[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Resistance and Capacity Behavior of Strong Electrolytes in Dilute Aqueous Solution.[1] I. Method for the Simultaneous Observation of Conductance and Dielectric Constant at High Radio Frequencies

BY ORLAN M. ARNOLD AND JOHN WARREN WILLIAMS

The interionic attraction theory has been utilized by Debye and Hückel[2] and by Onsager[3] to demonstrate that a square root law is the correct one to explain the change in the electrical conductance of very dilute solutions of strong electrolytes with concentration. In such systems variations in the mobilities rather than in the number of the ions are responsible for the observed conductance changes. At the time Debye and Hückel first proposed their conductivity theory Sand[4] realized that if changes in the mobilities of the ions were caused by electrostatic forces, then measurements at very high frequencies and at very high field strengths should lead to enhanced conductances since in either event the effect of such forces would be reduced. At the present writing the existence of such increased conductances under these conditions has been established experimentally and elaborate theories have been worked out to describe them. The experiments to be discussed in the following article were designed to test further the validity of the theory of Debye and Falkenhagen[5] which describes the frequency variation of conductance in dilute solutions of strong electrolytes.

The ordinary bridge methods such as are used for the determination of resistance and capacity at audio frequencies are not generally satisfactory at the lower radio frequencies and they fail entirely when observations at the higher radio frequencies are required. At such high frequencies the standard resistance coils react inductively and capacitatively, changes in the position of the contact on a slide wire produce changes in the ratio of such inductances and capacities in an unknown way, and the arrangement and length of the lead wires can give rise to uncertainties. From time to time there have been proposed methods, making possible the observation of conductance and/or capacity change at the radio frequencies.[6–10] The method finally adopted by us resembled that of Sack and his collaborators, but it differed in so many important respects that we feel it necessary to devote this first article to a brief description of the apparatus itself and the theory upon which its use is based. This comparator-resonance method made possible the simultaneous observation of resistance and capacity change with frequency, at the same time it was flexible as regards frequency change. It did not permit absolute measurements to be made, but it did accomplish a comparison of conductance and dielectric constant of two solutions, a standard and an unknown.

Description of Apparatus

A schematic diagram of the apparatus is given in Fig. 1. As indicated, there are three distinct circuits, a generator, (I); an intermediate circuit (II); and a comparator circuit, (III). In use all parts of this apparatus were clamped in fixed position on a firm table.

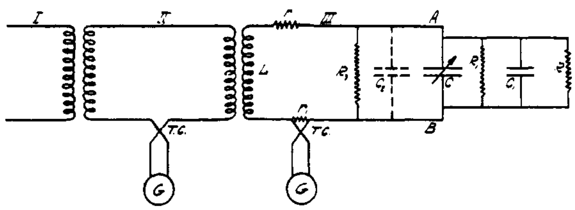

Fig. 1.—Schematic diagram of high frequency apparatus: L, inductance in the measuring circuit; C, capacitance of the variable precision condenser; R, resistance of the solution in the cell; R_1, resistance of the insulation of the precision condenser; R_2, resistance of the insulation of other parts of circuit; r, resistance of the leads in the measuring circuit; r_1 resistance of the heater in the thermocouple; C_1, capacitance of the measuring cell; C_2, capacitance between leads in the circuit; G, galvanometer; T. C., thermocouple.

A modified Hartley circuit, using an 01A tube, was found to be a satisfactory source of alternating current. In order to obtain uniform power output, good wave form and constant frequency at the high radio frequencies, it was

(1) More complete details of this work may be found in the thesis of O. M. Arnold, presented to the Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy and filed in the library of the University of Wisconsin, June, 1934.

(2) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

(3) Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

(4) Sand, *Phil. Mag.*, **45**, 281 (1923).

(5) Debye and Falkenhagen, *Physik. Z.*, **29**, 401 (1928).

(6) Sack, *ibid.*, **29**, 627 (1928); [Brendel, Mittelstaedt and Sack, *ibid.*, **30**, 576 (1929); Brendel, *ibid.*, **32**, 327 (1931)].

(7) Deubner, *ibid.*, **30**, 946 (1929).

(8) Wien, *Ann. Physik*, [5] **11**, 429 (1931).

(9) Malsch, *ibid.*, [5] **12**, 865 (1932).

(10) Zahn, *Z. Physik*, **51**, 350 (1928); Rieckhoff, *Ann. Physik*, [5] **2**, 577 (1929).

necessary to adjust inductance and capacity to one another, to adjust a variable grid leak resistance, and to maintain constant filament and plate supply. The wave length range used in the experiments was approximately 10 to 180 meters.

The intermediate circuit connected the generator with the comparator circuit. It consisted of two plug-in variable coupling coils and sensitive thermocouple connected in series. The indicating instrument used with the thermocouple was a Rawson multimeter. This intermediate circuit was not tuned to the oscillator for several reasons. First, too strong coupling, which causes unsteadiness of the power output and of the frequency in the oscillator and which results in greater fluctuation of current in the measuring circuit, may be thus avoided. Second, the disturbing effects due to the presence of harmonics are reduced. Third, greater possibility is afforded for more complete electrostatic shielding. The comparator circuit consisted of an inductance L, a thermocouple of high sensitivity (connected to a Leeds and Northrup Type R galvanometer), a precision condenser of low capacity C, a conductance cell C_1, or resistance R, connected as shown with very short leads. A beam of light reflected from the galvanometer mirror and focused on a curved scale of two meter radius and 4,140 divisions served to measure the energy in the circuit.

The thermocouples used were of the vacuum type, No. 22C, manufactured by the Western Electric Company. In each case they were placed directly in series with the circuit rather than in auxiliary detector circuits as is usually done. In a long series of experiments the ever present possibility of error due to slight mechanical displacement of primary and auxiliary circuits is thus avoided; in addition, the sensitivity of the current measurements is increased to the extent that very feeble currents can be used with success. The use of feeble currents is advantageous because heating effects in the conductance cells should be reduced as much as possible.

The shielding and grounding of the several circuits presented many difficulties and much attention was given to their solution. For the highest efficiency it was found necessary to shield separately the various parts of the apparatus. The generator, the thermocouples, the inductance of the comparator circuit with its coupling coil of the tank circuit and the precision condenser were enclosed in copper-lined boxes. An additional electrostatic shield was placed about the coupling coil of the intermediate circuit adjacent to the inductance of the comparator circuit in order to enhance the magnetic induction and reduce the electrostatic induction. Those parts of the circuits which were grounded were connected to a metal rod sunk in moist earth exterior to the building proper. All alternating current lines connected to single phase motors in the immediate vicinity of the apparatus were grounded or choked.

Theory of the Circuit and Measurements

The method of interpretation of precision condenser readings in terms of the dielectric constants of the solutions may be described as follows: For pure capacities connected as shown in Fig. 1, $\bar{C} = C' + C_1 + C_2$, when the cell is connected in parallel, and $\bar{C} = C'' + C_2$, when the cell is disconnected. Here C' and C'' are the precision condenser settings for the two observations and $\bar{C}$ is the total capacity of the circuit. It is further evident that $C'' - C' = C_1$. When dilute electrolyte solutions are introduced into the cells, the situation becomes much more complicated. Nevertheless, one may compare with reasonable correctness the susceptibilities of two solutions of the same electrical conductance, provided the latter is not too great, by making observations of the changes in the apparent capacity C_{1A}, defined as $C''_A - C'_A$. Thus, differences in C_{1A}, from solution to solution, using the same cell in identical position at the same wave length may be interpreted directly in terms of dielectric constant change when reference is made to the behavior of a standard solution of known dielectric constant and like electrical conductance. The capacity C_2 is small enough so that $\bar{C}$ may be considered equal to C'' when the cell is disconnected from the circuit.

Both galvanometer deflections and precision condenser settings are made use of for the evaluation of the conductances of the solutions. The mathematical treatment of the comparator circuit for the conductance problem is complicated. There will be considered a definition of the total impedance of the circuit and a definition of the impedance from point A to point B in the circuit; then there will be described the two specific cases, one in which the conductance cell or other resistance is removed from the circuit, and the other in which the cell or resistance is connected in the circuit. In all these considerations the resistance R_2 has been neglected, since $R_2 >> R$. In the equations I is the current in the comparator circuit, I' is the current in the intermediate circuit, E is the voltage in the comparator circuit, Z designates an impedance, D is a galvanometer deflection and k is a proportionality constant.

Definition of Total Impedance of Circuit.—We may begin our consideration with the following relations

$$kD = I^2$$
$$\bar{r} = r + r_1$$
$$z_1 = \bar{R}_0 + j\bar{X}_0$$

In these equations z_1, $\bar{R}_0$ and $\bar{X}_0$ symbolize total impedance, resistance and reactances from A to B, respectively. Now, by definition

$$(j\omega L + \bar{r} + z_1)I + j\omega MI' = 0 \qquad (1)$$

After substituting for z_1, rearranging the real and the imaginary terms, squaring and substituting E for MI', one obtains for the current I the expression

$$|I| = \frac{E}{\sqrt{(\bar{r} + \bar{R}_0)^2 + (\omega L + \bar{X}_0)^2}} = \frac{E}{z_T} \quad (2)$$

in which z_T is the total impedance.

The current I is the root mean square of the current amplitude. Since one is concerned with the current amplitude only, the phase angle may be neglected.

From equation (2) the total impedance may be expressed by the relationship

$$z_T^2 = (\bar{r} + \bar{R}_0)^2 + (\omega L + \bar{X}_0)^2$$

The total impedance is treated in the form of its square since it eliminates the square root term, and since the galvanometer deflection expresses the square of the current.

By further definition

$$\bar{X}_0 = \omega L_1 - (1/\omega\bar{C}_0)$$

where L_1 is the inductance and $\bar{C}_0$ is the total capacity, both across AB. Since L_1 is nearly if not exactly zero, the reactance for the part of the circuit from A to B may be expressed as $\bar{X}_0 = -1/\omega\bar{C}_0$. Thus, the expression for the total impedance of the circuit becomes

$$z_T^2 = (\bar{r} + \bar{R}_0)^2 + (\omega L - (1/\omega\bar{C}_0))^2 \quad (3)$$

Definition of Impedance from A to B.—The quantities $\bar{R}_0$ and $\bar{C}_0$ must be determined for substitution in equation (3).

The admittance, Y, from A to B may be written

$$Y = \frac{1}{\bar{R}} + j\omega\bar{C} = \frac{1 + j\omega\bar{C}\bar{R}}{\bar{R}}$$

or

$$\bar{z}_1 = \frac{\bar{R}}{1 + j\omega\bar{R}\bar{C}} = \frac{\bar{R}(1 - j\omega\bar{C}\bar{R})}{1 + \omega^2\bar{C}^2\bar{R}^2}$$

in which $\bar{R}$ represents R_1, R_2, and R in parallel, $\bar{C}$ is the effective capacity across AB, and $\bar{z}_1$ is the effective impedance, also across AB.

Rewriting the expression for $\bar{z}_1$, we have

$$\bar{z}_1 = \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2} - \frac{j\omega\bar{C}\bar{R}^2}{1 + \omega^2\bar{C}^2\bar{R}^2} = \bar{R}_0 + j\bar{X}_0 = \bar{R}_0 - \frac{j}{\omega\bar{C}_0}$$

The evaluation of $\bar{z}_1$ makes it possible to express z_T in terms of more readily accessible quantities. Since

$$R_0 = \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2} \text{ and } \frac{1}{\omega\bar{C}_0} = \frac{\omega\bar{C}\bar{R}^2}{1 + \omega^2\bar{C}^2\bar{R}^2}$$

substitution for $\bar{R}_0$ and $\frac{1}{\omega\bar{C}_0}$ in equation (3) gives

$$z_T^2 = \left(\bar{r} + \frac{\bar{R}}{1 + \omega^2\bar{C}^2\bar{R}^2}\right)^2 + \left(\omega L - \frac{\omega\bar{C}\bar{R}^2}{1 + \omega^2\bar{C}^2\bar{R}^2}\right)^2 \quad (4)$$

Case 1. Cell Not Connected.—In this case $\bar{R}_1$ is the only resistance to be considered for the evaluation of $\bar{R}$. Equation (4) becomes

$$z_{T_1}^2 = \left(\bar{r}_1 + \frac{R_1}{1 + \omega^2\bar{C}^2R_1^2}\right)^2 + \left(\omega L - \frac{\omega\bar{C}R_1^2}{1 + \omega^2\bar{C}^2R_1^2}\right)^2 \quad (5)$$

The subscript 1 is used for the total impedance of the circuit when the conductance cell or other resistance is not connected across AB. Since R_1 is high in magnitude, equation (5) reduces to

$$z_{T_1}^2 = \bar{r}_1^2 + \omega^2L^2 - \frac{2L}{\bar{C}} + \frac{1}{\omega^2\bar{C}^2} = \bar{r}_1^2 + \left(\omega L - \frac{1}{\omega\bar{C}}\right)^2$$

At resonance $\omega L = \frac{1}{\omega\bar{C}}$, and the impedance becomes

$$z_{T_1}^2 = \bar{r}_1^2 \quad (6)$$

Case 2. Cell Connected in Parallel with Precision Condenser.—The resistances contained in $\bar{R}$ appearing in equation (4) are now R and R_1. Since R_1 is large and may be neglected ($R_1 >> R$), the expression for the impedance assumes the form

$$z_{T_2}^2 = \left(\bar{r}_2 + \frac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2 + \left(\omega L - \frac{\omega\bar{C}R^2}{1 + \omega^2\bar{C}^2R^2}\right)^2$$

The subscript 2 indicates that the cell or resistance is now connected in the comparator circuit If the quantity $\omega^2\bar{C}^2R^2$ is large compared to 1, the expression reduces, at resonance, to

$$z_{T_2}^2 = \left(\bar{r}_2 + \frac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2 \quad (7)$$

Relationship between Galvanometer Deflection and Electrical Conductance.—From Ohm's law

$$I_1^2z_{T_1}^2 = E_1^2 \text{ and } I_2^2z_{T_2}^2 = E_2^2$$

Therefore

$$I_1^2z_{T_1}^2 = I_2^2z_{T_2}^2, \text{ since } E_1 = E_2 \quad (8)$$

The voltage is maintained constant for any set of observations having to do with a given solution.

From equations (6), (7) and (8) we have

$$\frac{I_1^2}{I_2^2} = \frac{z_{T_2}^2}{z_{T_1}^2} = \frac{kD_1}{kD_2} = \frac{\left(\bar{r}_2 + \frac{R}{1 + \omega^2\bar{C}^2R^2}\right)^2}{\bar{r}_1^2} \quad (9)$$

At any one frequency the total impedance of the circuit without the cell is always the same. Thus the numerical value for the resistance of any solution, as compared to that of a potassium chloride solution, may be obtained from the ratio which forms equation (9), provided the resistances of the two solutions are nearly of the same magnitude.

The solution of this expression for R in a series of measurements at any wave length is facilitated by the construction of an interpolation table for R and kD_2/kD_1, to be used at that wave length. The values of $\bar{r}$ and $\omega^2\bar{C}^2$ are constant for any wave length and may be obtained either by the proper calibration of the members of the circuit or by solving for one or the other by the substitution in the equation of known values of R and kD_2/kD_1. The latter known quantities must have been obtained from a series of measurements with a standard resistance. The quantities $\bar{r}$ and $\omega\bar{C}$ do not have to be precise for if approximate constant values are used throughout, the relative values of kD_2/kD_1 and R will be correct.

We wish to express our indebtedness to Professor Edward Bennett of the Department of Electrical Engineering of this University and to Dr. Ronold King of the Department of Physics of Lafayette College for their helpful advice.

Summary

A method is described which serves for the simultaneous observation of electrical conductance and dielectric constant of very dilute electrolyte solutions at high radio frequencies. The apparatus which was used may be described as being of the comparator-resonance type. It consists of three distinct units, a variable high frequency oscillator circuit, an intermediate circuit and a comparator circuit with thermocouple–galvanometer measuring system.

The mathematical theory of the circuits is considered. Dielectric constant change is calculated from a comparison of the resonance settings of the standard variable precision condenser in the comparator circuit with the conductance cell connected and disconnected. For the evaluation of electrical conductance change there are required observations of the comparator circuit galvanometer deflections, again at resonance and with the cell connected and disconnected. It is further pointed out that the method developed may be applied to the measurement of high frequency currents through other types of resistances.

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The Resistance and Capacity Behavior of Strong Electrolytes in Dilute Aqueous Solution. II. The Dispersion of Electrical Conductance[1]

BY ORLAN M. ARNOLD AND JOHN WARREN WILLIAMS

Some years ago it was pointed out by Debye and Falkenhagen[2] that as a necessary consequence of the postulated existence about any central ion of an ionic atmosphere with a finite time of relaxation, there must result an electrical conductance which is dependent upon the frequency of the field which is used to measure it. If an alternating field is applied, each ion in the solution will acquire a periodic motion. If the frequency is low enough (1000 cycles, for example) there will be produced in each instant a dissymmetry in the ionic atmosphere which corresponds to the momentary velocity of the ion. But if this frequency is increased to a point where the period of oscillation of the ion becomes comparable with the time required for the formation of its atmosphere any dissymmetry of the latter, necessary for the existence of the electrical force of relaxation, will decrease. Thus, depending upon the time of relaxation of the atmosphere about any particular ion there will be a frequency at which the dissymmetry of the atmosphere no longer can be formed in the normal way, and as the frequency is increased above this value the electrical force of relaxation will diminish and the mobility of the central ion will increase until such time as the frequency has been made so high that the dissymmetry of the ionic atmosphere disappears entirely.

The results of the calculations of Debye and Hückel[3] and of Onsager[4] for the molar conductance of a solution at zero, or very low, frequency may be expressed in the form

$$\bar{\Lambda} = \bar{\Lambda}_0 - \bar{\Lambda}_{I_0} - \bar{\Lambda}_{II}$$

Here $\bar{\Lambda}$ is the molar conductance of the solution at a finite concentration, $\bar{\Lambda}_0$ is the molar conductance at infinite dilution, $\bar{\Lambda}_{I_0}$ is the electrical

(1) A preliminary and incomplete report of this work has appeared in another place [Williams and Arnold, *Acta Physicochim.*, *U. R. S. S.*, **3**, 619 (1935)]. This report gives as well provisional data for the dielectric constants of very dilute electrolyte solutions at two high frequencies.

(2) Debye and Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).

(3) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

(4) Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).