An AC method of measuring the conductivity of dielectric liquids.

Henry E. Fischer
ABSTRACT

The problem undertaken in this thesis is the presentation of a method of measuring the conductivity of dielectric liquids in which the liquid is used as the parallel tank circuit of a modified Wien-bridge oscillator. The main advantage of this method is that the frequency of the voltage applied to the liquid can be varied by simply varying the oscillator frequency. This allows the selection of a frequency which is best suited to the liquid in regard to polarization and relaxation time.

An oscillator was designed, built and used in the laboratory to measure the conductivity of the dielectric liquids - distilled water, glycerin, and chloroform. The results of these measurements, which are presented in tabular form, agree well with published values for these liquids.
ACKNOWLEDGEMENTS

The author would like to express his gratitude to Dr. R. S. Carson for his suggestions and guidance throughout the course of this work.

Thanks to Mr. Welch of the Chemistry Department for his assistance in obtaining chemicals.

Thanks to the Electrical Engineering Department for the use of its laboratories and equipment.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>CHAPTER I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Statement of the Problem</td>
<td>1</td>
</tr>
<tr>
<td>B. Importance of the Subject</td>
<td>1</td>
</tr>
<tr>
<td>C. Reasons for the Investigation</td>
<td>3</td>
</tr>
<tr>
<td>CHAPTER II. REVIEW OF THE LITERATURE</td>
<td>4</td>
</tr>
<tr>
<td>CHAPTER III. THEORY OF OPERATION</td>
<td>7</td>
</tr>
<tr>
<td>A. Wien-Bridge Oscillators</td>
<td>7</td>
</tr>
<tr>
<td>B. Capacitance and Resistance in Parallel Plate Geometry</td>
<td>11</td>
</tr>
<tr>
<td>CHAPTER IV. DESIGN OF THE DEVICE</td>
<td>13</td>
</tr>
<tr>
<td>CHAPTER V. EXPERIMENTAL PROCEDURE AND RESULTS</td>
<td>18</td>
</tr>
<tr>
<td>A. Distilled Water</td>
<td>23</td>
</tr>
<tr>
<td>B. Glycerin</td>
<td>26</td>
</tr>
<tr>
<td>C. Chloroform</td>
<td>28</td>
</tr>
<tr>
<td>CHAPTER VI. CONCLUSION</td>
<td>31</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>33</td>
</tr>
<tr>
<td>VITA</td>
<td>35</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Basic Wien-bridge oscillator</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>Reactive section of the Wien bridge</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Schematic diagram of device</td>
<td>17</td>
</tr>
<tr>
<td>4.</td>
<td>Experimental arrangement of equipment</td>
<td>19</td>
</tr>
</tbody>
</table>
INTRODUCTION

A. Statement of the Problem

The problem of this thesis is to demonstrate a method to measure the conductivity of a dielectric liquid by employing a specially built Wien-bridge oscillator. This is to be accomplished by inserting a parallel-plate capacitor in a beaker of the liquid and using this in place of the normal parallel resistance-capacitance tank circuit. The frequency of oscillation will then be a function of the product of the resistance and capacitance of the liquid. By measuring the frequency, this product can be calculated and through parallel-plate geometry set equal to the permittivity divided by the conductivity of the liquid. Therefore, the conductivity can be calculated providing the dielectric constant is known.

B. Importance of the Subject

Accurate measurements of conductivities in the very low ranges are not obtainable with existing conventional methods. The usual alternating-current bridge method of measurement is not applicable because the bridges in general do not operate at low enough frequencies so that the period of the applied voltage is
long compared to the relaxation time of the liquid (1)*. Turning then to a direct current measurement of conductivity, the problem of polarization near the electrodes immediately presents itself. Although the use of platinized electrodes reduces the effect of electrode polarization, it is always present to some degree when measuring conductivity at low frequencies (usually below 1 kc) with the electrodes in contact with the liquid. This polarization is more pronounced when the frequency is lowered and/or the applied field is increased.

By measuring the conductivity using the method outlined in this thesis it is possible to vary the frequency and therefore satisfy the requirement that the period be large compared to the relaxation time of the liquid. Also the magnitude of oscillation will be kept at a minimum and therefore the applied field will be small to reduce polarization effects.

However, whether or not this method becomes generally acceptable as an accurate way of measuring conductivity, the mere fact that it is a different way is important in itself. This is true because of some additional light that might be shed on the vexing problem of conduction processes in dielectric liquids.

* Numbers in parenthesis refer to references listed in the bibliography.
C. Reasons for the Investigation

An interest in the methods used for measuring the conductivity of dielectric liquids led the author to this study. A further impetus, along this problem, was the designing and building of the device required to measure the conductivity in the way desired.
CHAPTER II

REVIEW OF LITERATURE

Electrical conduction in dielectric liquids has been under investigation for more than seventy years and over that period a diverse range of experiments have been reported. A review by Whitehead (2) in 1928 indicated that knowledge of the subject at that time was largely empirical. Subsequent reviews of the subject were made by Lewis (3) in 1957, by Sharbough and Watson (4) in 1960 and by Swan (5) in 1962. It is evident from these reviews that a considerable amount of information concerning the electrical conduction of liquids under a variety of conditions is available. However, as Swan (5) indicated, more detailed investigation of fundamental conduction processes are required to develop a satisfactory theory.

One of the main reasons for the lack of a successful theory to explain conduction processes in dielectric liquids is the considerable experimental difficulties involved in obtaining reliable evidence without significant interference from extraneous sources. Some extraneous sources of interference are the presence of electrodes in the liquid, the purity of the liquid, stray radiation, and magnitude and time of application of test voltage. In what follows, these are examined in somewhat greater detail.
Whenever electrodes are present in a liquid a space-charge layer will exist in the dielectric liquid close to the electrodes due to the equilibrium between the charge carriers emitted from the electrodes and those produced in the liquid (6). This layer will influence the charge transfer to the liquid and hence the conductivity measured. The only way to counteract this is to develop a theory to explain its effect and then take it into account in subsequent measurements.

The cleanliness and exterior composition of the submerged electrodes also affect conductivity. It is desirable that the electrodes be clean in order to prevent conduction by impurities. Platinum is the preferred material composing the exterior of the electrodes when dc measurements are made since the effect of polarization is reduced.

One possible way to reduce electrode effects is to keep the electrodes out of the liquid. Such a method is described by Usikov (7) in which the electrodes are placed on the outside of the glass container of liquid. Then assuming the resistance of the container is much greater than that of the liquid, the equivalent circuit is that consisting of a capacitor in series with the parallel resistance-capacitance of the liquid. However, there is still an electrode in contact with a dielectric (the container) and therefore some polarization will exist. Therefore, it is doubtful as to how great an advantage the electrodeless
method presents.

To insure having a sample of liquid that is pure as possible many precautions are taken by various investigators including putting the sample in a dry atmosphere for an extended period of time and continuous distillation.

Experimental results have shown that radiation including cosmic rays have a definite effect on conductivity, particularly at low field strengths. Proper shielding can help considerably to remove this effect.

Lastly, the conductivity measured varies with time of application and magnitude of a dc test voltage mainly because of polarization effects. Therefore, it is necessary to specify these variables for a quoted value of conductivity. Even so, the reproducibility of results by the same investigator using the same equipment and sample leave much to be desired. Results of different investigators under apparently comparable conditions often differ by several orders of magnitude. In spite of this, it is generally agreed in the literature that the dc method is here to stay. This is due to the fact that the ac bridge method would require an almost continuously variable frequency source and a bridge capable of measuring $10^{10}$ ohms and higher.
CHAPTER III

THEORY OF OPERATION

A. Wien-Bridge Oscillators

Figure 1 is the schematic diagram of a simple Wien-bridge oscillator. The Wien bridge is composed of $R_1$, $R_2$, $R_3$, $R_4$, $C_1$ and $C_2$. The reactive section of the Wien bridge, Figure 2, is the key to understanding the operation of the oscillator. The transfer function, $T = V_2/V_1$, at any angular frequency, $\omega$, is given by

$$T = \frac{R_2}{1 + j\omega C_2 R_2} \frac{1}{R_1 + \frac{1}{j\omega C_1} + \frac{R_2}{1 + j\omega C_2 R_2}} \tag{1}$$

which simplifies to

$$T = \frac{j\omega C_1 R_2}{(1 - \omega^2 C_1 C_2 R_1 R_2) + j(\omega C_1 R_1 + \omega C_2 R_2 + \omega C_1 R_2)} \tag{2}$$

Rationalizing this expression we have

$$T = \left[ C_1 R_2 \omega (\omega C_1 R_1 + \omega C_2 R_2 + \omega C_1 R_2) + j\omega C_1 R_2 (1 - \omega^2 C_1 C_2 R_1 R_2) \right]$$

$$\div \left[ (1 - 2 \omega^2 C_1 C_2 R_1 R_2 + \omega^4 C_1^2 C_2^2 R_1^2 R_2^2) \right.$$

$$+ (\omega C_1 R_1 + \omega C_2 R_2 + \omega C_1 R_2)^2] \tag{3}$$

Therefore, at any frequency, $\omega$, the phase shift, $\phi$, of $V_2$ with respect to $V_1$ is given by
Figure 1. Basic Wien-bridge oscillator.

Figure 2. Reactive section of the Wien bridge.
\[ \phi = \tan^{-1} \left( \frac{1 - \omega^2 C_1 C_2 R_1 R_2}{\omega (C_1 R_1 + C_2 R_2 + C_1 R_2)} \right) \]  

For zero phase shift, i.e., input in phase with output,
we have
\[ 1 - \omega^2 C_1 C_2 R_1 R_2 = 0 \]  
Therefore, the frequency of oscillation is
\[ f_0 = \frac{1}{2 \pi \sqrt{C_1 C_2 R_1 R_2}} \]

Inherent in the above equation is the assumption that the amplifier
contributes exactly 360° phase shift. This requires, among other
things, that the tubes be biased in their linear range and that
the coupling capacitors be large enough so that their reactance is
negligible at the frequency of oscillation.

It is customary practice to choose \( R_1 = R_2 = R \) and \( C_1 = C_2 = C \)
(8). Under these conditions \( f_0 = 1/2 \pi RC \) and the impedance of
the series arm of the reactive section of the bridge, \( Z_1 \), is
\( (1-j)R \) while the impedance of the parallel section, \( Z_2 \), is
\( (1-j)R/2 \). Therefore, since the impedance of the parallel branch
is one-half that of the series arm, only one-third of the input
current voltage across the bridge is applied to the grid of the tube.
Hence, a gain of three is needed in the amplifier to satisfy the
amplitude requirement for oscillation.

A zero in the bridge output could then be obtained at the
resonant frequency by setting \( R_3 = 2R_4 \). However, in the present case, where the bridge is to be used as part of an oscillator, the phase shift must be zero at the resonant frequency but the magnitude cannot be zero. This is accomplished by making \( R_3 \) slightly greater than \( 2R_4 \) to slightly unbalance the bridge. This then is the normal Wien-bridge oscillator configuration.

The only effect that \( R_3 \) and \( R_4 \), the non-reactive branch of the Wien bridge, have is that of heavy negative feedback which makes the gain adjustment less critical. Therefore, it is entirely possible to dispense with these resistors and to use some other negative feedback arrangement and/or to adjust the gain to the critical value.

An analysis by Whale (9) illustrates that for maximum frequency stability in a Wien-bridge oscillator the ratios \( C_2/C_1 \) and \( R_1/R_2 \) should be as large as possible. However, as these ratios become larger, the amplifier gain that is required for oscillation becomes greater. Therefore, the values obtainable for the above ratios ultimately depend on the gain that is available from the amplifier. Whale further displays graphically the results of varying these ratios by plotting \( |V_2/V_1| \) and phase shift versus frequency. \( |V_2/V_1| \) is that fraction of the total voltage applied to the bridge that is seen on the grid. Naturally it is desirable, for maximum frequency stability, that the maximum of the \( |V_2/V_1| \) curve be as sharp as possible at the resonant
frequency, \( f_0 \), and also, that the rate of change of phase shift with frequency be greatest at this frequency. The graphs show that there is very little deterioration in these optimum conditions if the ratios are changed from a number approaching infinity to one. Therefore, it can be concluded that as long as the parallel resistance and/or the series capacitance do not become appreciably larger respectively than the series resistance and the parallel capacitance, good frequency stability should be obtained.

In the device presented in this thesis the parallel resistance-capacitance tank circuit of the conventional Wien-bridge oscillator is replaced by a beaker containing the dielectric liquid in which a parallel plate capacitor has been immersed. This gives an equivalent resistance and capacitance in parallel.

B. Capacitance and Resistance in Parallel Plate Geometry

The capacitance of a parallel plate capacitor, neglecting fringing of the field at the edges of the plates, is

\[
C = \frac{\varepsilon A}{L} \tag{7}
\]

where \( \varepsilon \) = the permittivity of the medium between the plates

\( A \) = the cross sectional area of the plates

\( L \) = the distance between plates

The resistance of a rectangular block of material of length \( L \)
and cross section $A$ is

$$ R_2 = \frac{L}{\sigma A} \hspace{1cm} \text{(8)} $$

where $\sigma$ is conductivity of block material.

The product of (7) and (8) is

$$ R_2 C_2 = \left( \frac{L}{\sigma A} \right) \left( \frac{A \epsilon}{L} \right) = \frac{\epsilon}{\sigma} \hspace{1cm} \text{(9)} $$

and solving for $R_2 C_2$ from equation (6)

$$ R_2 C_2 = \frac{1}{(2 \pi)^2 f^2 R_1 C_1} \hspace{1cm} \text{(10)} $$

Equating (9) and (10)

$$ \frac{\epsilon}{\sigma} = \frac{1}{(2 \pi)^2 f^2 R_1 C_1} \hspace{1cm} \text{(11)} $$

Rewriting

$$ \sigma = \epsilon (2 \pi)^2 f^2 R_1 C_1 \hspace{1cm} \text{(12)} $$

Thus by measuring the frequency of oscillation of the oscillator and using known values of series resistance and capacitance, the conductivity can be calculated providing the permittivity is known.
CHAPTER IV
DESIGN OF THE DEVICE

The first requirement considered was that of designing the oscillator with a very large input impedance. This was necessary since the input impedance is in parallel with the impedance of the liquid tank circuit, and the former must be much greater than the latter if the resultant parallel impedance is to be, to a very close approximation, that of the liquid tank circuit. It is necessary that this approximation be close because the value for the impedance of the liquid tank circuit, used in the calculations of conductivity, is that of the aforementioned parallel combination. Thus, remembering that the liquid being used has a very high resistivity, it is apparent that the input impedance must be large.

To obtain the large input impedance a subminiature electrometer triode was used. This particular electrometer tube, Raytheon CK 5886, was used mainly because it was readily available to the author. To further increase the input impedance, the tube was employed as a cathode follower. Since the filaments of this tube are operated from a 1.5 volts dc supply (flashlight battery) a possible cause of 60 cycle interference was eliminated.

The insulated gate field effect transistor, which has only
recently become commercially available, is another device with a high input impedance. Although at present it is relatively expensive, it should be seriously considered in any future work with this method.

The second problem was that of designing a direct-coupled amplifier so that phase shift due to coupling circuitry would be nonexistent. To accomplish this end a simple transistor differential (difference) amplifier was employed. One input of the amplifier was from the cathode follower and the other input was biased at a dc voltage which could be varied by means of a potentiometer from the supply to ground. Two 2n2221 silicon npn transistors were used as the active elements of the amplifier. Since the amplifier would be operating at low but not zero (dc) frequency, drift due to temperature sensitivity of current gain, base-emitter voltage, and collector-base leakage current was not considered to be a overly critical factor. However, as a precaution, silicon transistors with correspondingly lower collector-base leakage current than that of germanium transistors were used. Also these transistors were of the epitaxial planar variety which reduces the drift due to collector-base leakage current and base-emitter voltage (10).

Since the supply voltage of the electrometer tube was only 20 volts, a common supply was used for the tube and the transistors simply by picking transistors with the appropriate voltage requirement.
Because the supply voltage for the entire circuit was common, the magnitude of the voltage at the cathode of the tube was such that direct coupling between it and the base of the first transistor was possible.

A theoretically possible Wien-bridge oscillator has been described up to this point, if the amplifier output is simply fed back to the bridge input, with some provision for adjusting the gain. However, an emitter follower stage is highly desirable. This is true because in the calculations made earlier under "Wien-Bridge Oscillators" the source impedance driving the bridge was assumed to be zero. If this is not the case, the transmission of the network is modified along with the frequency at which the bridge offers zero phase shift. For this reason an emitter-follower stage was added by direct coupling from the collector of the previous stage. For the emitter resistor a potentiometer was then used with the variable tap connected to the bridge input to give the necessary gain control.

One further refinement to the circuit was made. It was stated earlier that the resistive section of the bridge could be eliminated, as has been done here, since it only provides degenerative feedback. However, without a certain amount of degenerative feedback in the circuit the distortion of the waveshape is intolerable, due to limiting caused solely by the active devices, unless the gain is very critically adjusted. Therefore, a resistor
was included in the emitter of each transistor in the differential amplifier to provide sufficient degenerative feedback.

The circuit was then mounted on a chassis with two leads, made as short as possible, running to the capacitor in the liquid. The entire device was then enclosed in a shielded box with a hinged lid for easy access. The shielded box was used to prevent stray radiation from affecting the conductivity measurements.

It is desirable to have the oscillator oscillate at various frequencies with each liquid in order to see if frequency has any bearing on conductivity. Changing the frequency means changing the series resistance and/or series capacitance of the bridge. To facilitate doing this various resistors and capacitors were mounted on G-R plugs and then the desired value could be simply plugged in. Decade resistance boxes were not used because of shielding problems and inadequate ranges of resistance values. A schematic diagram of the completed device is illustrated in Figure 3.
Figure 3. Schematic diagram of device
CHAPTER V

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental part of this problem consists of using the previously described device to measure the conductivity of three dielectric liquids, namely, distilled water, glycerin, and chloroform. The choice of liquids was made on the basis of availability and expected range of conductivity. The values of conductivity obtained were then compared to published values of conductivity for the liquids.

It should be emphasized at this point that the above comparison cannot be used to determine the detailed accuracy of the method. This is true since different samples of a liquid can differ appreciably in purity and also because the way in which the published values of conductivity were obtained is not specified, i.e., whether the applied voltage was dc or if ac what frequency. However, the object of this experiment is not to demonstrate the accuracy of this method but rather to show the feasibility of it. Many additional steps would have to be taken, to obtain the most accurate conductivity reading for the liquid, including the platining of the capacitor plates and some means of controlling the purity of the liquid under test such as continuous distillation.

In spite of the above mentioned shortcomings, the published
values of conductivity are useful in that they provide about the only means of comparison available since the conductivities of the liquids in this experiment are beyond the range of readily accessible equipment on campus at the present time.

Figure 4 is a block diagram of the experimental arrangement of equipment. The oscilloscope was used to amplify the oscillator signal sufficiently to drive the frequency counter and to provide a visual display of the oscillator output for adjustment of amplifier gain and bias. The gain was maintained at the minimum value necessary for oscillation. This was done to keep the active devices in the oscillator from presenting any significant phase shift which would limit the accuracy of the equation for resonant frequency derived earlier.

Figure 4. Experimental arrangement of equipment.
Several values of series resistance and capacitance were used in the oscillator for each of the liquids. In every case the values used for these elements in the subsequent calculation were obtained by an impedance bridge measurement. The bridge is accurate to within ±1% of the dial reading for resistance and capacitance.

It was outlined earlier that certain ratios of series resistance and capacitance to parallel resistance and capacitance were desirable. In order to pick series resistors in line with these ratios, a dc resistance measurement was made across the terminals of the capacitor submerged in each liquid to give an indication of the parallel resistance. Similarly the parallel capacitance was taken as the product of the relative dielectric constant of the liquid and the capacitance of the parallel plate capacitor in air.

It was mentioned in the introduction that the period of the applied dc voltage must be long compared to the relaxation time of the liquid. Therefore, the period of the oscillator frequency must be compared to the relaxation time of every liquid to ensure meeting this criteria. To facilitate this comparison the following argument was used to come up with an easy way of determining this relaxation time.

For the parallel plate capacitor submerged in a dielectric
liquid the following differential form of Maxwell's equation holds
\[ \nabla \times \vec{H} = \vec{J}_{\text{total}} = \vec{J}_{\text{cond}} + \vec{J}_{\text{disp}} \]

(1)

where \( \vec{J}_{\text{cond}} \) is the conduction current density due to the resistance between the plates and \( \vec{J}_{\text{disp}} \) is the displacement current density due to the capacitance. Since

\[ \vec{J}_{\text{cond}} = \sigma \vec{E} = \left( \sigma / \varepsilon \right) \vec{D} \]

(2)

and

\[ \vec{J}_{\text{disp}} = \frac{\partial \vec{D}}{\partial t} \]

(3)

(1) can be written as

\[ \nabla \times \vec{H} = \left( \sigma / \varepsilon \right) \vec{D} + \frac{\partial \vec{D}}{\partial t} \]

(4)

Taking the divergence of both sides yields

\[ \nabla \cdot \nabla \times \vec{H} = \frac{\sigma}{\varepsilon} \nabla \cdot \vec{D} + \frac{\partial}{\partial t} (\nabla \cdot \vec{D}) \]

(5)

but since

\[ \nabla \cdot \nabla \times \vec{H} = 0 \]

(6)

and

\[ \nabla \cdot \vec{D} = \rho \]

(7)

(5) becomes

\[ 0 = \frac{\sigma}{\varepsilon} \rho + \frac{\partial \rho}{\partial t} \]

(8)

which yields upon solving for \( \rho \)

\[ \rho = \rho_0 e^{-\frac{\sigma}{\varepsilon} t} \]

From (9) it is seen that

\[ \varepsilon / \sigma = \chi \] (the relaxation time)

(10)
However, equation (9), page 12, is

\[ R_2 C_2 = \frac{\varepsilon}{\sigma} \] .......(11)

Equating (10) and (11) we obtain

\[ R_2 C_2 = \gamma \] .......(12)

where \( R_2 C_2 \) is the product of the resistance and capacitance of the parallel liquid tank circuit. Therefore, the period of the oscillator frequency should be large compared to \( R_2 C_2 \) or equivalently the frequency of oscillation should be small compared to \( \frac{1}{R_2 C_2} \).

The value obtained for conductivity, using this method, is dependent on the accuracy of equation (6), page 9, which is

\[ f_0 = \frac{1}{2\pi \sqrt{R_1 C_1 R_2 C_2}} \]

Therefore, to illustrate that this equation does hold for the particular oscillator designed in this thesis, the frequency of the oscillator was measured, using the frequency counter, and calculated, using the above equation, with actual resistors and capacitors in the parallel tank circuit. The results are as follows:

<table>
<thead>
<tr>
<th>( \frac{R_1}{(k \ \Omega)} )</th>
<th>( \frac{R_2}{(k \ \Omega)} )</th>
<th>( C_1 ) (pf)</th>
<th>( C_2 ) (pf)</th>
<th>( f ) (measured) (cps)</th>
<th>( f ) (calculated) (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1570</td>
<td>890</td>
<td>430</td>
<td>980</td>
<td>210</td>
<td>208</td>
</tr>
<tr>
<td>1690</td>
<td>1780</td>
<td>216</td>
<td>212</td>
<td>425</td>
<td>428</td>
</tr>
<tr>
<td>1570</td>
<td>890</td>
<td>212</td>
<td>216</td>
<td>631</td>
<td>630</td>
</tr>
<tr>
<td>3.42</td>
<td>3.38</td>
<td>980</td>
<td>970</td>
<td>46478</td>
<td>47800</td>
</tr>
</tbody>
</table>
Thus in the low frequency range, the range of interest for low conductivity dielectrics and the range in which chloroform and glycerin fall, the agreement between the measured frequency and the calculated frequency is very good.

To check the effect of any stray capacitance on the measured value of frequency, a small (about 13 pf.) capacitor was connected from ground to the different points of the circuit to see if any frequency change would occur. The results were negative, so stray capacitance should not be a critical factor.

A. **Distilled Water**

The distilled water tested was a commercial grade, purchased locally, and was used directly from the container without any further distillation.

The relative dielectric constant of water is 81 and the dc resistance measured across the terminals of the submerged 10 picofarad capacitor was 4 kilohms. Therefore, the resistance and capacitance of the parallel tank, \( R_2 \) and \( C_2 \), were on the order of 4 kilohms and 810 picofarads respectively.

Distilled water was unique in that the conductivity increased somewhat with time. In several runs it was noticed that this was predominantly true only during the first 20 minutes.
after which the conductivity remained quite steady. A typical
fun follows:

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Frequency (cps)</th>
<th>$\sigma x 10^6$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>43087</td>
<td>1.05</td>
</tr>
<tr>
<td>1</td>
<td>43720</td>
<td>1.08</td>
</tr>
<tr>
<td>2</td>
<td>44325</td>
<td>1.11</td>
</tr>
<tr>
<td>3</td>
<td>44926</td>
<td>1.14</td>
</tr>
<tr>
<td>4</td>
<td>45368</td>
<td>1.16</td>
</tr>
<tr>
<td>5</td>
<td>45693</td>
<td>1.18</td>
</tr>
<tr>
<td>6</td>
<td>45797</td>
<td>1.18</td>
</tr>
<tr>
<td>8</td>
<td>45910</td>
<td>1.19</td>
</tr>
<tr>
<td>10</td>
<td>46076</td>
<td>1.20</td>
</tr>
<tr>
<td>15</td>
<td>46814</td>
<td>1.24</td>
</tr>
<tr>
<td>20</td>
<td>47480</td>
<td>1.27</td>
</tr>
</tbody>
</table>

Here the values of $R_1$ and $C_1$ (the series resistor and capacitor) are
4.65 kilohms and 430 picofarads respectively.

Since this time dependency was not, to my knowledge, noticed
by any other investigator it would seem reasonable to suspect
that the cause for it was peculiar to this method. Probably
the most obvious thing to suspect would be oscillator drift.
This was checked by inserting a fixed resistor and capacitor
in place of the liquid and observing the frequency. The oscillator
frequency was monitored continuously over a time span of 25 minutes
with the extremes of frequency being 33690 cps. and 33706 cps.
This is only a span of 16 cps. compared to approximately 4,500 cps.
with the liquid present. Therefore, the explanation for the time
dependency of conductivity can be localized to the beaker of
liquid containing the capacitor. It can be concluded then, that
if this result is not representative of the liquid, it must be due
to some interaction between the liquid and the capacitor plates.

To eliminate erroneous results due to the preceding phenomena, all following conductivity measurements for water were taken after the oscillator had been in operation for at least 20 minutes. Such a set of readings follow.

<table>
<thead>
<tr>
<th>$R_1$ (k$\Omega$)</th>
<th>$C_1$ (pf)</th>
<th>Frequency (cps)</th>
<th>$\sigma \times 10^6$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.48</td>
<td>430</td>
<td>51900</td>
<td>1.14</td>
</tr>
<tr>
<td>4.40</td>
<td>430</td>
<td>48546</td>
<td>1.26</td>
</tr>
<tr>
<td>4.65</td>
<td>980</td>
<td>47480</td>
<td>1.27</td>
</tr>
<tr>
<td>3.48</td>
<td>980</td>
<td>36638</td>
<td>1.30</td>
</tr>
<tr>
<td>4.40</td>
<td>980</td>
<td>33944</td>
<td>1.40</td>
</tr>
<tr>
<td>4.65</td>
<td>980</td>
<td>33270</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Below is a sample calculation of relaxation time and conductivity for $R_1 = 3.48$ kilohms and $C_1 = 430$ picofarads. From equation (10), page 12:

$$R_2C_2 = \frac{1}{(2\pi)^2 t^2 R_1 C_1}$$

$$R_2C_2 = \frac{1}{(2\pi)^2 (5.19 \times 10^4)^2 (3.48)(.43)10^{-6}}$$

$$R_2C_2 = \frac{1}{159,200}$$

and from equation (12), page 22:

$$R_2 C_2 = \gamma = \frac{1}{159,200}$$

Therefore, the oscillator frequency should be small compared to 159,200 cps and this is seen to be the case in the frequency range used in the above calculations of conductivity. Also using equation (12), page 12.
\[ \sigma = \varepsilon (2\pi)^2 f^2 R_1 C_1 \]
\[ = (81)(8.85 \times 10^{-12})(51900)^2(3.43)(.43)10^{-6}(2\pi)^2 \]
\[ = 1.142 \times 10^{-6} \text{ mhos} \]

In analyzing the values of conductivity obtained for distilled water it should first be noted that they agree well with the published value of approximately \(10^{-6} \Omega^{-1} \text{cm}^{-1}\) (11). Also the conductivity decreases with increasing frequency of oscillation.

B. Glycerin

The relative dielectric constant of glycerin is 56 and the dc resistance measured across the terminals of the submerged 10 picofarad capacitor was 1.6 megohms. Therefore, \(R_2\) and \(C_2\) were on the order of 1.6 megohms and 560 picofarads respectively.

Glycerin was also unique among the liquids measured in that it is highly viscous. Because of this property, small air bubbles were likely to form around the capacitor plates when the glycerin was poured into the beaker. One way to minimize this is simply to pour in the liquid very slowly and then by rotating the capacitor plates try to free the air pockets, that did form, so that they would rise to the surface. Another way to get rid of these air bubbles is to place the beaker containing the liquid and the capacitor under the bell jar and then reduce the air pressure.
inside sufficiently to cause them to rise to the surface.

A typical set of data for a sample that was not placed under the bell jar follows:

<table>
<thead>
<tr>
<th>$R_1$ (M$\Omega$)</th>
<th>$C_1$ (pf)</th>
<th>Frequency (cps)</th>
<th>$\sigma \times 10^8$ ((\Omega^{-1}) cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.37</td>
<td>980</td>
<td>206</td>
<td>2.73</td>
</tr>
<tr>
<td>2.61</td>
<td>980</td>
<td>230</td>
<td>2.65</td>
</tr>
<tr>
<td>2.18</td>
<td>980</td>
<td>252</td>
<td>2.66</td>
</tr>
<tr>
<td>1.57</td>
<td>930</td>
<td>294</td>
<td>2.60</td>
</tr>
<tr>
<td>2.61</td>
<td>430</td>
<td>350</td>
<td>2.68</td>
</tr>
<tr>
<td>2.18</td>
<td>430</td>
<td>386</td>
<td>2.73</td>
</tr>
<tr>
<td>0.89</td>
<td>980</td>
<td>392</td>
<td>2.62</td>
</tr>
<tr>
<td>1.57</td>
<td>430</td>
<td>451</td>
<td>2.68</td>
</tr>
<tr>
<td>0.89</td>
<td>430</td>
<td>603</td>
<td>2.72</td>
</tr>
</tbody>
</table>

The relaxation time for this sample is

$$\tau = \frac{1}{R_1 C_1} = \frac{1}{(2 \pi f)^2 R_1 C_1}$$

$$\tau = \frac{1}{(2 \pi )^2 (392)^2 (0.89)(0.98) \times 10^{-3}}$$

$$\tau = \frac{1}{5280}$$

Again the oscillator frequencies used are small compared to 5280 cps. as required.

As can be seen from the table that the conductivity of glycerin unlike that of distilled water does not vary in any particular way with frequency. The small random fluctuations, amounting to about a 4.8% deviation, cannot be counted as significant and the value of conductivity measured here is in good agreement with the published value of $6 \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ (12).
The following data is for a sample of glycerin that was placed under the bell jar:

<table>
<thead>
<tr>
<th>$R_1$ (M$\Omega$)</th>
<th>$C_1$ (pf)</th>
<th>Frequency (cps)</th>
<th>$\sigma X 10^8$ (S$-1$ cm$-1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.37</td>
<td>980</td>
<td>220</td>
<td>3.13</td>
</tr>
<tr>
<td>2.61</td>
<td>980</td>
<td>243</td>
<td>2.96</td>
</tr>
<tr>
<td>2.18</td>
<td>980</td>
<td>267</td>
<td>2.93</td>
</tr>
<tr>
<td>1.57</td>
<td>430</td>
<td>312</td>
<td>3.04</td>
</tr>
<tr>
<td>2.61</td>
<td>430</td>
<td>372</td>
<td>3.04</td>
</tr>
<tr>
<td>2.18</td>
<td>430</td>
<td>410</td>
<td>3.08</td>
</tr>
<tr>
<td>0.89</td>
<td>980</td>
<td>415</td>
<td>2.94</td>
</tr>
<tr>
<td>1.57</td>
<td>430</td>
<td>481</td>
<td>3.06</td>
</tr>
<tr>
<td>0.89</td>
<td>430</td>
<td>644</td>
<td>3.10</td>
</tr>
</tbody>
</table>

Again, there is no trend of conductivity with frequency, however, the readings are slightly larger than previously. These larger readings are as expected since air bubbles in the liquid reduce the effective cross sectional area of the liquid through which current must pass. Therefore, conductivity is increased by the removal of these air bubbles.

C. Chloroform

The relative dielectric constant of chloroform is 4.9 and the dc resistance measured across the terminals of the submerged 10 picofarad capacitor was 9 megohms. Therefore, $R_2$ and $C_2$ were considered as approximately 9 megohms and 49 picofarads respectively.

Chloroform provides a striking example of a liquid whose value of conductivity is somewhat in doubt. Published values range from
10^{-8} \text{ cm}^{-1} \text{ cm}^{-1} \text{ cm}^{-1} \text{ cm}^{-1} (12) to 10^{-11} \text{ cm}^{-1} \text{ cm}^{-1} \text{ cm}^{-1} \text{ cm}^{-1} (13) with the most common values found in the literature between 2.5 \times 10^{-10} \text{ cm}^{-1} \text{ cm}^{-1} and 10^{-10} \text{ cm}^{-1} \text{ cm}^{-1}. The above mentioned value of 10^{-11} \text{ cm}^{-1} \text{ cm}^{-1} was reached only after 4\frac{1}{2} months of continuous distillation.

A set of conductivity measurements on chloroform follows:

<table>
<thead>
<tr>
<th>$R_1$ (M $\text{cm}$)</th>
<th>$C_1$ (pf)</th>
<th>Frequency (cps)</th>
<th>$\sigma \times 10^{-10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.00</td>
<td>55</td>
<td>249</td>
<td>9.38</td>
</tr>
<tr>
<td>12.00</td>
<td>55</td>
<td>288</td>
<td>9.36</td>
</tr>
<tr>
<td>9.40</td>
<td>55</td>
<td>361</td>
<td>9.34</td>
</tr>
<tr>
<td>16.00</td>
<td>24</td>
<td>385</td>
<td>8.36</td>
</tr>
<tr>
<td>6.70</td>
<td>24</td>
<td>412</td>
<td>8.34</td>
</tr>
<tr>
<td>12.00</td>
<td>24</td>
<td>468</td>
<td>8.45</td>
</tr>
<tr>
<td>9.40</td>
<td>24</td>
<td>553</td>
<td>8.43</td>
</tr>
</tbody>
</table>

The relaxation time for chloroform is

$$\tau = \frac{R_1 C_1}{(2 \pi)^2 f^2 R_1 C_1}$$

$$\tau = \frac{1}{(2 \pi)^2 (3.61 \times 10^2)^2 (2.4)(1.6) 10^{-4}}$$

Again, it is seen that the frequencies at which the conductivity was measured are low compared to the reciprocal of the relaxation time. Also, the conductivity generally decreases with increasing frequency as was also characteristic of distilled water.

The actual value of conductivity measured tends to be roughly about five times recent published values. However, when measuring
conductivity on the order of $10^{-10}\text{cm}^{-1}$ it is reasonable to assume that the purity of the liquid and the cleanliness of the equipment will tend to have a considerable influence on the results. Because of this and the fact that the author had available only the minimum means of controlling these factors, the readings obtained can be considered to be quite good.
CHAPTER VI

CONCLUSION

In choosing a parallel plate capacitor to use in the liquid, the design of the capacitor plates should be taken into account as a possible source of error. This is due to the fact that in this method parallel plate geometry is made use of which assumes, among other things, that the plates have the same shape and be lined up vertically, i.e., directly on top of one another.

The range of frequencies over which the conductivity for the various liquids was measured is, relatively speaking, quite small. This was done purposely in order to avoid any phenomena associated with polarization on the one extreme and relaxation time on the other.

The amount of error due to the circuit itself, excluding the capacitor and the beaker of liquid, is undoubtedly very small. This statement is based foremost on the fact that the calculated and measured values of frequency, mentioned in Chapter V, were in very close agreement. This means that the frequency of this oscillator is virtually completely determined by the elements in the reactive section of the Wien bridge, i.e., the frequency is independent of the rest of the circuit. Still another basis for the statement at the beginning of this paragraph, is that an
oscilloscope was used to observe the waveform at all times. This allowed on the spot adjustment of gain and bias to correct for any distortion present.

In line with the above paragraph, it should be pointed out that there was one noticeable exception to the frequency being determined entirely by the reactive section of the bridge. This was that the frequency varied slightly with adjustment of the gain. Since this effect was greater with water, the reason for it was probably the fact that adjustment of the gain varies the Thevenin impedance of the source driving the bridge, and this impedance is in series with the series arm of the bridge. For water, with the amplifier at half gain, these impedances are of the same order of magnitude. This problem can be handled by building a larger gain amplifier so that the gain control can be set at a minimum, thereby, keeping the Thevenin impedance lower.

Another refinement to the amplifier, which would make adjusting the gain somewhat easier, would be to use a potentiometer with a larger number of turns for the gain control.

As an extension of the material presented in this thesis, the author suggests the building of a larger gain amplifier, the using of a specially constructed, platinized capacitor and the development of some means for better controlling the purity of the liquid under test.
BIBLIOGRAPHY


VITA

The author was born on March 15, 1937 in Washington, Missouri. He lived on a farm about five miles west of Washington, and attended Ziegenmeyer's, a one room country school, for his primary education. His secondary education was obtained at St. Francis Borgia High School in Washington, from which he was graduated in May, 1955.

The author enlisted in the United States Navy in February, 1956, and served for four years as an electronic technician attaining the rank of second class petty officer before his discharge.

He received his Bachelor of Science Degree in Electrical Engineering from the University of Missouri at Rolla in June, 1964. He entered Graduate School at the University of Missouri at Rolla in September, 1964 under a NASA Traineeship.

The author is a member of Eta Kappa Nu, Tau Beta Pi and Phi Kappa Phi.