

An Oscillographic Method for the Study of Solution Behavior at Radio Frequencies¹

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From a study of the analytical implications of solution theory, it was concluded that experimental data were required to determine what property of solutions in a high frequency electric field would be most suitable as an indicator property for analytical purposes. An oscillographic apparatus was designed and constructed for measuring both the dielectric constant and the conductivity of electrolyte solutions at radio frequencies. The method is applicable both with immersed electrodes and with non-immersed electrodes.

The behavior of solutions of electrolytes in a high frequency field is of significance from the analytical as well as from the theoretical standpoint. It is important to know how the dielectric constant, the conductivity and other related quantities vary with concentration in order that a wise choice may be made of an indicator property for analytical purposes. This subject is of interest in radio frequency extensions of conventional conductometric titrations employing immersed electrodes and also in ascertaining the true nature of the measurements in the newer field of high frequency titrations without immersed electrodes.

A study of the analytical implications of solution theory led to the conclusion that experimental data are required as a basis of this selection of the most suitable solution property. This conclusion is based upon the fact that theory is not well developed for solutions of concentrations commonly encountered in regular analysis and even for certain very dilute solutions.

Several methods, including the classical bridge methods, have been employed for evaluating the dielectric constant and the conductivity of electrolyte solutions, but these methods are generally of limited applicability. The Henriquez resonance method (6) (7), which has been adopted and modified by numerous workers (1) (2) (3), is useful for determining the dielectric constant of very low conductivity liquids. Methods developed by Drude employing immersed Lecher wires are useful for very high frequency investigations of conducting liquids; the Wyman modification (11) provides for such dielectric constant measurements of conducting liquids. Grubb and Hunt (5) have employed a grid dip method at about eighty megacycles in which immersed electrodes are connected to an inductance and tuned to resonance with a micrometer screw, thus measuring dielectric constants of solutions up to about 0.005 normal. Surber (10) has determined the dielectric constant of medium and high loss liquids at microwave frequencies with a variable length liquid column in a section of wave guide. Forman and Crisp (4) investigated energy loss and dielec-

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tric constant changes with concentration for a number of electrolyte solutions over a wide range of concentrations at wave lengths varying from 0.80 to 11 meters. The calorimetric method for measuring energy loss has been described further (9). Although these and similar methods have been very useful in some applications, it seemed that some other method would be desirable to provide simultaneous dielectric constant and conductivity measurements over wide ranges of electrolyte concentrations. The present study represents an attempt to develop such a method.

Description of Method

The phase difference between two sine wave voltages at high frequency can be measured with a cathode ray oscillograph, as discussed by Seely (8). The measurement is based upon the interpretation of the Lissajous patterns which result from the impression of two sine wave voltages of identical frequency across the two pairs of deflecting plates. This principle has been used in the present study.

The circuit diagram is indicated in figure 1. Figure 2 shows the equivalent circuit with immersed electrodes. In the apparatus as constructed here, a war surplus BC-457A transmitter, converted for operation from the 110 volt a-c lines, was used as the source at 4.5 megacycles. Resistor R is a plaque resistor, whose inductance was empirically compensated with mica and air condensers with the aid of a radio frequency bridge so that it is pure resistance (98 ohms) at the 4.5 megacycle frequency employed. A Dumont type 274 oscillograph was used with the input voltages applied directly to the deflection plates rather than passing them through the amplifiers first.

The Lissajous patterns were photographed with a Dumont type 314 Oscillograph-Record camera. Each complete photograph consisted of a triple exposure, one of the Lissajous pattern and one of each axis obtained by shorting the x and y input terminals in turn. A diagrammatic representation of the complete photograph is shown in figure 3 along with an identification of the quantities which are measured in this study. A is the distance from the origin to the intercept of the ellipse with the vertical axis, and e_2 is the maximum vertical deflection. Likewise, e_1 is the maximum horizontal deflection. The distances A, e_1 and e_2 were measured on each photograph (35 mm. frame) with the aid of the Wilder MicroProjector, model AM-20. Additional experimental quantities, R and ω (2π times the frequency) are constant for all measurements.

It is not, of course, necessary to follow all of these constructional and operational details completely in order to use the method presented in this study.

Analysis of Circuit with Immersed Electrodes

The cell employing immersed electrodes, figure 2, is considered to be electrically equivalent to a parallel r-C combination, and the numerical values of C and of r are the desired quantities. It is now necessary to derive the proper mathematical relationships between the measured quantities, A, e_1 , e_2 , R and ω , and the desired quantities, r and C. This may be done as follows. A graphical construction of the tracing shows that e_1 and e_2 are proportional, respectively, to the maximum voltages applied to

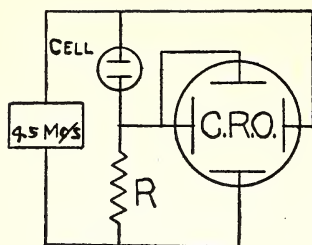


Fig. 1

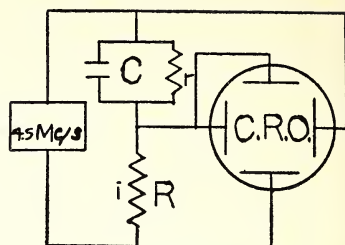


Fig. 2

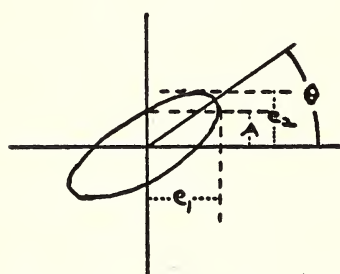
 $\theta \equiv \text{TRACE ANGLE}$

Fig. 3

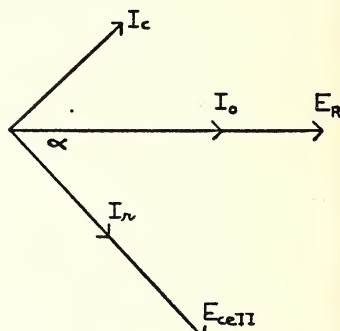


Fig. 4

the horizontal and to the vertical deflection plates. Because of this reason and the fact that the oscillograph amplifiers are not used, and assuming essentially identical deflection sensitivities (or correcting for specific sensitivities in tube employed),

$$\frac{e_1}{e_2} = \frac{E_{ce11}}{E_R} \quad (\text{in which } E_{ce11} \text{ and } E_R \text{ are, respectively the voltages appearing across the cell and the resistor } R \text{ of figure 1})$$

$$\frac{e_1}{e_2} = \frac{Z_{ce11}}{R} \frac{I_{ce11}}{I_R}$$

$$\frac{e_1}{e_2} = \frac{Z_{ce11}}{R} \quad (\text{since the same current flows through } R \text{ and the cell})$$

$$Z_{ce11} = \frac{Re_1}{e_2} \quad (\text{equation 1})$$

The current through the cell must divide vectorially between r and C , so

$$\overline{I_{ce11}} = \overline{I_r} + \overline{I_c}$$

$$\frac{\overline{E_{ce11}}}{Z_{ce11}} = \frac{\overline{E_r}}{r} + \frac{\overline{E_c}}{X_c}$$

$$\frac{1}{Z_{ce11}} = \frac{1}{r} + \frac{1}{X_c} \quad (\text{since the same voltage is across parallel parts of the cell})$$

$$\frac{1}{Z_{ce11}} = \sqrt{\left(\frac{1}{r}\right)^2 + (wc)^2} \quad (\text{changing from vectorial quantities to quantities of magnitude only})$$

Rearranging,

$$Z_{ce11} = \frac{R}{\sqrt{1 + \omega^2 C^2 r^2}} \quad (\text{equation 2})$$

Seely proves (13) that $\sin \alpha = \frac{A}{e_2}$ (equation 3), in which α is the phase difference angle between e_1 and e_2 , i.e., between E_{ce11} and E_R . A further relationship between $\sin \alpha$ and the desired quantities, C and r , may be derived with the aid of the vector diagram, figure 4. Take the total current flow through R and the cell, I_c , as the reference vector. The same current flows through R and the cell, So I_R and I_{ce11} are vectorially identical to I_o .

$$\overline{I_o} = \overline{I_R} = \overline{I_{ce11}}$$

The voltage across R must be in phase with the current through R , since R is pure resistance at the frequency employed; thus the E_R vector lies along the reference vector. The currents through C and r are 90° apart, with I_c leading I_r , and these two currents must vectorially equal the total current through the cell. Furthermore, the voltage across the cell must be in phase with the current through its resistive component, so the vector for the voltage across the cell, $\overline{E_{ce11}}$, must have the same direction as the vector $\overline{I_r}$. Angle α is by earlier definition the phase difference angle between the voltages across the cell and R , so it is the angle indicated in figure 4 between $\overline{E_R}$ and $\overline{E_{ce11}}$.

$$\cos \alpha = \frac{I_r}{I_{ce11}} \quad (\text{from figure 4})$$

$$\cos \alpha = \frac{\frac{E_r}{r}}{\frac{E_{ce11}}{Z_{ce11}}}$$

$$\cos \alpha = \frac{Z_{ce11}}{r} \quad (\text{since } E_r \text{ and } E_{ce11} \text{ are equal})$$

$$\text{Substituting equation 2, } \cos \alpha = \frac{1}{\sqrt{1 + \omega^2 C^2 r^2}}$$

$$\text{But, } \sin \alpha = \sqrt{1 - \cos^2 \alpha}$$

$$\text{So, } \sin \alpha = \sqrt{1 - \left(\frac{1}{\sqrt{1 + \omega^2 C^2 r^2}}\right)^2}$$

$$\sin \alpha = \frac{\omega Cr}{\sqrt{1 + \omega^2 C^2 r^2}} \quad (\text{equation 4}) -$$

Combining equation 1, 2, 3, and 4 and solving for C and r, the following equations are obtained:

$$C = \frac{A}{e_1 R \omega} \quad (\text{equation 5})$$

$$r = \frac{\frac{e_1}{e_2} R}{\sqrt{1 - \left(\frac{A}{e_2}\right)^2}} \quad (\text{equation 6})$$

Equations 5 and 6 relate the desired quantities, C and r, to the experimentally measurable quantities, A, e_1 , e_2 , R and ω . It should be emphasized that the significance of C and of r is this: a pure capacitance and a pure resistance of these magnitudes, when connected in parallel and substituted for the cell, would result in a phase difference the same as that observed experimentally with the conductivity cell. If the assumption of the equivalent circuit, figure 2, is correct, the magnitudes of C and of r are directly proportional to the dielectric constant and the resistance, respectively, of the solution combined with the particular sensing element and linking field used. This assumption may be supported by the experimental results obtained upon solutions of known properties.

Analysis of Circuit with Non-immersed Electrodes

With non-immersed electrodes as in the new type of high frequency methods of analysis, the equivalent circuit is the same as that in figure 2 with an additional capacitance, C_g , in series with the parallel r-C combination. The measured quantities, A, e_1 , e_2 , R and ω , must be related mathematically to the quantities C_g , r and C of the equivalent circuit of the cell. Then the value of C_g must be measured experimentally (e.g., by filling the cell with mercury and measuring its capacitance with a conventional capacitance bridge—this is, in effect, shorting the r-C portion of the equivalent circuit of the cell so that the C_g factor represents the entire cell). Although this derivation need not be carried through here, it may be performed by rewriting the C_g , r and C quantities into an equivalent parallel resistive-capacitive impedance and then proceeding as in the case of immersed electrodes.

Conclusions

The error in this type of measurement may be as much as two or three per cent because of several factors: the pairs of deflecting plates may not be exactly at right angles to each other; curvature of outer deflection field regions; non-linear responses of deflection; random errors in measurement of the several quantities on the photographed pattern; non-uniform film shrinkage.

This apparatus has been constructed and tested experimentally. The experimental data have served to show the feasibility of the method if stray reactances are minimized to a readily obtainable degree.

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