier

⁹ This advantage, of a resonance setting independent of the resistance, can be obtained in a more simple circuit. If an alternating p. d. is applied across the coil in Fig. 1 instead of being induced in the circuit, the condition for minimum current from the source is independent of the parallel resistance. Experimentally, however, this condition could not be obtained at radio frequencies because it was impossible to keep the frequency of the source constant with such coupling.

condenser was controlled by a long glass rod to remove the body capacity of the operator. The grid galvanometer was of high sensitivity and had a coil of low moment of inertia to give quick response. The galvanometer suspension was twisted so that the normal grid current gave zero reading on the scale. This greatly magnified the amount of any variations which were observed by a lamp and scale arrangement, the scale being about 15 feet from the galvanometer.

The oscillator and resonance circuits were about 15 feet apart and were coupled through a long horizontal antenna from the oscillator and a short vertical one from the other. The strength of the coupling could be varied by changing the distance between the ends of the two antennae. The coupling was made so loose that the secondary circuit produced no detectable effect on the grid current of the oscillator. Such loose coupling was found quite necessary as will be shown later.

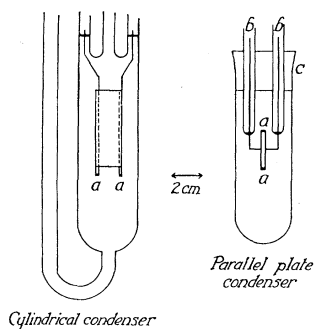


Fig. 4. Diagram of the test condensers drawn to scale. *aa*—glass spacers, *bb*—capillaries, *c*—rubber stopper.

The inductance of the coil and antenna in the secondary circuit was about seven microhenries.¹⁰ A mica condenser of about $700 \mu\mu\text{f}$ served as the series condenser. A G. R. C. precision condenser was used as the standard variable condenser. This was also operated by a long arm to remove body capacity. Two condensers were used for the liquids tested and diagrams of them are shown in Fig. 4. The electrodes of each were of platinum. The effective

¹⁰ This experimental arrangement did not conform exactly to the conditions assumed in developing the theory of the circuit because here the emf was induced in the antenna instead of in the coil. It was assumed that the effect of the antenna, whose capacity was very small was of an added inductance and that the emf was induced in the circuit, which would then give the same result as obtained above for the resonance condition. The reason for this assumption was that the resonance observed was series resonance which results from an emf induced in the circuit. If the effect of the antenna had been to apply a p. d. across the coil, i.e., between the antenna terminal and the grounded side of the coil, parallel resonance would have been obtained which was not the case experimentally. It is possible that the use of the antenna may have caused a small error; it was used in the preliminary work of this paper because it provided a convenient arrangement for securing coupling variations and at the same time proper shielding. It has been eliminated in an improved form of the apparatus for more extensive work now in progress.

capacity in air of the parallel plate condenser was $2.6 \mu\mu\text{f}$ and of the cylindrical condenser $14.1 \mu\mu\text{f}$.

The grid and filament were connected to the terminals of the variable condenser with as short leads as the dimensions of the apparatus permitted. The blocking condenser in the grid circuit prevented a leak current flowing through the conducting liquid. The various low impedance by-pass condensers made the effect of the voltmeter on the secondary circuit that of a small capacity in parallel with a high resistance. Neither of these effects as seen from the theory of the circuit would have any bearing on the changes to be measured. The potentiometer on the *C* battery permitted adjustment of the bias to give the maximum change in the plate current for a given p. d. impressed on the grid. The second tube in the voltmeter circuit served as a direct current amplifier. The galvanometer in the plate circuit of this tube was of the same type as that in the grid circuit of the oscillator. Its suspension was likewise twisted to give zero reading when normal plate current was flowing. All tubes used were of the 201-A type.

It was found that steadier readings were obtained by grounding one side of the system as shown in the diagram. The test condenser was immersed in a constant temperature water bath which was kept at 25.0°C .

Benzene was used as a standard liquid and the dielectric constants of of water and water solutions were determined with respect to the dielectric constant of benzene. This latter was determined by a method devised to give directly the absolute value of the dielectric constants of non-conducting liquids. The method, in brief follows.

STANDARDIZATION OF BENZENE

A condenser of gold plated parallel plates, separated by small glass spacers was placed in parallel with a coil of 2 henries inductance. The natural period of this system was measured by Hubbard's arrangement of the drop chronograph.¹¹

If L is the inductance of the circuit and C the capacity, excluding that between the plates, A the area of one of the plates, d the thickness of the glass spacers, the natural period of the system is given by

$$T = 2\pi(L(C + kA/4\pi d))^{1/2}$$

The period as obtained from the chronograph readings is

$$T = s/(2gh)^{1/2}$$

where s is twice the distance in cm between two successive nodes on the discharge curve, h the average distance the projectile has fallen as it strikes the levers and g the acceleration of gravity. Then

$$s^2 = 8\pi^2ghL(C + kA/4\pi d)$$

¹¹ J. C. Hubbard, Phys. Rev. 9, 529 (1917).

If d is changed to d_1 by using a new set of glass spacers and s_1 is the new value of s then

$$s_1^2 - s^2 = Bk(1/d_1 - 1/d)$$

where B is a constant. If the dielectric is now changed from k to k_1 and the readings repeated, s' and s'_1 being the new nodal intervals the relation between the dielectric constants is

$$k_1 = k(s_1'^2 - s'^2)/(s_1^2 - s^2)$$

The intervals are measured directly from a micrometer screw and if k for air is taken as unity the absolute value of the dielectric constant of the liquid results directly. This method of using glass spacers of different thicknesses to eliminate lead corrections was first used by Powers and Hubbard in a resonance method.¹²

Four sets of glass spacers gave four independent values for the dielectric constant of benzene. The average value was 2.239 ± 0.005 . The measurements were taken at a frequency of 7.7×10^3 and temperature 25°C . It was assumed that there was no change in this value between this frequency and 2.7×10^6 , an assumption which seems justified because of the non-polar nature of benzene. This result is in good agreement with recent determinations of this constant. Sayce and Briscoe¹³ give 2.2389 and Harriss¹⁴ 2.2482, at 25°C . These values are about two percent lower than those generally accepted by handbooks prior to 1925.

The conductivity of water was too high to permit its use as a dielectric in this circuit.

RESULTS

The dielectric constant of water was determined with respect to that of benzene using the resonance circuit. The calculation was made from the equation

$$(k_1 - 1)/(k_2 - 1) = c_1/c_2$$

where k_1 and k_2 are the dielectric constants of water and benzene, and c_1 and c_2 the changes made in the setting of the standard condenser for maximum reading of the voltmeter caused by introducing each liquid into the test condenser. The average value for water obtained by using both condensers shown in Fig. 4 was 79.5 ± 0.5 . The average conductivity of the water was 2×10^{-6} mhos per cm, but variations one-half to five times this value made no measurable change in the dielectric constant.

The values for methyl alcohol and glycerine were found to be 34.0 and 50.6. These values are slightly lower than those generally listed in handbooks. Kahlbaum c. p. materials were used.

¹² Powers and Hubbard, *Phys. Rev.* **15**, 535 (1920).

¹³ L. A. Sayce and H. V. H. Briscoe, *Chem. Soc. J.* **127**, 315 (1925).

¹⁴ H. Harriss, *Chem. Soc. J.* **127**, 1049 (1925).

Tests of the method with sugar solutions gave the results in Table I. These values agree very closely with those reported by Harrington¹⁵ but are higher than those published by Furth.¹⁶ At a concentration of one mol per liter Furth's result is about 10 percent higher, this difference decreasing in the weaker solutions.

The method was next tested with KCl solutions and the results obtained are also shown in Table I. With solutions stronger than 0.003 N in the parallel plate condenser and 0.0005 N in the cylindrical condenser the p. d. across the standard condenser was too small to be measured. The resistance

TABLE I. Dielectric constants of KCl and sugar solutions.

KCl			Sugar	
Conc. mols/l	Ratio— k of solution to k of water		Conc. mols/l	K_s/K_w
	parallel plate condenser	cylindrical condenser		
0.00025	0.988	0.989	0.10	0.978
0.0005	0.978	0.978	0.25	0.967
0.001	0.989	—	0.50	0.943
0.002	1.001	—	0.75	0.915
0.003	1.019	—	1.00	0.887

of the solution in each condenser in this limiting case was about 100 ohms. The probable error of the results was about one-half of one percent for water, the sugar solutions and the most dilute KCl solutions and about one and one half percent for the strongest solutions.

The agreement of the two readings from the larger condenser with those of the smaller is considered as evidence that the condition for maximum p. d. across the condenser is independent of the parallel resistance. The resistance of a solution in the cylindrical condenser was about one-fifth the resistance of the same solution in the other condenser. A direct test of this point was not possible because a variable resistance without some capacitive or inductive effect could not be found. For example, a General Radio "non-inductive" resistance box in parallel with the standard condenser changed the setting for maximum deflection 82 $\mu\mu\text{f}$ when the resistance was one 100-ohm coil and 132 $\mu\mu\text{f}$ when the resistance was ten ten-ohm coils.

In 1924 Furth¹⁷ published data from a force method showing a dependence of the dielectric constant of NaCl solutions on the applied field. Although he corrected this data in 1927¹⁸ a test of the point seemed interesting because measurements of the strengths of applied fields could be made readily with the tube voltmeter. Furthermore a change in the dielectric constant of polar substances is expected in strong fields although not likely in the small fields which were used in this work. No change was found in the dielectric constant

¹⁵ E. A. Harrington, Phys. Rev. **8**, 581 (1916).

¹⁶ R. Furth, Ann. d. Physik **70**, 64 (1923).

¹⁷ R. Furth, Phys. Zeits. **25**, 676 (1924).

¹⁸ R. Furth, Zeits. f. Physik **44**, 256 (1927).

of water in fields varying between 58 volts per cm and one-half volt per cm and no change was found in a 0.0005 N KCl solution in fields from three to one-fourth volts per cm. These field values were the maximum or peak values. The different fields were obtained by varying the output of the oscillator.

When the coupling between the oscillator and secondary circuit was increased to give a small, sharp dip in the grid galvanometer of the former at resonance, quite different results were obtained. The readings from the two condensers no longer agreed. A typical example of this disagreement is shown in the curves *I* and *J* in Fig. 5. *I* was obtained with the parallel plate condenser and *J* with the cylindrical condenser. Curve *A* is the graph of the

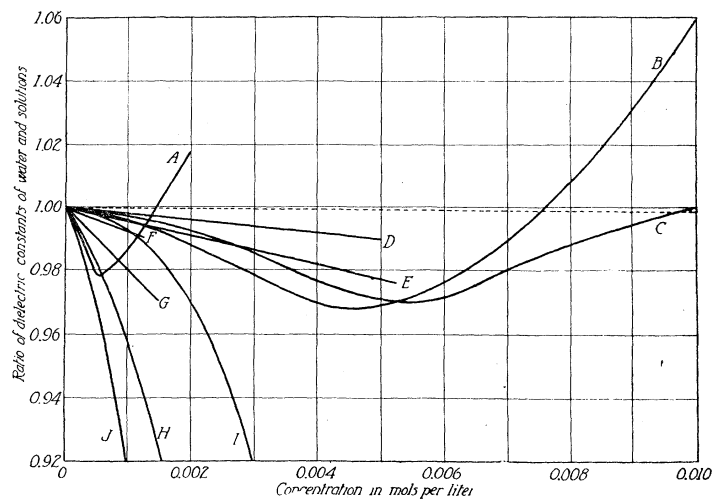


Fig. 5. Dielectric constants of KCl solutions as reported by different observers. *A*—Astin, resonance method at 3×10^6 ; *B*—Carman and Schmidt, force method at 500; *C*—Pechold, force method at 50; *D*—Schancke and Schreiner, Nernst bridge method at 10^6 ; *E*—Sommer, Nernst bridge method at 10^6 ; *F*—Sach, Nernst bridge method at 10^6 ; *G*—Walden, Ulich and Werner, resonance at 10^8 ; *H*—Lattey, resonance method at 10^7 ; *I* and *J*—Astin, same method as curve *A* with closer coupling. *I*—with parallel plate condenser, *J*—with cylindrical condenser. The dotted line indicates the lowering predicted by Hückel.

data in Table I. The other curves are the dielectric constants of KCl solutions as reported by other experimenters. The conditions under which *I* and *J* were obtained were such that the additional transfer of energy between the primary and secondary circuits gave measurable deflections of the voltmeter at concentrations twice the highest obtained in curve *A*.

CONCLUSIONS

An estimate of the average activity coefficient of KCl ions obtained from the data in Table I and Hückel's equation

$$k = k_0 - 2\delta\gamma$$

gave $\delta = 1900$. k and k_0 are the dielectric constants of the solution and pure solvent and γ the concentration in mols per liter. That this value is higher than those obtained from the data of other observers is evident from a glance at Fig. 5. The lowering of the dielectric constant predicted by Hückel is shown by the dotted line. In spite of the wide variety of results which have been reported none agrees even as to order of magnitude with this predicted lowering. Voight reports no lowering but since his result consists of a single reading at 0.0013 N it bears little weight.

Since it was possible to make the curve I agree more or less closely with F , G and H (I is merely a typical curve, it could be made to take different shapes and positions by additional changes in coupling) it is suggested that perhaps some of these results are in error because of coupling effects. Hellman and Zahn¹⁹ have already criticised the work of Walden, Ulich and Werner because of tight coupling between the resonance and thermocouple circuits. None of the observers using resonance and bridge methods whose curves are listed records tests as to the constancy of the frequency of the a.c. source; it has merely been assumed constant. A more extensive test of this point is under way using heterodyne methods to note frequency variations and using crystal control to insure a certain degree of stability. The use of the vacuum tube voltmeter in the present work made it possible to work at looser coupling than if a thermocouple had been used. Other experimenters have used thermocouples as resonance indicators.

Hellman and Zahn use a decrement method and eliminate many of the difficulties which are present in resonance methods. They are able to measure much stronger solutions than has been hitherto possible but their method does not apply to very dilute solutions. With NaCl (they have not worked with KCl) the most dilute solution they could measure was 0.05 N. Since the interesting region, or at least the region where results will be most easily interpreted, is the very dilute region where ionization is complete, they extrapolated their results to cover solutions weaker than 0.05 N. Their results decrease slightly at first, reach a minimum, and then increase. Because of the initial decrease they assume a linear lowering from zero concentration to their initial concentration. In view of the many discrepant results in this region through which they extrapolate, their assumption seems unwarranted. The results for NaCl differ as widely as for KCl, even the two force methods yield very different data for the former salt.

Since it was possible to extend the limiting concentration of the present method twofold by a slight increase in coupling it is believed that the useful range can be considerably extended by using sources of much stronger output. This work together with a study of the effect of frequency changes is already under way.

Appreciation is expressed to Professor W. A. Lynch for his frequent and valuable counsel and to Professor J. C. Hubbard of Johns Hopkins University for suggesting the problem.

¹⁹ H. Hellman, and H. Zahn, *Phys. Zeits.* **26**, 680 (1925).