[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE MEASUREMENT OF DIELECTRIC CONSTANTS.

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Received May 19, 1921.

This preliminary paper contains a description of a bridge method for measuring dielectric constants of liquids in which use is made of audion bulbs both as a source of exciting current and as a means of determining the balance point of the bridge. Our interest in the dielectric constant is due to the suspected close relationship that exists between this constant and the solvent power of liquids. That there is a relation between the swelling powers of liquids and their dielectric constants is apparent from a casual review of the experimental data. However, there are many exceptions to the rule and our effort is directed toward the possibility of finding a more general relationship.

Accordingly, we planned first to measure the dielectric constants of a series of liquids and mixtures of the same and also the swelling power, or as it is incorrectly called the "solvent" power, that these exerted upon a certain sample of cellulose nitrate.

Our choice of a suitable method for the measurement of dielectric constant was greatly influenced by the result of a year's work in this field by one of the authors. This work (unpublished) was done in University College, London, together with Professor F. G. Donnan and resulted in the conviction that there is no satisfactory method for the measurement of dielectric constant of liquids possessing a specific conductivity greater than that of conductivity water. In this work the Drude[1] method as well as Schmidt's[2] modification was carefully investigated, using a well constructed apparatus in which special attention was paid to the exciting energy and the end-point detectors. A 30cm. spark induction coil was employed, operated with a mercury break interrupter. This induction coil was connected to a Tesla converter, the energy from which was used to excite the primary circuit of the testing apparatus. Neon tubes were prepared and the most sensitive ones were used in determining the end-point. The results of the experiments with this apparatus showed that neither from the standpoint of precision nor from the standpoint of the ability to measure the dielectric constants of conducting liquids, does this apparatus have the advantages which have been claimed for it over other methods. When liquids that possessed a conductivity only slightly greater than that of conductivity water were used, the minima became very obscure, and furthermore during the measurement a large increase in the temperature of the liquid was observed, indicating that energy

[1] Drude, *Z. physik. Chem.*, **23**, 267 (1897).

[2] Schmidt, *ibid.*, **27**, 343 (1898).

absorption was taking place. This energy absorption increased with the increase in frequency of the electric wave. This is important from the chemist's viewpoint since it is commonly understood that an increase in the frequency of the electric wave enables one to measure the dielectric constant of a conducting liquid.

Many experiments were made with the well-known bridge method as developed by Nernst.[3] Special attention was given here to the source of alternating current. Electrically driven tuning forks of various frequencies within the telephonic range were used, as well as a variety of other well-known interrupters. The sharpest minima, however, were obtained with a small Wehnelt break. All manner of changes in the apparatus did not develop an arrangement which was especially satisfactory. The principal objection was the lack of precision. The sources of current producing the more symmetrical electric waves gave minima which extended over a large portion of the setting scale.

From a theoretical consideration of the distribution of an alternating current in a Wheatstone bridge, we decided to use as our source of alternating current an apparatus which would furnish a symmetrical wave. This is an important factor in the measurement of dielectric constant for the assurance of a sharp and true minima. Professor Flemming[4] has given it consideration in his statement, "It may be pointed out incidentally that no accurate balance or well defined zero can be obtained unless the electromotive force applied to the bridge has a very true sine wave form. Hence no arrangement such as a buzzer, hummer or current interrupter of any kind can be substituted for the sine curve alternator or for an alternator and a wave filter."

We used a frequency of about 1000 cycles per second since this is within the telephonic range and gives a pitch easy to detect and since there is nothing to be gained by using a higher frequency. The work of one of us cited above showed that there is greater energy absorption at higher frequencies. Flemming has treated this matter theoretically and has shown that greater dissipation of current due to the dielectric occurs at higher frequencies. With a slightly conducting liquid in our cell we have to measure the capacity similar to that of a leaky condenser. Flemming has shown that the energy loss in a poor dielectric due to an alternating current can be divided into two parts, the first due to conductivity which is probably electrolytic in nature and the second to a conductivity which is nearly proportional to the frequency. The first is the regular direct current conductance while the second has been called an alternating current conductance.

In the method worked out by Nernst, the ratio arms of the bridge

[3] Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

[4] Fleming, *Proc. Phys. Soc. London*, [2] **23**, 117 (1911).

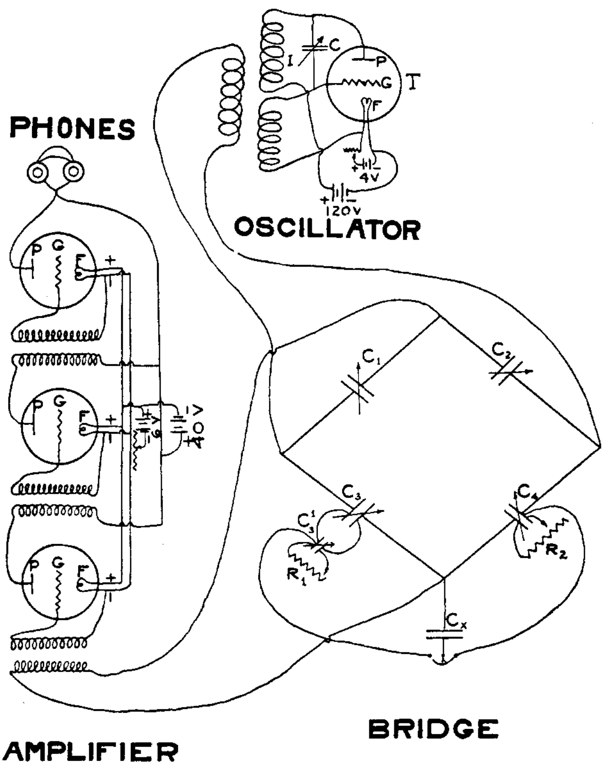
consisted of two resistances and the other arms consisted of an unknown capacity which was balanced by a measuring condenser. In order to make the impedance in the ratio arms of the same magnitude as the impedance in the balancing arms, it was necessary to use very large resistances with the possibility of introducing self-induction into those arms of the bridge. We used air condensers in all four arms. Air condensers are to be desired because of their more constant capacity and the smaller chance for leakage.

Since, with a conducting solution in our dielectric cell condenser, we had to balance a leaky condenser, we used a non-inductive resistance shunted around the measuring condenser in the balancing arm of the bridge. Although Flemming[4] has shown that it is not possible to duplicate a leaky condenser by means of a condenser and a resistance in parallel, we were able to prove that up to a certain limiting value of shunted conductivity it was possible to obtain true values of the capacity of the condenser.

Much attention has been given by conductivity workers and workers on the bridge method for the measurement of dielectrics to the phone used to detect the minima. The minimum current possible in the bridge is determined by the current necessary to excite the phones. This minimum current is still large enough to cause trouble in the matter of heating effects, polarization, etc. A small current is to be desired, but using a small current and one of symmetrical wave form much difficulty is experienced in reaching a minimum. To overcome this difficulty we used the thermo-ionic amplifier of recent development. With this improved apparatus, consisting of a source of alternating current of symmetrical wave form, a symmetrical bridge, each arm of which offered an impedence of the same magnitude, and with an extremely small current flowing through the bridge, the use of which was made possible by the amplifier in connection with the telephones, we hoped for an improvement in the accuracy of our measurements.

The Vreeland oscillator is without doubt the best source of alternating current of sine wave form, but the cost of the Vreeland oscillator led us to turn to the electron tube as our source of current. By an arrangement in which an electron tube, a condenser and an induction coil are connected in a circuit, it is possible to obtain an alternating current of symmetrical wave form. With this arrangement by properly varying the plate voltage, the temperature of the filament, the capacity and the induction, it is possible to obtain different currents varying from a few tenths of a milliampere or less to 25 amperes and with a frequency varying from ½ cycle per second to 50 million cycles per second.[5]

[5] Hall and Adams, This Journal, 41, 1515 (1919).



DIELECTRIC CONSTANT APPARATUS

We used the "Marconi Vacuum Tube" type V.T.1. In the drawing, T is the vacuum tube, C the condenser, and I the induction coils. The audion plate was charged with 120 volts by dry cells while the filament was heated with a current of 0.7 ampere and 4 volts supplied from lead storage cells. The two induction coils consisted of about 300 turns of No. 32 wire each wound around a laminated iron core. The lead to the bridge was coupled to this with about 50 turns on the secondary coil. At C are two variable Murdock condensers connected in parallel. By adjustment of these condensers we obtained a frequency of about 1000 cycles per second. During the first part of our work we used the laboratory current to charge the plates in the electron tubes both in the amplifier and in the oscillator. Great difficulty was experienced from external noises caused from other electrical apparatus running in the building which tended to obscure the minimum and greatly tried the patience of the operator; but when dry cells were used to supplant the laboratory current the results were most gratifying.

In the construction of the bridge, two variable Murdock air condensers were used in the ratio arms.[6] The condensers had a capacity of about 0.0005 microfarad and the scales were divided into 180 divisions. In any series of measurements these condensers were set and the moving pointer sealed by means of sealing wax. These condensers

[6] These condensers as well as most of the wireless apparatus were purchased from the Wireless Specialty Co. of Boston.

are represented by C_1 and C_2 in the drawing. In the measuring arm of the bridge were the following parts.

1. A variable vernier condenser, C_3 in the drawing, "DeForest" type, with a capacity of 0.0015 microfarad. The ccale was divided into 100 divisions. The vernier had a capacity of about 180 degrees per scale division. The pointer on this scale was extended about 75 cm. to an enlarged scale of some 2200 divisions of 1 mm. each, thus enabling us to set the condenser with a much greater precision. In making a measurement, the setting was made on the large scale and then the accuracy of the scale was tested by means of the vernier condenser. The vernier was moved by means of a lever operated from the center of the room. This was done to prevent the introduction of capacity into the bridge from the operator's body. If after making a setting on the large scale, the vernier, by a small movement to the right and to the left, passed through a minimum, we assumed the setting to be correct.

2. Connected in parallel with this measuring condenser was a second Murdock condenser, C_3', from which about half of the plates had been removed. The recording pointer of this condenser was also extended to an enlarged scale. It was possible to use the large condenser for changes in dielectric from 2 to about 26 and over and the small condenser for changes from 2 to 7, gaining a 5-fold increase in sensitivity. The vernier setting-lever was used for testing the setting of the minimum when either condenser was used. When C_3 was used, C_3' was locked in a fixed position, the scale of C_3 calibrated and the measurements made. When it was desired to use C_3' as the measuring condenser, C_3 was locked and the small condenser scale was calibrated.

3. R_1 is a non-inductive resistance made by filling a conical glass tube with "Mangani" solution (121 g. of mannitol plus 41 g. of boric acid). The resistance of this tube could be varied by varying the distance between the electrodes or by moving a plunger down into the ground glass conical part of the tube, thereby decreasing the cross section. The stem of the plunger fitted into a hard rubber cap which was threaded. The small thread on the screw of the cap made possible a very sharp setting of the resistance. This was extremely important when any great conductivity was possessed by the liquid being measured. In some cases it was found that turning the cap one or two mm., involving the very slight accompanying displacement of the plunger in the tube, entirely obscured the minimum. Previous workers have called attention to the importance of the resistance used to compensate the conductivity. It has been suggested that as the conductivity increased and the electrodes in the liquid resistance were moved closer together, a capacity was introduced in the resistance tube which involved an error in the capacity of the measuring condenser. That this is not the true explanation can easily be shown by a consideration of the voltage consumption in the measuring arm of the bridge. A simple calculation is sufficient to illustrate this point.

Consider the bridge, with capacities C_1 and C_2 balanced against capacities C_3 and C_4 the latter being shunted with resistances R_1 and R_2 respectively. Then $Z_1/Z_2 = Z_3/Z_4$ where Z is the impedance; if $C_1 = C_2$, and both C_1 and C_2 are air condensers, $Z_1 = Z_2$, and therefore $Z_3 = Z_4$.

Let us suppose that C_4 is composed of 2 concentric cylinders 0.2 cm. apart and having an electrode surface of 50 sq. cm. Furthermore, let the dielectric be alcohol having a dielectric constant of 25 and a specific conductivity of 1×10^{-7} mho.

The capacity of such a condenser is $Ka/4\pi d$ 900,000 = 0.00055 mf. The resistance of such a cell is therefore $(50/0.2) \times 10^{-7} = 2.5 \times 10^{-5}$ mho $= 0.4 \times 10^5$ ohm.

The impedance of the above capacity and resistance in parallel may be most easily calculated by obtaining the vectorial sum of the admittances due to capacity and resistance. The admittance due to capacity at a frequency of 1000 is 2π. $1000C = 2 \times 3.1416 \times 1000 \times 5 \times 10^{-10} = 3.1 \times 10^{-6}$. Therefore the admittance of the combination is $\sqrt{(2.5 \times 10^{-5})^2 + (3.1 \times 10^{-6})^2} = 2.52 \times 10^{-5}$. The impedance is $1/2.52 \times 10^{-5} = 0.396 \times 10^5$ ohm.

This calculation shows that the impedance of the whole bridge arm is largely determined by that of the resistance alone and that the quantity which we wish to measure, the capacity, only slightly affects the total impedance. In other words, an accurate measurement of capacity cannot be made at a frequency of 1000 cycles per second if the impedance due to resistance is less than that due to capacity. This is an important consideration for the determination of the limit of conductivity. It has been commonly overlooked in dielectric-constant measurements of conducting solutions.

4. In the fourth arm of the bridge was a condenser, C_4, shunted by a Mangani solution resistance. This condenser acted as a tare condenser and the resistance was used to balance the conductivity of the liquid when the dielectric cell condenser was placed on the C_3 arm of the bridge in the differential method of measurement which was used. Our purpose in finally adopting the differential method was to eliminate any errors due to an unsymmetrical arrangement of the bridge such as different self-inductances of the wires, mutual capacities of the condensers, etc. Also by the differential method twice the ordinary displacement on the measuring scale is obtained for a given change in dielectric.

The dielectric cell was composed of two co-axial platinum cylinders, 2.2 cm. × 6.3 cm. and 1.9 cm. × 6.3 cm., respectively, which were set in the ground glass stopper of a glass cup. This cup was mounted on a hard rubber base. The platinum cylinders were firmly fastened at each end to prevent any possible displacement during a set of measurements. These cylinders as well as the cup were easily cleaned between measurements by washing several times with alcohol and ether and then drying in a stream of air. It was so arranged that the whole dielectric cell could be placed in a holder in a thermostat if at any time the accuracy of the work should demand close temperature control. The dielectric cell was arranged by means of a rocking commutator so that it could be placed in parallel first with C_4 and a reading taken and then in parallel with C_3 and the difference in reading taken. During the calibration of the scale and during any series of measurements, C_1, C_2, and C_4 were sealed, C_3 being the only condenser whose capacity was changed.

The amplifier was a two-step type triode E to which a third step was added by means of an amplifying transformer and an electron tube, thus giving a 1000 fold amplification. The plates were charged at 40 volts from dry cells and the filaments were heated by a current of 0.7 ampere and 6 volts from lead storage cells. This amplifier was used in connection with a set of Baldwin wireless telephones. These telephones have non-adjustable mica diaphragms and were especially suited for wireless work for the reception of very weak signals. Their resistance was 2000 ohms. In any determination, the amplifier was adjusted by changing the temperature of the filaments to give the greatest sensitivity and then was not changed during an entire calibration and set of measurements. This was in keeping with the care always exercised during a set of readings to vary nothing but the liquid in the dielectric cell and the capacity of the measuring condenser. It was only by employing the greatest precaution along these lines that consistent and comparable results could be obtained. For instance, before the rocking commutator was used in the differential method of measurement, a wire was moved from C_4 to C_3 in order to change the dielectric cell from parallel with C_4 to parallel with C_3. It was discovered that the movements of this fine short wire caused the shifting of the minimum many divisions on the recording scale. Again, before the final setting was made by the use of the vernier condenser lever operated at a distance from the bridge, it was found that effects produced by the operator's body either entirely obscured the minimum or shifted it a few hundred divisions.

The first set of measurements on the bridge was made for the purpose of determining the sensitivity of the apparatus. Before using the differential method it was found that we were able to get very sharp minima when the ratio of the condensers in the ratio arms was other than one to one. This made it possible to magnify the deflection of the dielectric cell on the measuring condenser. With benzene in C_4, the dielectric cell, C_3 the measuring condenser gave in 4 experiments, 430, 430, 430, and 390; with ether it gave 840, 905, 1070, and 1205, respectively.

In the last measurement a change in dielectric of from 2.22 to 4.35 caused a change on the setting scale of the measuring condenser of 815 divisions, which means (setting to one division on the scale and one division is one millimeter) that one division on the scale is equivalent to a change in dielectric of 0.0026. These measurements could be made on C_3'. When made on C_3' which possessed a 5-fold sensitivity, one scale division was equivalent to a change in dielectric of 0.0005. No attempt was made to carry this study further as it was not desired to reach this sensitivity. For our measurements we needed a sensitivity which would keep the readings of a change in dielectric of from 2 to 26 on the scale.

A set of measurements was made by the differential method and the same satisfactory balancing of the bridge was obtained.

Investigation was next made of the effect of an added non-inductive resistance to an air condenser whose capacity was being measured by the differential method. This resistance was balanced out by a resistance in parallel to the condenser in the balancing arm.

	a.	*b.*	*a − b.*	*diff.*
Condenser alone	497	293	204	..
Condenser plus resistance in parallel	505	260	245	41

As the resistance decreased, the difference between the true capacity and the observed capacity increased. Next a 22,000-ohm resistance was shunted around the condenser whose capacity was being measured. As the capacity was increased, the amount that the minimum was shifted due to the shunted resistance decreased. It was also found that there was less shifting of the minimum due to the shunted resistance if the ratio condensers as 1:1. The reason for this can be seen from the following calculation.

If the impedance of the ratio arms is the same, *i. e.*, if $C_1 = C_2$, then $C_3 = C_4$ in the presence of conductivity due to R only on condition that C_3 is shunted with an equal resistance. On the other hand, if C_1 does not equal C_2, the ratio of C_3 to C_4 will not equal the ratio of C_1 to C_2 even under the condition that R_3 is equal to R_4. A single calculation is sufficient to bring out this point.

Let $C/C_2 = a/b$; then $Z_3/Z_4 = b/a$; or $A_3/A_4 = a/b$ (1)
where Z is the impedance, and A is the admittance. Further let $R_3 = R_4 = x$. A = the vectorial sum of $C_3 + (1/x)$.

$$= \sqrt{C_3^2 + (1/x^2)}; \quad \text{and } A = \sqrt{C_4^2 + (1/x^2)}.$$

$$\text{From Eq. 1 } a\sqrt{C_4^2 + 1/x^2} = b\sqrt{C_3^2 + 1/x^2}.$$

$$\text{Squaring, } a^2 C_4^2 + \frac{a^2}{x^2} = b^2 C_3^2 + \frac{b^2}{x^2}$$

$$b^2 C_3^2 - \frac{a^2 - b^2}{x^2} + a^2 + C_4^2 \tag{2}$$

$$\frac{b^2 C_3^2}{a^2 C_4^2} = 1 + \frac{a^2 - b^2}{a^2 C_4^2 x^2}$$

$$\frac{C_3^2}{C_4^2} = \frac{a^2}{b^2} + \frac{a^2(a^2 - b^2)}{b^2 a^2 C_4^2 x^2}$$

$$\frac{C_3}{C_4} = \frac{a}{b} + \sqrt{\frac{a^2 - b^2}{b^2}} - \frac{1}{C_4 x}. \tag{3}$$

From this general equation one can see that the ratio of C_3 to C_4 is equal to the ratio of C_1 to C_2 only when the product $C_4\,x$ is large. Inasmuch as C is the capacity of the condenser being measured we can increase the product only by working with dielectrics of small conductivities, that is of large values of x. In other words, it is possible to obtain a greater sensitivity by making the ratio of the ratio condensers greater than 1; however, this cannot be done for liquids having appreciable conductivity.

The effect of the introduction of the maximum conductivity of the Mangani resistance tubes shunted around an air condenser was studied. As shown by the following observation, no appreciable shifting of the minimum resulted.

	a.	b.	a – b.
Air condenser alone	1488	321	1167
Air condenser plus maximum conductivity of resistance tube	1498	330	1168

The same results were obtained when the dielectric cell was used.

	a.	b.	a – b.
Dielectric cell alone,			
Empty	1636	1588	48
Filled with ether	1701	1523	178
Dielectric cell plus maximum conductivity of resistance tube,			
Empty	1633	1585	48
Filled with ether	1700	1522	178

In all measurements of dielectric constants only those liquids were measured whose conductivity could be balanced out with the tested Mangani solution resistances.

The condensers in the ratio arms were now set at 90, *i. e.*, at a ratio of 1:1, condensers C_1, C_2, and C_4 were sealed, C_3 was locked into position and the scale on C_3 was calibrated by filling the dielectric cell with the above liquids. The calibration curve is given on the chart with the curves for the dielectric measurements.

CALIBRATION DATA.

Liquid.	D. C.	*a.*	*b.*	*a - b.*
Carbon tetrachloride	2.25	1268	1160	108
Ether	4.35	1320	1115	205
$C_6H_6 + C_6H_5NO_2$	15.9	1380	860	720
Alcohol	25.8	1795	640	1155

The following tables give the results of the dielectric measurements of the different mixtures with interpolation values from the curves. The points on the calibration curve were re-checked between measurements so as to assure no change in the values of the bridge. The liquids were not allowed to stand exposed to the air during a measurement, because in some cases the conductivity increase due to the absorption of water vapor from the air was such as to introduce an error in the observed value of the capacity of the dielectric cell. The conductivity of alcohol was observed to increase considerably upon exposure to the air for a few seconds. At the end of a half hour or less the conductivity had increased beyond that which could be balanced out with the maximum conductivity of the Mangani resistances.

DIELECTRIC CONSTANTS OF MIXTURES OF BENZENE IN ETHYL ALCOHOL

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	2.28	40	10.8	80	20.6
10	4.3	50	13.1	90	23.2
20	6.5	60	15.5	100	25.8
30	8.6	70	18.0		

DIELECTRIC CONSTANTS OF MIXTURES OF ETHER IN ALCOHOL.

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	4.35	40	10.9	80	20.6
10	5.7	50	13.1	90	23.2
20	7.2	60	15.5	100	25.8
30	8.9	70	18.0		

DIELECTRIC CONSTANTS OF MIXTURES OF CARBON TETRACHLORIDE IN ALCOHOL.

Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.	Alcohol % by weight.	Dielectric constant.
0	2.25	40	14.5	80	22.6
10	5.4	50	17.0	90	24.2
20	8.6	6	19.1	100	25.8
30	11.7	70	20.9		

Summary.

1. A bridge method for the measurement of dielectric constants is described.

2. Preliminary measurements of the dielectric constants of mixtures of ethyl âlcohol and benzene, ethyl alcohol and ether, and ethyl alcohol and carbon tetrachloride are given.

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