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Relative Permittivity as a Function of Co-solvent and Impedance Spectroscopy for Quantifying  
Anions in Solution

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A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

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by

Yahya Sami Alseiha

December 2018

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Dr. Dane W. Scott

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Dr. Catherine McCusker

Keywords: Relative Permittivity, Impedance Spectroscopy, Nyquist Plot, Resistivity and  
Conductivity

## ABSTRACT

Relative Permittivity as a Function of Co-solvent and Impedance Spectroscopy for Quantifying  
Anions in Solution

by

Yahya Sami Alseiha

This work measured relative permittivity from 15.0 to 55.0 °C of aqueous solutions containing acetone or tetrahydrofuran using a BI 870 dielectric meter. A cubic polynomial fit resulted in coefficients for calculating permittivity as a function of temperature and mole fraction. Literature values for other co-solvent system resulted in similar polynomial coefficients. Using BI 870, permittivity measurements of ionic solutions were not possible because of high conductivity. A simple method using impedance spectroscopy measured these solutions. Impedance decreases with increasing temperature and decreases with increasing ionic strength. Due to the temperature dependence of impedance, all measurements were at 25.0 °C. Anions including bicarbonate, sulfate, acetate, and carbonate were determined using this method. Detection limits were at parts per trillion (ppt) levels. A simple sensor based on smaller stainless steel cylinders and a circuit to determine impedance is currently being developed in combination with an anion exchange column.

## DEDICATION

This work is dedicated to my parent, my wife, my parent-in-laws, my kids, my siblings, my aunts, my uncles, my cousins, and my grandparents and all my friends.

## ACKNOWLEDGEMENTS

First and foremost, I would like to thank God for giving me the knowledge, strength, opportunity and ability to accomplish this research satisfactorily. Without his blessings, this work would not be possible. I would like to express my profound gratitude to my research advisor Dr. Dane Scott. This journey to complete this research would not be possible without him. Also, I would like to thank my committee members Dr. Bishop and Dr. McCusker for their suggestions and comments resulting this thesis. I also thank the East Tennessee State University Office of Sponsored Research and Programs.

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## LIST OF ABBREVIATIONS

AC	Alternating Current
DMF	Dimethylformamide
EIS	Electrochemical Impedance Spectroscopy
EPA	Environmental Protection Agency
fM	Femtomolar
IC	Ion Chromatography
ppb	Parts Per Billion
ppm	Parts Per Million
ppt	Parts Per Trillion
Z	Impedance

## CHAPTER 1

### INTRODUCTION

#### Purpose of Research

Hydrolysis of acetic anhydride results in acetic acid and the reaction rate in pure water is well understood. To quantify the effect of solute-solvent interactions using tetrahydrofuran as a co-solvent, relative permittivity values of different aqueous solutions of tetrahydrofuran and water are required and were measured. These were obtained using Brookhaven's BI 870 dielectric constant meter. Pure water and aqueous solutions using acetone as a co-solvent were measured and compared to literature values to validate the method of measurement. Relative permittivity values of some water co-solvent systems are available in published literature. These values were fit as a function of mole fraction instead of molarity to compare to other co-solvent systems. All values fit a cubic polynomial permitting calculation of relative permittivity as a function of mole fraction over a temperature range from 15.0 and 50.0 °C. Another use for permittivity explored was determining the concentration of ions in solution.

A primary reason for this effort is a method for detecting and measuring nitrate in ground water near agricultural centers. Ideal systems are low cost, robust, maintenance free and wireless.<sup>1</sup> The main electrochemical techniques for determining concentration of ions are conductivity, ion selective electrode and pulsed amperometry.<sup>2-4</sup> The detection limits for these techniques are between ppb to ppt levels, which is below the maximum contaminant level established by the EPA, and depend on the ion being measured.<sup>2-5</sup> Pulsed amperometry methods are excellent for species that can be oxidized and reduced requiring a reference electrode.<sup>2,6</sup> Different metal electrodes used for pulsed amperometry include silver, gold and platinum.<sup>2,3,7</sup> Ion selective electrodes are easily polluted by other species such as organics in real water samples.<sup>1,7</sup>

Different metal electrodes and modifications such as polymer treatment have been used to circumvent these problems.<sup>7,8</sup> In attempt to circumvent these issues permittivity measurements of solutions of low ionic strength were explored. However, the method for measuring solutions with low ionic strength was not successful due to conductivity of the solution interfering with the electrical measurement performed by the BI 870.

Interestingly, the probe of the BI 870 connected to an electrochemical workstation was successful in using impedance measurements to determine the concentration of ions in solution. This method involves an electrical measurement across two stainless steel cylinders with solution between them. The result of this work uses the BI 870 probe and an electrochemical workstation to determine the concentration of ions in solution. Detection limits obtained are comparable to ion conductivity and pulsed amperometry.<sup>2</sup> Stainless steel is more robust in the presence of real samples and impedance measurements do not require a reference electrode. As such, the method of calibrating impedance measurements following ion exchange should result in further development of an in-situ sensor for monitoring ions in water.

### Relative Permittivity

One important property of a solution is relative permittivity, ( $\epsilon$ ), which is the dielectric response of a material or solution to an applied electrical field.<sup>9</sup> In 1948 Hasted et al. conducted the first organized experimental study of the dielectric properties of different concentrations of salt in water.<sup>10</sup> Dielectric constants of aqueous electrolyte solutions depend on hydration, complexation characteristics of ions, electric conductivity, structure saturation and kinetic depolarization.<sup>11</sup>

### The Relative Permittivity of Pure Water Compared to Other Solvents

In most cases, polarity has a direct relationship with relative permittivity.<sup>12</sup> As a general

rule, if polarity is high so will relative permittivity. Table 1 is a list of pure water and relative permittivity values for liquids at 20.0 °C.<sup>12,13</sup> For example, water is highly polar having a relative permittivity value of 80.2 while hexane is non-polar having a dielectric constant of 1.89.<sup>13</sup>

Table 1. Relative permittivity of pure water and solvents at 20.0 °C<sup>12,13</sup>

<b>Solvent</b>	<b>Relative permittivity</b>
Water	80.20
Methanol	32.35
Ethanol	25.00
n-propanol	20.81
Isopropanol	18.62
Acetone	19.56
Hexane	1.890

#### Temperature and Relative Permittivity

Temperature is a factor that dramatically affects the relative permittivity of a solvent. In general, the dielectric constant for a pure solvent is inversely related to temperature.<sup>13,14</sup> This is due to molecules having more random thermal motion as temperature increases meaning molecules are less aligned in an applied electric field causing relative permittivity to decrease.<sup>12</sup> Table 2 shows the relative permittivity values of pure water listed in the CRC Handbook of Chemistry and Physics. This data is from the work of Malmberg and Maryott which used an equal ratio arm and capacitance-conductance bridge operated at frequencies below 100 kilocycles per second to measure relative permittivity values of pure water over the temperature range 0.00 to 100.0 °C.<sup>14,15</sup>

Table 2. Relative permittivity of water at different temperatures listed in the CRC Handbook<sup>13,15</sup>

T(°C)	Relative Permittivity
10.0	83.96
20.0	80.20
30.0	76.60
40.0	73.17
50.0	69.88
60.0	66.73
70.0	63.73
80.0	60.86
90.0	58.12
100.0	55.51

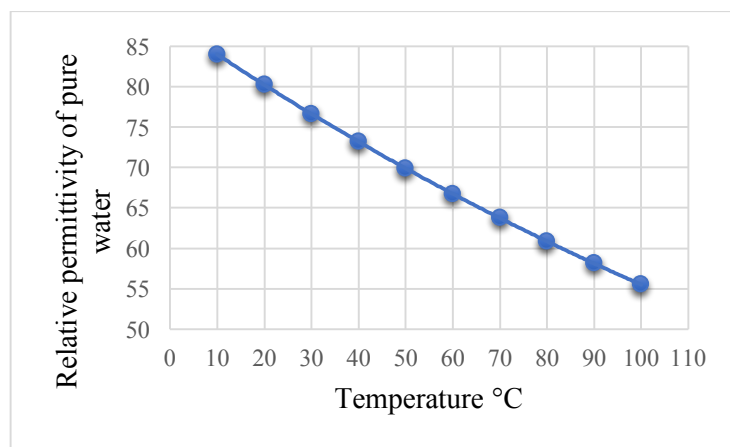


Figure 1. Relative permittivity values of pure water and temperature fit to a cubic polynomial using Malberg and Maryott's data<sup>13,15</sup>

The data collected by Malmberg and Maryott plotted in Figure 1 was fit to a polynomial because the slope of permittivity and temperature decreases at higher temperatures.<sup>14</sup> The general polynomial is:

$$\varepsilon = a + bX + cX^2 + dX^3 \quad (1.1)$$



In this equation, X can be temperature or mole fraction of a co-solvent in water. Linear regression of the data provides the coefficients of the polynomial (a-d) and these values are given in equation (1.2).<sup>14</sup>

$$\varepsilon = 87.74 - 0.4008t + 9.398(10^{-4})t^2 - 1.41(10^{-6})t^3 \quad (1.2)^{14}$$

Equation (1.2) can be used to calculate the relative permittivity of pure water over a temperature range of 0.00 to 100.0 °C. Today, there are simple instruments, such as Brookhaven Instruments BI 870 dielectric constant meter, available to measure relative permittivity values of water co-solvent solutions with reasonable accuracy. The BI 870 was used to measure relative permittivity of pure water. Comparing experimental coefficients to those in equation (1.2) offers a method to validate the technique of measuring relative permittivity of water co-solvent systems.

#### Relative Permittivity Measurements of Water Co-Solvent Systems

Co-solvent systems for reactions are of interest and relative permittivity values of these mixtures are needed.<sup>16</sup> An example is measurement of the relative permittivity of water and methanol, ethanol and propanol as co-solvent solutions using developed microwave frequencies.<sup>16</sup> Yet another example is use of dielectric relaxation spectroscopy which was used to measure aqueous solutions of 1,4-dioxane.<sup>17</sup>

#### Relative Permittivity and Ionic Strength

In 1948, Hasted et al. were the first scientists who studied dielectric properties of aqueous solutions of salts.<sup>10</sup> Their experiment demonstrated that the relative permittivity of a solution decreases when the salt concentration increases which is called dielectric decrement. The reason behind the inverse relationship between the relative permittivity and the salt concentration is the local electric field created by electrostatic interaction between ions and an external applied

field.<sup>18</sup> Polar molecules in water create a local ionic field around them, which generates a hydration shell around them. This lowers the sensitivity of water molecules to the external field, which decreases the relative permittivity.<sup>10,18</sup> The relative permittivity of salt concentrations is linear up to 1.5 M. Equation (1.3) shows this relationship.<sup>10</sup>

$$\varepsilon = \varepsilon_{\omega} - \alpha c \quad (1.3)$$

Where  $\varepsilon$  is the dielectric constant,  $\varepsilon_{\omega}$  is the dielectric constant of pure water,  $c$  is the concentration of salt and  $\alpha$  is the total excess polarization of the ionic species. This equation is not valid for salt concentrations higher than 1.5 M most likely due to ionic strength having a greater effect on the degree of excess polarization.<sup>10</sup> Gavish and Promislow developed equation (1.4) for salt concentrations greater than 1.5 M.<sup>10</sup> The equation presumes that the presence of ions causes a local electric field to develop.<sup>10</sup>

$$\varepsilon(c) = \varepsilon_{\omega} - \beta L \left( \frac{3\alpha}{\beta} c \right) \quad (1.4)$$

Where  $\varepsilon(c)$  is the dielectric constant as a function of salt concentration  $c$ ,  $\varepsilon_{\omega}$  is the dielectric constant of pure solvent,  $\alpha$  is the total excess polarization of the ions,  $\beta$  is the relative difference between an effective ion-pair dipole moment and the water dipole moment, and  $L$  is the Langevin function which can be determined using equation (1.5).<sup>10</sup>

$$L(v) = \coth(v) - \frac{1}{v} \quad (1.5)$$

Equation (1.4) provides means of determining the dielectric constant with a high degree of accuracy for concentrations of salts. Figure 2 shows a comparison of experimental relative permittivity values fit to equation (1.4) on the left and with calculated values (in color) on the right.<sup>10,19</sup>

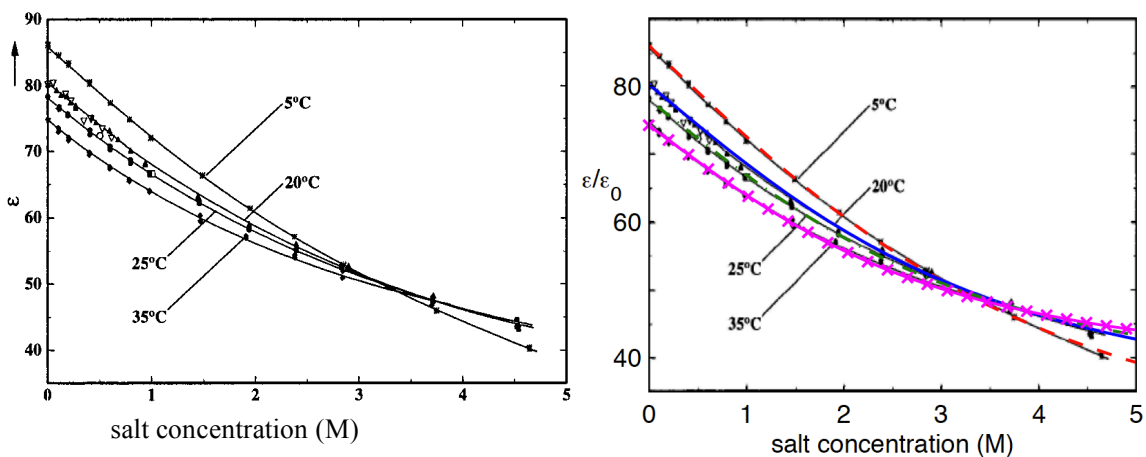


Figure 2. Experimentally fit relative permittivity values (left) and calculated relative permittivity values (right) of different molar NaCl solutions and temperature using equation (1.4)<sup>10,19</sup>

Plots in Figure 2 fit to equation (1.4) result in values of  $\alpha$  and  $\beta$  at different temperature listed in Table 3.<sup>10</sup>

Table 3. Values for  $\alpha$  and  $\beta$  and legend for each temperature in Figure 2

T(°C)	$\alpha$	$\beta$	Legend
5.00	13.7	70.25	(- -)
20.0	12.0	52.94	(--)
25.0	11.5	47.91	(.-.)
35.0	10.7	40.12	(-x)

In this work, using the BI 870 of solutions with ions caused current to flow interfering with the method of measurement. However, the probe attached to an electrochemical workstation permitted electrochemical impedance measurements to quantify ions in solution.

### Electrochemical Impedance Spectroscopy

Impedance spectroscopy (also referred to as electrochemical impedance spectroscopy, EIS) is an electrochemical technique that measures a current-voltage response.<sup>20,21</sup> Experimentally, impedance spectroscopy is performed by applying a constant initial voltage. A sine wave potential of different frequencies is superimposed on the base potential. Both current

and potential are measured to obtain the real and imaginary impedance values. It is also a method where an impedance of cell is plotted against the frequency.<sup>22</sup> This spectroscopy method provides valuable electrical information including charge transfer and electrical properties of reactions and materials.<sup>23</sup> Equation (1.6) shows how to determine impedance for resistor and capacitor in parallel.<sup>24</sup>

$$\vec{Z} = \frac{R_1}{(1+j2\pi f R_1 C_1)} \quad (1.6)$$

This results in impedance having a real ( $Z'$ ) and imaginary ( $Z''$ ) component in units of ohms. A plot of these two values results in a Nyquist plot shown in Figure 3.<sup>25</sup>

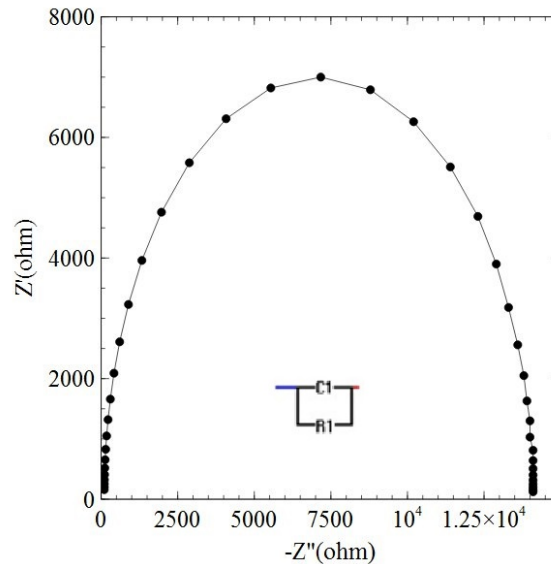


Figure 3. Nyquist plot of the real ( $Z'$ ) and imaginary ( $Z''$ ) component of impedance for a capacitor and resistor in parallel using sample data from EIS Spectrum Analyzer Software<sup>25</sup>

Impedance, denoted as  $Z$ , is the expression or measure of the ability of an electric circuit or any other electronic component to resist the flow of electric current. Impedance is a circuit element that is represented by two scalar quantities, resistance and reactance.<sup>26</sup> In this case, impedance is more of a resistance phenomenon where the resistance is the ability of the circuit to

resist the flow of an electrical current.<sup>26</sup> The reactance is the non-resistive component of impedance in AC circuit. In this work, the real impedance is the most useful value, which is the diameter of the semi-circle.<sup>23</sup> This value is obtained by fitting the Nyquist plot to a model electrical circuit, in which the solution being measured is represented by a capacitor and resistor in parallel. Electrochemical impedance software is open source which fits the Nyquist plot. The result is a regression fit providing the capacitance and real impedance and error of the experimentally measured solution.

### Current Applications of EIS

Applications of EIS include the study of metal corrosion, adsorption and desorption on an electrode surface, discharge and charging batteries and ion mobility in batteries and super-capacitors.<sup>27</sup> Measurements obtained by Electrochemical impedance spectroscopy used with coaxial-like electrodes functioned as a sensor.<sup>28</sup> The sensor was used in frequency range between 20 Hz to 2 MHz for specific electrolyte solutions having low conductivity to determine electrical properties. The sensor was most efficient for solutions not less than 0.05 mM for potassium and sodium chloride.<sup>28</sup> Also, the method most comparable to this work involved two stainless steel parallel plates used to investigate dilute solutions of lithium chloride.<sup>29</sup> This technique was used to measure the lithium chloride solutions over a frequency range of 1 kHz to 13 MHz. However, no detection limit was reported. Heavy metals including mercury ions have been determined with a detection limit of 10 ppt using Electrochemical impedance spectroscopy.<sup>30,31</sup> To achieve this low detection limit Zhang and his team developed an extremely sensitive and selective DNA biosensor using a gold electrode and sulfhydryl groups to determine the mercury ions using EIS.<sup>31</sup> Another example is a DNA biosensor made of an electrode modified with polyaniline and gold nanoparticles for silver ions with a detection limit of 10 fM using EIS.<sup>32</sup> In addition, EIS is

also used to study friction processes in industries and automobiles applied to electrochemical reactions in fuel cells, capacitors, resistors and inductors.<sup>27</sup> Others use EIS for studying catalytic reaction kinetics. Additionally, impedance spectroscopy can be used to study solutions of low ionic strength. Impedance measurements are also temperature dependent.<sup>33</sup>

### Resistivity and Impedance of Pure Water and Ions in Solutions

Increasing temperature of pure water increases its conductivity due to the concentration of hydronium and hydroxide ions increasing with temperature.<sup>34</sup> Resistivity measures the ability of pure water to resist electric current, which is the inverse of conductivity. Generally, pure water is a poor conductor of electric current or rather an insulator. However, not even “de-ionized” water is completely free of ions. This is due to water being in equilibrium with hydroxide and hydronium ions. Therefore, the resistivity of pure water is dependent on the sum of concentration and ion specific conductivity of each ion present. The resistivity of pure water can be calculated using equation (1.7).<sup>33</sup>

$$\rho_{H_2O}^{-1} = 10^{-3} d (\lambda_{H^+} + \lambda_{OH^-}) \sqrt{K_w} \quad (1.7)$$

where  $\rho_{H_2O}$  is the resistivity of pure water in  $\Omega \cdot \text{cm}$ ,  $\lambda_{H^+}$  and  $\lambda_{OH^-}$  are specific ion conductivities which are 349.19 and 199.18  $\text{S} \cdot \text{cm}^2/\text{mole}$  respectively at 25.0 °C,  $d$  is specific gravity and  $K_w$  is the equilibrium constant of water, which is  $1.00 \times 10^{-14}$  at 25.0 °C. The square root of  $K_w$  results in the concentration for each ion being  $1.00 \times 10^{-7} \text{ M}$ .<sup>33,35</sup> Using these values, the resistivity of pure water is 18.2  $\text{M}\Omega \cdot \text{cm}$  at 25.0 °C. Knowing the resistivity, the real impedance can be calculated with the area and thickness of sample being measured given in equation (1.8).<sup>36</sup>

$$Z_{re} = \frac{\rho l}{A} \quad (1.8)$$

Where  $l$  is the thickness of sample between the electrodes in cm and  $A$  is the contact area in  $\text{cm}^2$ . Different ionic solutions have different impedance values due to different quantities, types and charges. In some cases, solution impedance can only be determined from EIS spectra. Water with high concentrations of ions has a lower impedance.<sup>37</sup> This relationship exists due to the solution being a better conductor because of a greater amount of ions in solution.

## CHAPTER 2

### EXPERIMENTAL

#### Materials and Equipment

All chemicals were used as received from the manufacturer. Sodium chloride, sodium bicarbonate, potassium carbonate, sodium acetate and sodium sulfate were obtained from Fisher Scientific. A Millipore Direct Q UV3 purifier system generated 18.2 M $\Omega$ ·cm water used to prepare and measure all solutions. A Vernier temperature probe was used to monitor temperature. A BI 870 dielectric constant meter and probe from Brookhaven Instruments was used for relative permittivity measurements. The probe consisted of outer and inner stainless-steel cylinders separated by Teflon posts shown in Figure 4.



Figure 4. Stainless-steel probe from BI 870 dielectric meter also used for impedance measurements

The CHI 604E was used for electrochemical impedance spectroscopy. The probe connected to a CHI 604E electrochemical workstation using the reference and working electrode leads was used for impedance spectroscopy measurements of the solutions. The data generated a



Nyquist plot, which was fit using EIS Spectrum Analyzer Software to obtain the real impedance and error.

### Relative Permittivity Measurements

The BI 870 measured the relative permittivity of aqueous co-solvent solutions. This instrument has a relative error of 2.0%. The measured signal is a sine wave that is 10 kHz with an amplitude of 0.7 V. All solutions were prepared using 18.2 M $\Omega$  water prepared by starting with tap water treated by Culligan® systems followed by a Millipore Direct Q UV3 system. Ultrapure water, 40 ml, was put in a cylindrical glass cell provided with the BI 870. The solution was stirred ensuring homogeneity. A Vernier temperature probe was positioned in the middle of the probe's cylinders. To increase temperature a water bath with ice was used on a hotplate. Once the temperature of the solution to be measured dropped to less than 15.0 °C, the hot plate was turned on maintaining a heating rate of 1.0 °C/minute from 15.0 to 55.0 °C. The relative permittivity values were recorded every 5.0 °C. To validate the method pure water was measured and compared to known values discussed previously. To further validate the method, water and acetone co-solvent solutions were measured from 15.0 to 55.0 °C. The water mole fraction ranged from 0.3 to 1.0.

### Impedance Methods

The BI 870 probe was connected to the CHI 604 E workstation to obtain impedance measurements of pure water.

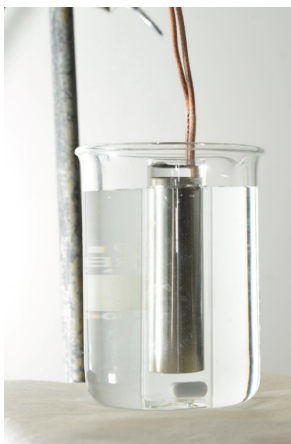


Figure 5. The water bath, probe and leads of the BI 870 probe for impedance measurements

Figure 5 shows the experimental setup. A Vernier temperature probe was above the stainless-steel probe to monitor the solution's temperature. An AC impedance used an initial applied potential of 0.2 V and sine amplitude of 0.1 V over a temperature range from 25.0 to 60.0 °C. Real and imaginary impedance data was collected over a frequency range from 1 to 100 kHz. Each spectrum was imported as a text file into EIS Spectrum Analyzer Software to fit the Nyquist plot providing real impedance, capacitance and respective errors of the solution represented as a resistor and capacitor in parallel configuration.

The same procedure was used for solutions of low ionic strength ranging from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-9}$  M. A stock solution of  $1.0 \times 10^{-4}$  M was prepared and serial dilution resulted in standards for measurement. This included solutions of sodium chloride, 5.844 ppm to 58.44 ppt, sodium bicarbonate, 8.400 ppm to 84.00 ppt, potassium carbonate, 13.82 ppm to 138.21 ppt, sodium acetate 8.203 ppm to 82.03 ppt and sodium sulfate, 14.20 ppm to 142.04 ppt. To determine the effect of 1:1 compared to 2:1 electrolytes solutions  $1.0 \times 10^{-5}$  M solutions of sodium chloride, sodium acetate, sodium bicarbonate, potassium carbonate and sodium sulfate were measured at 25.0 °C.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### Relative Permittivity of Pure Water

Table 4 lists relative permittivity values experimentally obtained using the BI 870 for pure water at different temperatures.

Table 4. Relative permittivity of pure water vs temperature

Temperature °C	Relative permittivity
15.0	80.9
20.0	79.7
25.0	78.5
30.0	77.2
35.0	76.0
40.0	74.8
45.0	73.5
50.0	72.2
55.0	70.9

A plot of the values in Table 4 is shown in Figure 6.

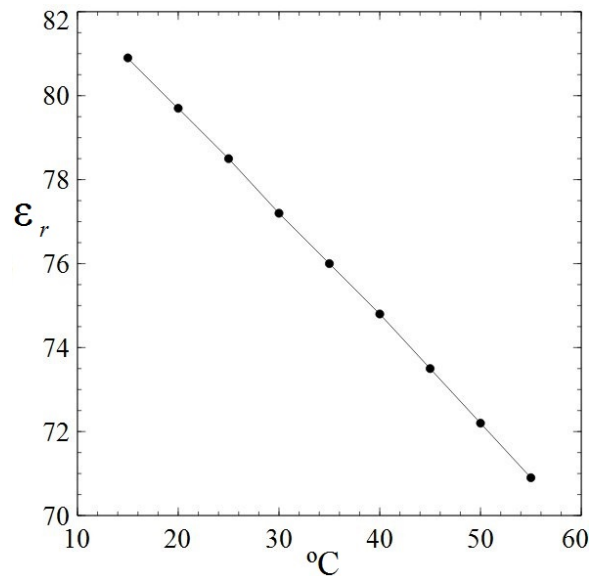


Figure 6. Experimental relative permittivity values of pure water as a function of temperature fit to a cubic polynomial

The data was fit to a cubic polynomial given in equation (1.1) in which  $X$  is temperature and compared to the work by Malmberg and Maryott. The cubic polynomial coefficients of the experimental data for pure water using the BI 870 is given in equation (3.1).

$$\varepsilon_s = 84.6(\pm 0.2) - 0.25(\pm 0.2)t + 3.6(\pm 5.9) \times 10^{-4}t^2 - 6.1(\pm 5.6) \times 10^{-6}t^3 \quad (3.1)$$

The coefficients obtained by Malmberg and Maryott are given in equation (3.2).<sup>14,38</sup>

$$\varepsilon = 87.74 - 0.4008t + 9.938 \times 10^{-4}t^2 - 1.41 \times 10^{-6}t^3 \quad (3.2)$$

The first term in equations (3.2) and (3.3) is a constant and differ by 3.6%. The remaining coefficients agree within error. The measured relative permittivity at 25.0 °C should be 79.3 according to Brookhaven instruments.<sup>39</sup> From equations (3.1) and (3.2) the relative permittivity is 78.4 and 78.3 respectively. This is a 0.1 % difference and within the 2.0 % absolute error of the instrument. Another example agreeing with this result is the reported value of pure water being 78.33.<sup>40</sup> As a result, the method of measuring relative permittivity values using the BI 870 is valid. The polynomial coefficients permit calculating the relative permittivity of pure water as a function of temperature.

#### Relative Permittivity Using Acetone as a Co-Solvent

Solutions of different mole fractions of acetone were prepared and measured using the same procedure as pure water. As expected, the measured relative permittivity decreased with increasing temperature and using lower mole fractions of water. Tables 9 through 15 in Appendix 1 provide relative permittivity values as a function of mole fraction of acetone in water from 15.0 to 55.0 °C. Figure 7 shows a plot of relative permittivity measurements as a function of mole fraction and temperature.

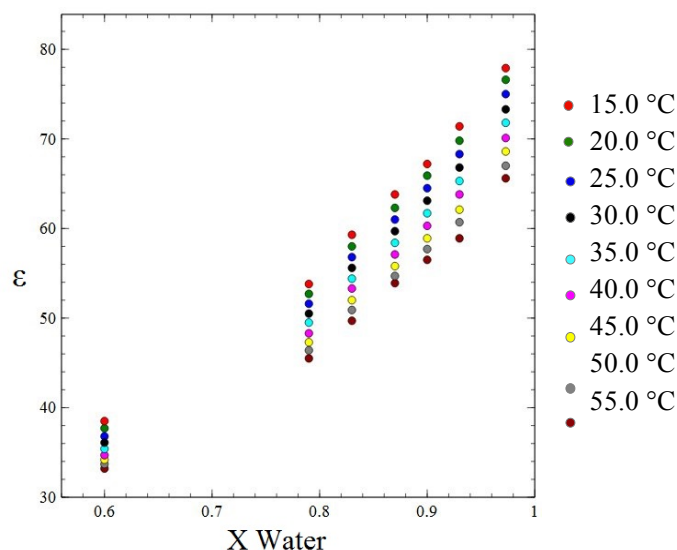


Figure 7. Plots of relative permittivity for water with acetone as a co-solvent system from 15.0 °C (red top) to 55.0 °C (dark red bottom)

These values were fit to the cubic polynomial expression given in equation (1.1) where  $X$  is mole fraction of water. Table 5 lists the cubic polynomial coefficients. These coefficients allow calculating relative permittivity as a function of mole fraction. The overall error in the temperature and mole fraction of water used was  $\pm 0.22$  °C and  $\pm 0.001$  respectively. The  $R^2$  values for all plots fit a cubic polynomial and are all higher than 0.995.

Table 5. Polynomial coefficients a-d of relative permittivity of acetone in water using mole fraction

T (°C)	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	$R^2$
15.0	18.8	23.8	-17.8	56.8	0.9997
20.0	17.4	29.9	-30.8	63.7	0.9998
25.0	16.2	33.9	-39.0	67.7	0.9998
30.0	15.0	38.7	-47.9	71.6	0.9999
35.0	13.9	43.2	-57.2	76.0	0.9999
40.0	12.8	47.0	-64.8	79.4	0.9998
45.0	10.9	56.3	-81.6	87.3	0.9997
50.0	9.9	59.6	-86.7	88.7	0.9996
55.0	9.1	61.4	-89.5	88.9	0.9985

Literature data of relative permittivity values for acetone in water results in a dielectric constant of 45.8 for a water mole fraction of 0.75 at 30.0 °C, which is only 2.18 % higher compared to 47.2 in this work.<sup>12</sup> As mentioned earlier, the relative error of the instrument is 2-10 % for binary solvent systems according to Brookhaven Instruments, meaning these values are identical within error.<sup>39</sup>

Solutions of different mole fractions of tetrahydrofuran were prepared and measured using the same procedure. Tables 16-21 in Appendix 2 provide relative permittivity values as a function of mole fraction tetrahydrofuran in water and temperature. Appendix 3 contains tables of the cubic polynomial coefficients determined following the same procedure using acetone as a co-solvent. Literature data was used to fit and determine the coefficients for methanol, ethanol, isopropanol, acetonitrile, N,N-dimethylformamide (DMF) and 1,4-dioxane.<sup>12,40-42</sup>

#### Trends Among the Polynomial Coefficients

The coefficients a-d and temperature for acetone as a co-solvent is plotted in Figure 8.

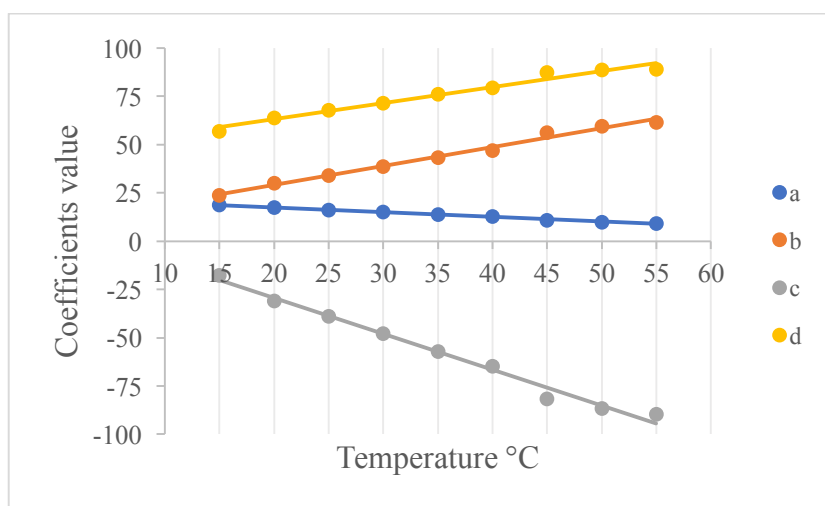


Figure 8. Plot of coefficients a-d for acetone co-solvent systems and temperature

Interestingly, for acetone in water over all temperatures measured coefficient a is positive while c is negative and both decrease with increasing temperature. Coefficients b and d are both positive and increase with temperature. Comparison of Tables 22-29 show that these trends for the polynomial coefficients vary widely and are dependent on the co-solvent present. Overall, the polynomial coefficients result in relative permittivity values decreasing as temperature increases for all water co-solvent systems measured. One possibility is that the change in polynomial coefficients with increasing temperature represent a measure of the change in dipole moment which results in decreasing alignment in an electric field which causes the relative permittivity to decrease.<sup>12,43</sup> Relative permittivity measurements of salt solutions using the BI 870 was attempted. However, the instrument is only accurate for solutions with a conductivity lower than or equal to 10  $\mu\text{S}/\text{cm}$ .<sup>39</sup> As a result, the probe of the BI 870 was used for EIS measurements to determine the real impedance of pure water and solutions of low ionic strength. The detection limit and effect of 1:1 and 2:1 electrolytes were explored.

#### Impedance of Pure Water as a Function of Temperature

EIS experiments of pure water from 25.0 to 60.0 °C generated Nyquist plots shown in Figure 9. EIS software analyzer fit the real and imaginary impedance to determine the real resistance and capacitance of the solution.

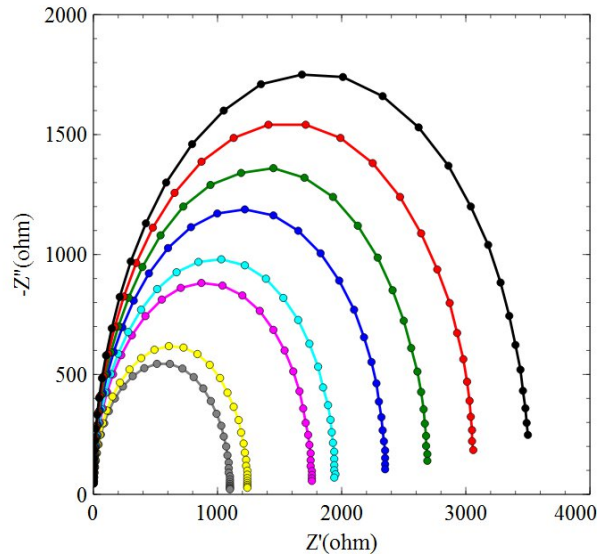


Figure 9. Nyquist plots for pure water from 25.0 °C (black curve) to 60.0 °C (gray curve)

The diameter of the semi-circle is the value of real impedance. Appendix 4 lists the real impedance values and error for pure water as function of temperature from 25.0 to 60.0 °C. A plot of these values is shown in Figure 10.

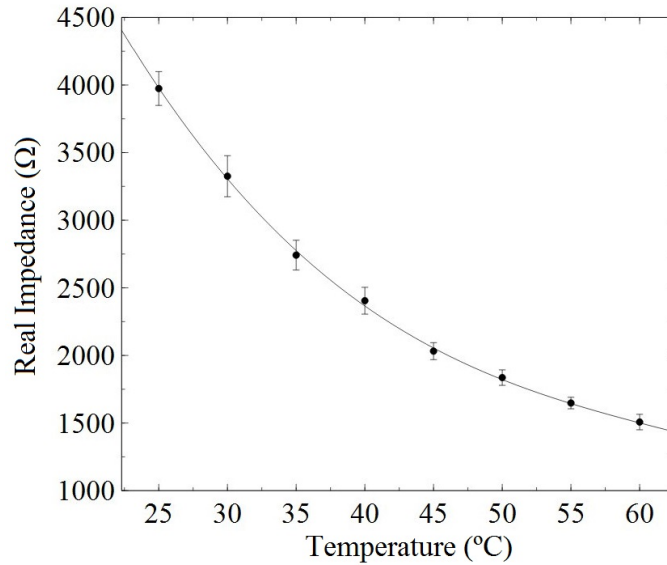


Figure 10. Real impedance as function of temperature for pure water



The polynomial equation for fitting the plot in Figure 10 results in coefficients provided in equation (3.3):

$$Z_{re} = 10,220(\pm 250) - 370(\pm 19)T + 5.4(\pm 0.5)T^2 - 0.029(\pm 0.004)T^3 \quad (3.3)$$

Where  $Z_{re}$  is the real impedance in ( $\Omega$ ) and T is the temperature in degrees Celsius ( $^{\circ}\text{C}$ ). The polynomial fit results in a 0.9993 coefficient of determination. Due to the temperature dependence of impedance, all measurements of low ionic strength solutions were measured at 25.0  $^{\circ}\text{C}$ . The real resistance from the fit of Nyquist plots was obtained for sodium chloride, sodium bicarbonate, potassium carbonate, sodium acetate and sodium sulfate. Tables 31-35 in Appendix 5 provide the impedance values and error for ppb solutions at 25.0  $^{\circ}\text{C}$ . This data was used to calibrate the probe and EIS measurements for determining concentration of anions and detection limits.

#### Calibration and Detection Limits

The graph of real impedance in ohms versus concentration results in a logarithmic curve with excellent correlation. However, a linear relationship is desired due to the future goal of developing a simple programmable electronic circuit for converting measured real impedance to concentration. This was found to be possible by plotting real impedance and the negative natural logarithm of concentration of the ion. Figure 11 shows the calibration plot for chloride using sodium chloride solutions at 25.0  $^{\circ}\text{C}$ .

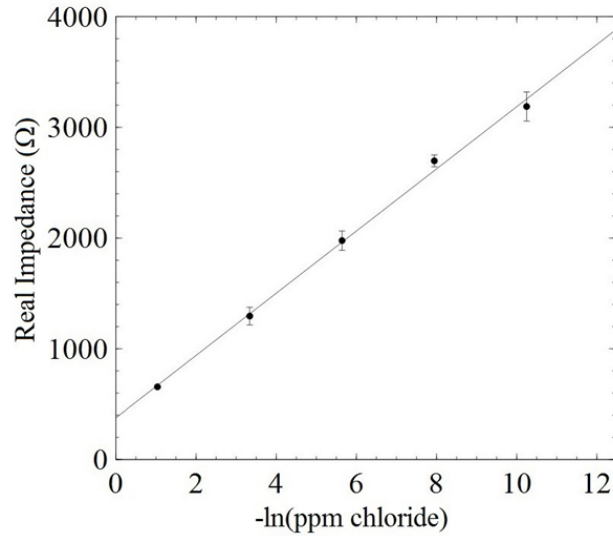


Figure 11. Real impedance and -ln ppm of chloride from sodium chloride at 25.0 °C

Using this method, all calibration plots were linear. The detection limit is defined as three times the standard deviation (3s) divided by slope (m) which results in units of concentration.<sup>44</sup> In Figure 11 low concentrations of chloride are closer to 12 and higher concentration of chloride approach zero which is opposite a normal calibration plot for signal and concentration. As such, the detection limit is found by subtracting three times the standard deviation of the impedance measurement from that of pure water and calculating concentration in units of parts per trillion (ppt). The resulting equation for the detection limit of an ion is shown in equation (3.4).

$$\text{Detection Limit in ppt} = \left[ e^{-\left(\frac{3.853\Omega - 3s}{m}\right)} \right] \frac{(1 \times 10^6 \text{ ppt})}{1 \text{ ppm}} \quad (3.4)$$

Detection limits for carbonate, bicarbonate, chloride, acetate and sulfate were calculated and given in Table 6.

Table 6. Detection limits for anion concentrations measured at 25.0 °C

<b>Ion</b>	<b>Detection Limit (ppt)</b>	<b>R<sup>2</sup></b>
Carbonate	16	0.9942
Bicarbonate	129	0.9998
Chloride	13	0.9996
Acetate	128	0.9943
Sulfate	2.0	0.9965

Using a Metrohm 761 Compact IC, detection limits for chloride are known to be 500 ppt and 30 ppt for sulfate.<sup>45</sup> Obtained detection limits are similar to ion chromatography. As such, the method of impedance spectroscopy following separation may offer a new and novel method for determining the concentration of ions.

#### Effect of 1:1 and 2:1 Electrolytes

Table 7 lists the values for the specific ion conductivities in S·cm<sup>2</sup>/mole for cations and anions considered in this work.<sup>46,47</sup>

Table 7. Specific ion conductivities values in S·cm<sup>2</sup>/mole<sup>46,47</sup>

<b>Ion</b>	<b><math>\lambda</math></b>	<b>ion</b>	<b><math>\lambda</math></b>
Sodium	50.11	Carbonate	72.0
Potassium	73.5	Sulfate	79.8
Chloride	76.35	Acetate	40.9
Bicarbonate	44.5		

Measurements of different 1:1 and 2:1 electrolytes were performed. An example of a 1:1 electrolyte is sodium chloride resulting in one sodium ion and one chloride ion. A 2:1 electrolyte is sodium sulfate. The solutions were measured at the same concentration and temperature,  $1 \times 10^{-5}$  M and 25.0 °C. For comparison to calculated impedance values, measurement of distance between the probe cylinders and surface area of the inner cylinder were required. The

measurement of area of the inner cylinder was  $27.3 \text{ cm}^2$ , and  $l$ , the distance between the inner and outer cylinder, 0.1 cm. The ratio of  $l$  and  $A$ , which is a constant, was calculated to be  $3.7 \times 10^{-3} \text{ cm}^{-1}$ . Using this value, the impedance values of salt solutions were significantly higher compared to measured values. The measured impedance of pure water at  $25.0 \text{ }^\circ\text{C}$ ,  $3,853\Omega$ , and resistivity of pure water,  $18.2 \text{ M}\Omega\cdot\text{cm}$ , resulted in ratio of  $2.1 \times 10^{-4} \text{ cm}^{-1}$ . This is significantly less than the value determined by geometric measurements. This is most likely due to inactive sites of the metal probe. The calculated impedance values were determined by first finding resistivity using equation (3.5).<sup>48</sup>

$$\rho_{MX}^{-1} = 10^{-3}d(C\lambda_{M^+} + C\lambda_{X^-}) \quad (3.5)$$

where  $\rho_{MX}$  is the resistivity of the salt in  $\Omega\cdot\text{cm}$ ,  $\lambda_{M^+}$  and  $\lambda_{X^-}$  are specific ion conductivities in for the cation and the anion in  $\text{S}\cdot\text{cm}^2/\text{mole}$  respectively at  $25.0 \text{ }^\circ\text{C}$ ,  $d$  is specific gravity and  $C$  is the concentration in molar. The calculated impedance values were found using equation (1.8) and the measured cell ratio, length over area  $\left(\frac{l}{A}\right)$ ,  $2.1 \times 10^{-4} \text{ cm}^{-1}$ . Table 8 lists the measured impedance, error, sum of specific ion conductivity and calculated impedance  $1 \times 10^{-5}$  M salt solutions.

Table 8. Experimental and calculated real impedance for  $1.0 \times 10^{-5}$  M solutions at  $25.0 \text{ }^\circ\text{C}$ <sup>35,49</sup>

Salt	Impedance ( $\Omega$ )	Error ( $\pm\Omega$ )	Calculated Impedance ( $\Omega$ )
Sodium chloride	656	23	166.85
Sodium bicarbonate	850	12	222.90
Sodium acetate	698	8	231.84
Potassium carbonate	573	31	96.347
Sodium sulfate	472	39	117.21

Table 8 shows the measured real impedance values for 1:1 and 2:1 electrolytes. All calculated impedance values are less than measured values. This is due to calculated values being based on conductivity which has units of inverse resistance. The measured values are higher due to impedance being a combination of resistance and reactance.

## CHATER 4

### CONCLUSION

The relative permittivity of pure water was determined using Brookhaven Instruments BI 870 dielectric constant meter. Results were compared to experimental relative permittivity values for water and water-acetone co-solvents system to validate the method. After method validation, the instrument was used to measure the relative permittivity of water-tetrahydrofuran co-solvent systems. A third order polynomial fit resulted in coefficients to calculate the relative permittivity as a function of temperature and mole fraction. Based on literature values, polynomial coefficients for acetonitrile, ethanol, methanol, isopropanol DMF and 1,4-dioxane co-solvents were determined. This method was attempted for ionic solutions. However, due to current induced by the BI 870 and conductivity of the solutions measurement was not possible. The probe for the BI 870 was used with the CHI 604 E Electrochemical workstation for AC impedance measurements.

Impedance of pure water as a function of temperature was measured. As the temperature increases impedance decreases and fit to third order polynomial. The same molar concentration of salt solutions were measured at 25.0 °C to compare measured impedance to calculated values based on molar conductivity. Detection limits were found to be at the ppt level. This work shows that impedance spectroscopy has detection limits are lower than ion chromatograph and similar to pulsed amperometry. This is promising as no reference electrode is required.<sup>50</sup> A stainless-steel cylinder is more robust potentially lowering the cost of detector for ions and maintenance costs. Ongoing work is developing a circuit and LCD screen to output ion concentrations in ppt. The theoretical circuit shown in Figure 12 is a model for the current circuit being tested in Figure 13.

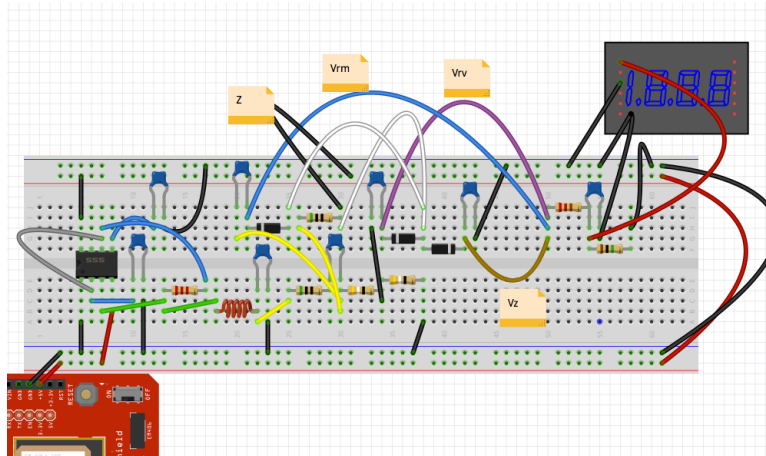


Figure 12. Theoretical circuit needed for measuring ions in solution

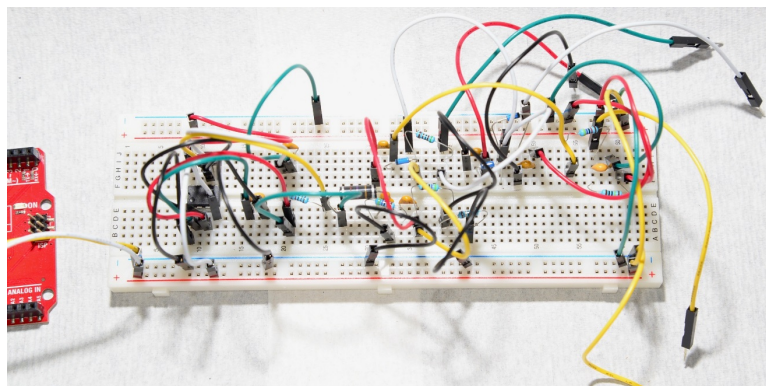


Figure 13. Current circuit development for testing

Use of this circuit to determine concentration of different ions in solution would require use of ion exchange resin for separation. Once developed, the system can be calibrated for output of concentration in ppt. This technology may find use in water quality or chemical monitoring systems.

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## APPENDICES

### APPENDIX A: Relative Permittivity Values for Mole Fractions of Acetone in Water as a Function of Temperature

Table 9. Relative permittivity of 0.60 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	38.5
20.0	37.7
25.0	36.8
30.0	36.1
35.0	35.4
40.0	34.7
45.0	34.2
50.0	33.7
55.0	33.2

Table 10. Relative permittivity of 0.21 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	53.8
20.0	52.7
25.0	51.6
30.0	50.5
35.0	49.5
40.0	48.3
45.0	47.3
50.0	46.4
55.0	45.5

Table 11. Relative permittivity of 0.17 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	59.3
20.0	58.0
25.0	56.8
30.0	55.6
35.0	54.4
40.0	53.3
45.0	52.0
50.0	50.9
55.0	49.7

Table 12. Relative permittivity of 0.13 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	63.8
20.0	62.3
25.0	61.0
30.0	59.7
35.0	58.4
40.0	57.1
45.0	55.8
50.0	54.7
55.0	53.9

Table 13. Relative permittivity of 0.10 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	67.2
20.0	65.9
25.0	64.5
30.0	63.1
35.0	61.7
40.0	60.3
45.0	58.9
50.0	57.7
55.0	56.5

Table 14. Relative permittivity of 0.07 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	71.4
20.0	69.8
25.0	68.3
30.0	66.8
35.0	65.3
40.0	63.8
45.0	62.1
50.0	60.7
55.0	58.9

Table 15. Relative permittivity of 0.027 mole fraction of acetone in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	77.9
20.0	76.6
25.0	75.0
30.0	73.3
35.0	71.8
40.0	70.1
45.0	68.6
50.0	67.0
55.0	65.6



APPENDIX B: Relative Permittivity Values for Mole Fractions of Tetrahydrofuran in Water as a  
Function of Temperature

Table 16. Relative permittivity of 0.692 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	10.2
20.0	9.8
25.0	9.5
30.0	9.2
35.0	8.9
40.0	8.7
45.0	8.4
50.0	8.2
55.0	8.0

Table 17. Relative permittivity of 0.51 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	17.4
20.0	16.9
25.0	16.5
30.0	16.1
35.0	15.7
40.0	15.3
45.0	14.9
50.0	14.6
55.0	14.3

Table 18. Relative permittivity of 0.41 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	22.3
20.0	21.6
25.0	21.0
30.0	20.5
35.0	20.0
40.0	19.5
45.0	19.1
50.0	18.7
55.0	18.4

Table 19. Relative permittivity of 0.31 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	29.6
20.0	28.6
25.0	27.8
30.0	27.1
35.0	26.7
40.0	25.8
45.0	25.4
50.0	25.3
55.0	24.8

Table 20. Relative permittivity of 0.17 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	45.5
20.0	44.6
25.0	43.4
30.0	42.4
35.0	41.5
40.0	40.7
45.0	40.0
50.0	39.3
55.0	39.0

Table 21. Relative permittivity of 0.13 mole fraction of tetrahydrofuran in water

<b>Temperature °C</b>	<b>Permittivity</b>
15.0	48.7
20.0	48.4
25.0	47.8
30.0	47.1
35.0	46.5
40.0	45.7
45.0	45.2
50.0	44.8
55.0	44.6

APPENDIX C: Polynomial Coefficients Other Aqueous Co-Solvent Systems

Table 22. Polynomial coefficients and coefficient of determination for interpolating relative permittivity of tetrahydrofuran in water

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
15.0	-26.6	208	-371	271	0.9989
20.0	-25.4	199	-358	264	0.9993
25.0	-25.5	198	-356	262	0.9995
30.0	-25.8	198	-355	259	0.9995
35.0	-25.3	193	-345	252	0.9994
40.0	-23.7	183	-328	242	0.9990
45.0	-21.5	167	-297	223	0.9982
50.0	-18.9	150	-267	205	0.9976
55.0	-14.8	124.6	-219.5	178	0.9966

Table 23. Polynomial coefficients for interpolating relative permittivity of methanol in water<sup>12</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
20.0	18.3	44.7	-16.1	23.6	1.000
30.0	26.2	42.6	-15.3	23.3	1.000
40.0	26.8	29.4	1.4	15.7	1.000
50.0	24.0	33.8	-7.15	19.3	1.000
60.0	22.7	31.5	-5.5	18.1	0.9999

Table 24. Polynomial coefficients for interpolating relative permittivity of ethanol in water<sup>12</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
20.0	24.9	21.8	-17.3	50.7	0.9999
40.0	22.1	17.3	-10.8	44.4	1.000
50.0	20.8	17.0	-12.7	44.6	0.9999
60.0	19.5	15.5	-11.2	42.6	0.9999
80.0	14.3	30.6	-39.9	55.4	0.9999

Table 25. Polynomial coefficients for interpolating relative permittivity of propanol in water<sup>12</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
20.0	20.7	26.7	-84.1	116.7	0.9998
40.0	18.1	26.3	-82.2	110.5	0.9998
50.0	16.9	26.0	-82.8	109.2	0.9998
60.0	15.7	25.3	-80.1	105.3	0.9997
80.0	13.7	23.8	-77.3	99.8	0.9997

Table 26. Polynomial coefficients for interpolating relative permittivity of isopropanol in water<sup>12</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
20.0	18.5	22.3	-71.9	111	0.9998
40.0	16.1	22.1	-70.9	105	0.9998
50.0	14.9	21.1	-67.4	101	0.9998
60.0	13.9	20.9	-66.9	98.1	0.9998
80.0	11.8	19.7	-62.3	90.9	0.9998

Table 27. Polynomial coefficients for interpolating relative permittivity of DMF in water<sup>18</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
15.0	41.6	28.3	-36.4	50.0	0.9961
25.0	40.0	3.5	41.8	-5.6	0.9978
40.0	33.7	43.8	-64.4	57.9	0.9956

Table 28. Polynomial coefficients for interpolating relative permittivity of 1,4-dioxane in water<sup>41</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
0.0	0.47	56.0	-193	222	0.9984
10.0	0.48	55.0	-190	215	0.9982
20.0	0.40	56.6	-196	217	0.9975
30.0	0.52	52.8	-182	203	0.9978
40.0	0.55	51.6	-178	196	0.9977
50.0	1.6	24.1	-87	121	0.9973
60.0	0.25	58.5	-203	211	0.9914
70.0	0.63	47.9	-166	178	0.9971
80.0	0.66	46.3	-162	173	0.9968

Table 29. Polynomial coefficients for interpolating relative permittivity of acetonitrile in water <sup>40</sup>

<b>T (°C)</b>	<b><i>a</i></b>	<b><i>b</i></b>	<b><i>c</i></b>	<b><i>d</i></b>	<b>R<sup>2</sup></b>
15.0	37.6	14.1	3.8	27.1	0.9997
20.0	36.7	15.5	0.7	27.9	0.9997
25.0	36.0	15.4	0.4	27.3	0.9998
30.0	35.2	15.0	0.9	26.0	0.9998
35.0	34.5	14.8	0.6	25.5	0.9998
40.0	33.8	15.4	-1.5	26.1	0.9998
45.0	33.1	15.2	-1.9	25.7	0.9998
50.0	32.3	14.7	-1.3	24.6	0.9998
55.0	31.7	14.5	-1.7	24.3	0.9998
60.0	31.1	13.8	-1.1	23.4	0.9998

APPENDIX D: Impedance Measurements for Pure water as a Function of Temperature

Table 30. Real impedance values ( $\Omega$ ) of pure water from 25.0 to 60.0 °C

<b>Temperature (°C)</b>	<b>Real Impedance (<math>\Omega</math>)</b>	<b>Error (<math>\pm\Omega</math>)</b>
25.0	3974	139
30.0	3326	92
35.0	2742	81
40.0	2405	71
45.0	2032	58
50.0	1836	53
55.0	1648	37
60.0	1507	33

APPENDIX E: Impedance Measurements for Salts in Aqueous Solution as a Function of  
Temperature

Table 31. The ppb amounts of prepared sodium chloride solutions and impedance determined by fitting Nyquist plots at 25.0 °C

<b>Concentration ppb</b>	<b>Impedance <math>\Omega</math></b>	<b>Error <math>\pm\Omega</math></b>
5,844	68.40	0.3
584.4	656.0	19
58.44	1,431	131
5.844	1,977	219
0.584	2,697	87

Table 32. The ppb amounts of prepared sodium bicarbonate solutions and impedance determined by fitting Nyquist plots at 25.0 °C

<b>Concentration ppb</b>	<b>Impedance <math>\Omega</math></b>	<b>Error <math>\pm\Omega</math></b>
8,400	237.0	5
840.0	850.0	103
84.00	2,177	78
8.400	2,363	52

Table 33. The ppb amounts of prepared potassium carbonate solutions and impedance determined by fitting Nyquist plots at 25.0 °C

<b>Concentration ppb</b>	<b>Impedance <math>\Omega</math></b>	<b>Error <math>\pm\Omega</math></b>
1,382	574.0	31
138.2	906.0	40
13.82	1,181	27
1.382	2,000	26
0.1382	2,695	83



Table 34. The ppb amounts of prepared sodium acetate solutions and impedance determined by fitting Nyquist plots at 25.0 °C

<b>Concentration ppb</b>	<b>Impedance <math>\Omega</math></b>	<b>Error <math>\pm\Omega</math></b>
820.3	699.0	8
82.03	1,219	21
8.203	2,203	28
0.8203	2,401	119

Table 35. The ppb amounts of prepared sodium sulfate solutions and impedance determined by fitting Nyquist plots at 25.0 °C

<b>Concentration ppb</b>	<b>Impedance <math>\Omega</math></b>	<b>Error <math>\pm\Omega</math></b>
14,204	72.00	1
1,420.4	477.0	34
142.04	1,689	89
14.204	2,165	48
1.4204	2,518	52

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