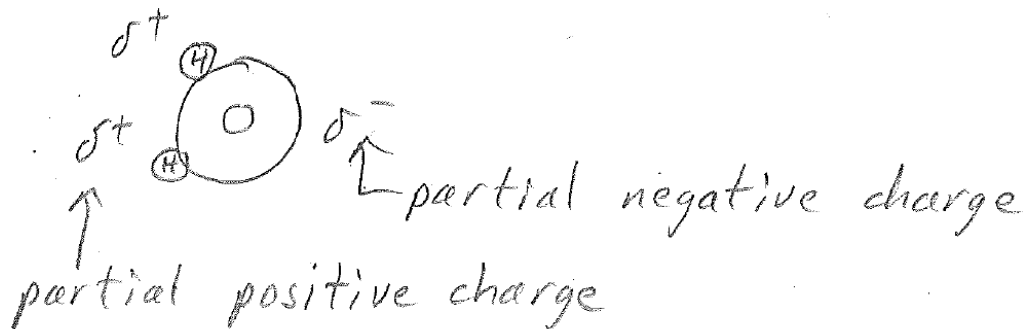


Resistive Sensing of Aqueous Solutions

1. Background

Water: H_2O → a molecule with a polar covalent bond

Physically:



Therefore, as a polar compound, H_2O has a permanent dipole, which causes ionic compounds (salts) to dissolve in it.

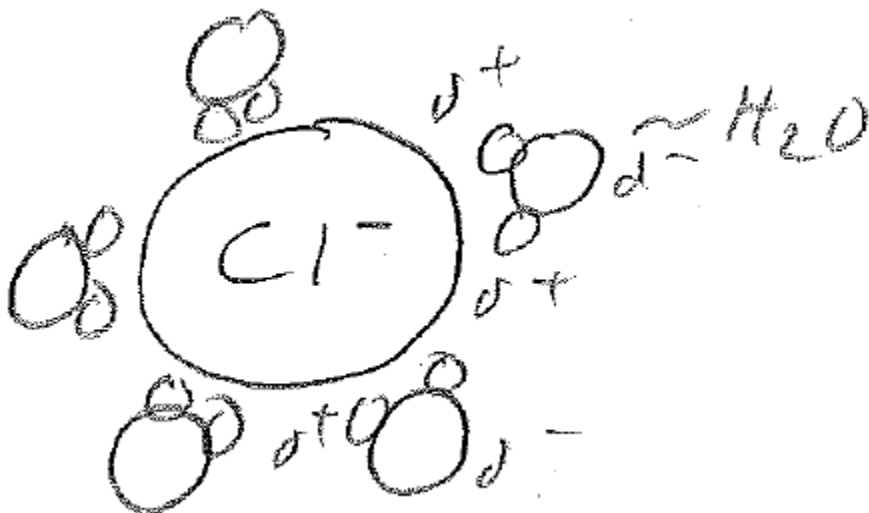
Example: table salt: $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

Na^+ is a cation and Cl^- is an anion

In water: $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

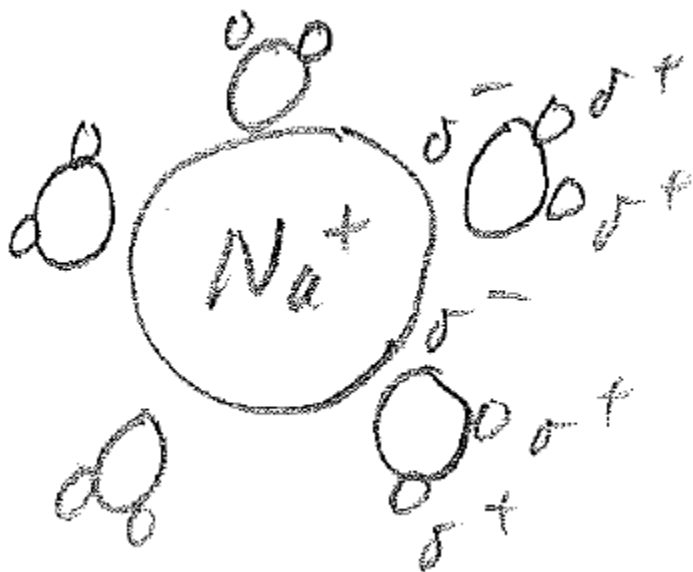
$\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ are hydrated ions

$\text{Cl}^-(\text{aq}) \rightarrow$ hydrated anion:



Observe that the partial positive charge on the H_2O molecules is drawn to the Cl^- anion in the exaggerated drawing. The resulting composite structure is called a hydration shell or a hydration sphere.

Similarly, the partial negative charge on the H_2O molecules is drawn to the Na^+ anion in the exaggerated drawing below, also forming a hydration shell. $\text{Na}^+(\text{aq}) \rightarrow$ hydrated cation:



Note: atom sizes are NOT to scale

2. Applying an electric field across the solution

$\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ act as mobile charge carriers, like electrons and holes in a semiconductor.

However, ion charge carriers are slow compared to electrons and holes. Therefore, an aqueous solution is a much lower frequency electrical system.

The higher the NaCl concentration, the higher the number of mobile charge carriers, and the higher the electrical conductivity.

The symbol for electrical conductivity is σ , the same symbol used for tensile stress in mechanical systems.

For low salt concentrations:

$\sigma \propto \text{ion concentration}$:

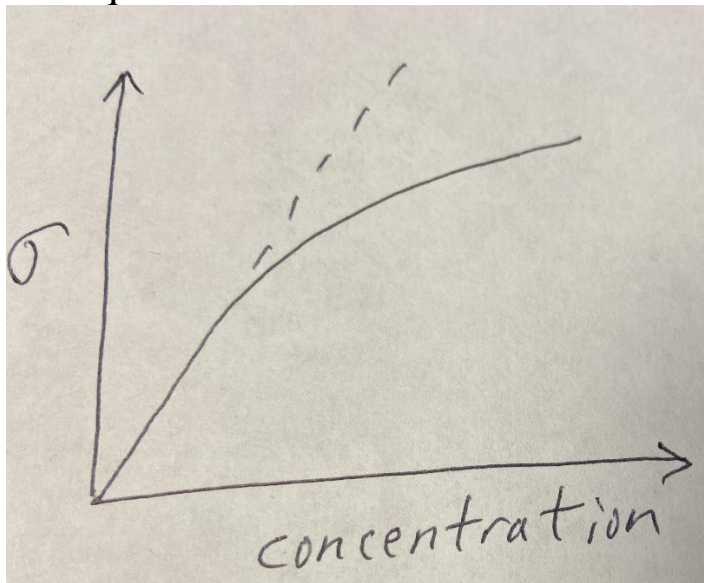
$$\sigma = \sum_{i=1}^n \lambda_i C_i$$

where: σ = solution electrical conductivity (EC)

λ_i = ionic conductivity of the i^{th} ion type

C_i = molar concentration of the i^{th} ion type

For high concentrations: ions will interact with each other, invalidating this equation:



By measuring EC, the concentration of dissolved salts can be determined.

3. Temperature effects

EC is affected by temperature nonlinearly. However, for $0^{\circ}\text{C} \leq T \leq 30^{\circ}\text{C}$, a linear model is:

$$\sigma_T = \sigma_{25}[1 + a(T - 25)]$$

Where: σ_{25} is the EC at 25°C

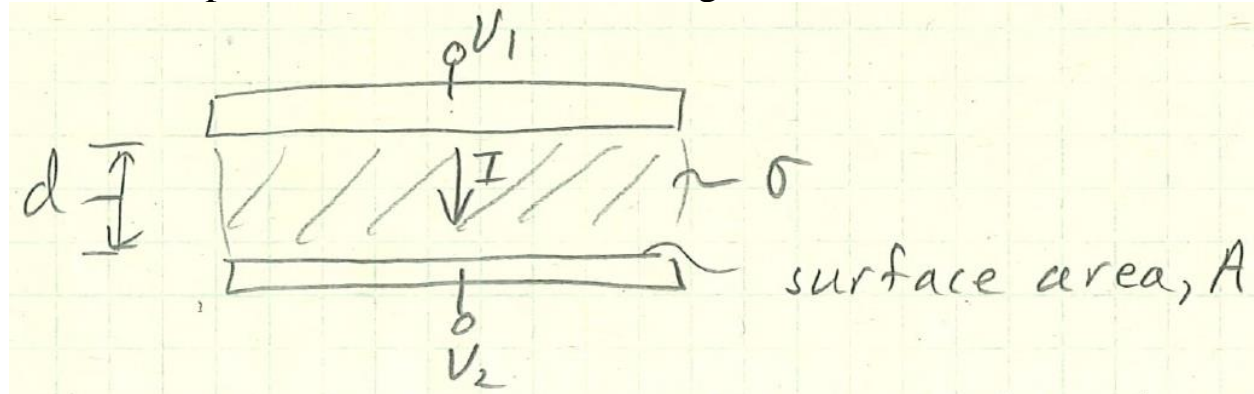
“a” is a temperature compensation factor, $[a] = 1/^{\circ}\text{C}$

Various values for “a” are found in publications: 0.0191, 0.02, 0.025, 0.0187, etc. However, all are approximately $a = 0.02$.

Often, σ_{25} is calculated and used for comparison.

4. Measuring EC of an aqueous solution

Consider 2 parallel electrodes in a homogeneous solution:



Assumptions: $A \gg d^2$, and a uniform current density

Therefore: $R = \frac{d}{\sigma A}$

Conductance: $G = \frac{1}{R} = \frac{\sigma A}{d} = \sigma \kappa$

The sensor's cell constant, κ , is a function of the sensor's geometry, and is independent of concentration or temperature.

$$[\kappa] = \text{m}$$

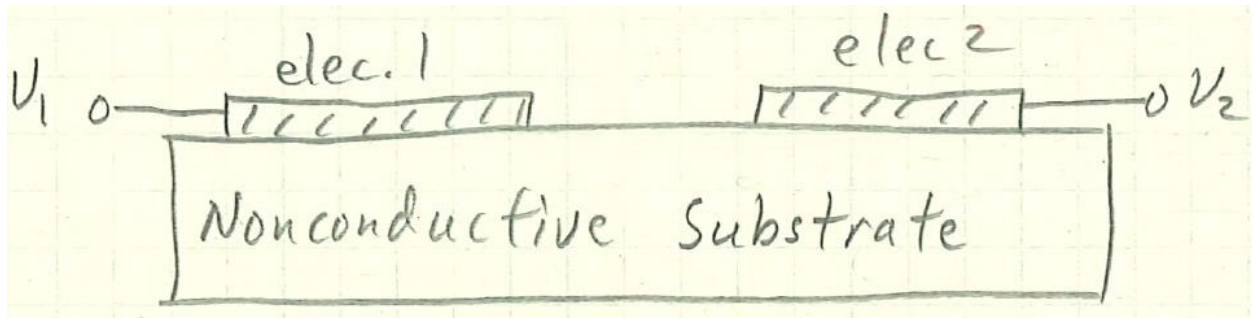
$$[G] = \text{S}$$

$$[\sigma] = \text{S/m}$$

If κ is known, you can measure G (or R) and calculate σ .

a. Flat electrode sensor

Consider:



This type of electrode structure is easy to build in MEMS or on a PCB.

However, it has a non-uniform current density. Therefore, κ is difficult to calculate.

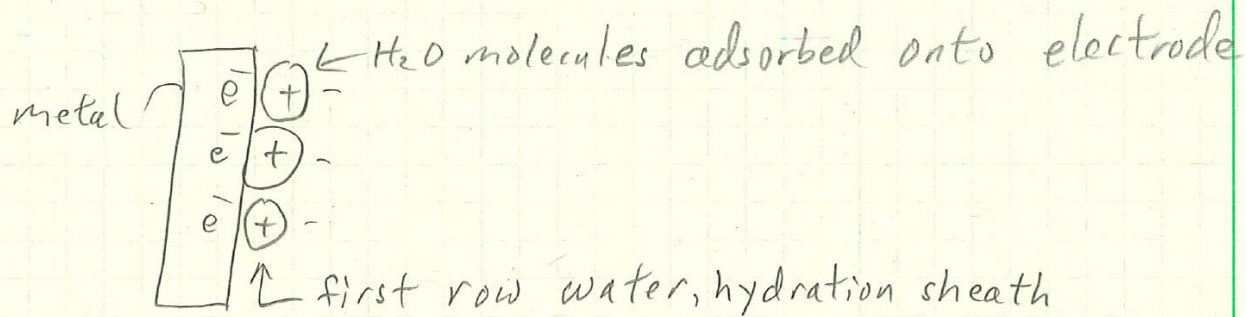
But, you can use an EC sensor of known κ and measure EC with it. Then measure G with the flat electrode sensor. Then calculate κ for the flat electrode sensor:

$$\kappa = \frac{G}{\sigma}$$

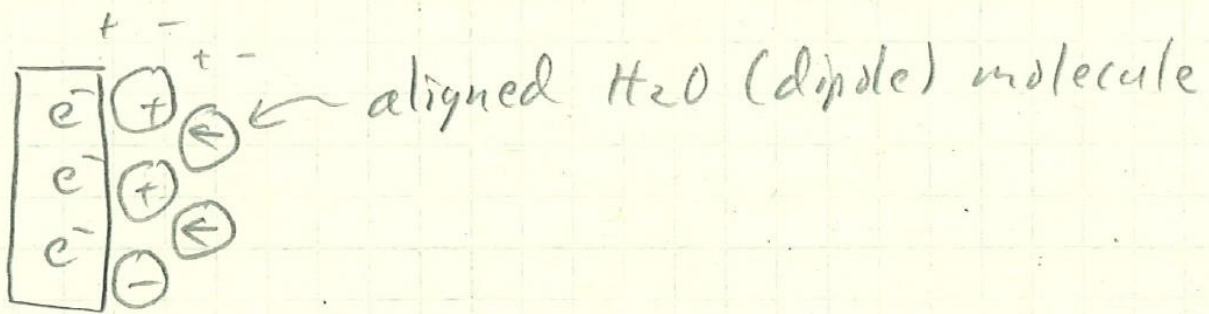
With now knowing κ for the flat electrode sensor, the sensor can be used to determine σ from any G measurement.

5. Frequency effects

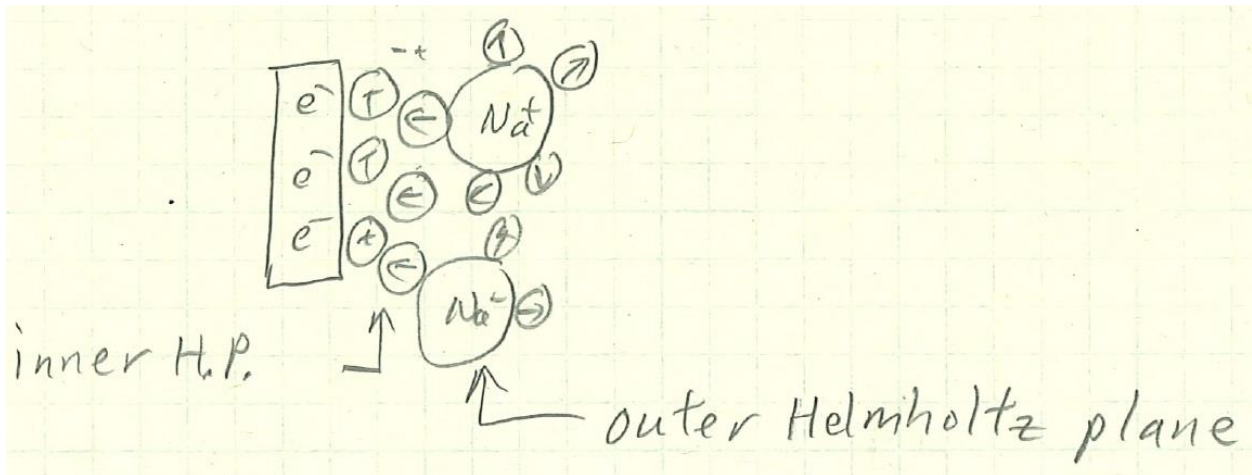
When a metal electrode is put in water, a water molecule making contact with the metal will transfer an electron to the metal, leaving the water molecule with a positive charge.



Other water molecules (dipoles) will be attracted to the H₂O molecules on the electrode, and will align with them.



Cations will be attracted to the aligned dipoles and will form hydrated cations there:

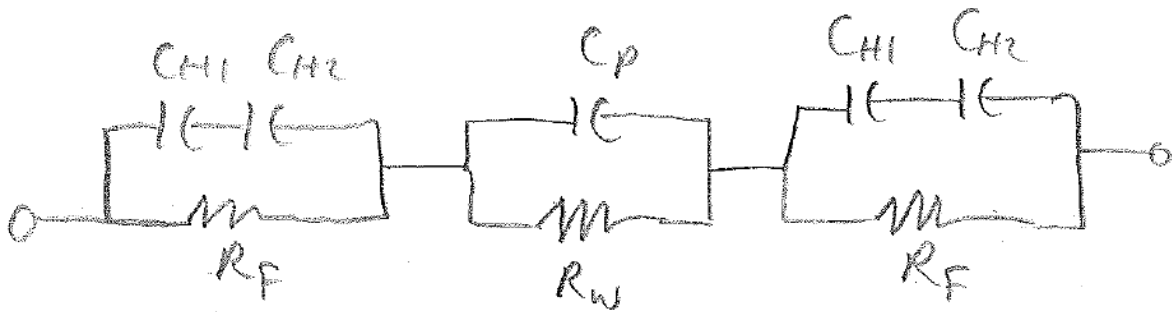


Some Na⁺ ions will also chemically bond to the metal, forming an inner Helmholtz plane.

The 2 Helmholtz planes together form the “electrical double layer,” or EDL, which is two capacitors in series (C_{H1} and C_{H2}), and in parallel with

the resistance (R_F) between the electrode and the water when a voltage is applied. The subcircuit consisting of C_{H1} , C_{H2} , and R_F is called the Faradaic impedance.

Circuit model:



$$\frac{1}{\frac{1}{C_{H1}} + \frac{1}{C_{H2}}} > C_p$$

The Faradaic impedance of the EDL results in an EC measurement error at DC and low frequencies.

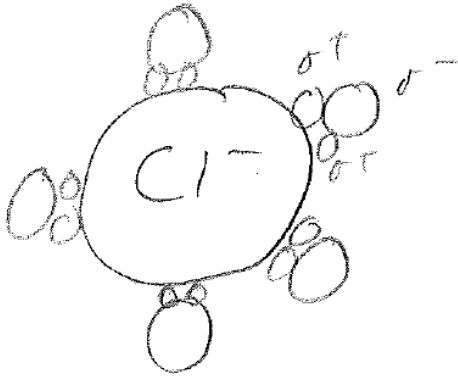
Measuring EC at a sufficiently high frequency shorts across the EDL for a more accurate EC reading.

But too high of a measurement frequency will result in shorting across the small parasitic capacitance, C_p .

Choose some measurement frequency that ~ shorts C_{H1} and C_{H2} , but not C_p . The goal is to measure R_w with the sensor. The exact frequency used depends on the sensor. With the sensors I have developed, 1 MHz seems to work well.

6. More on hydration shells

A hydrated anion:



Mechanically, a hydration shell is a SMD with a mechanical ω_n and Q .

The lower the concentration, the larger the hydration shell around each ion: the larger its mass and the lower its ω_n .

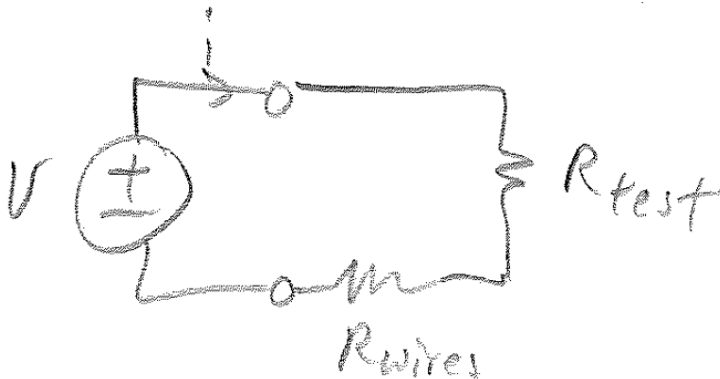
If the dipole-like hydration shell is electrically excited at its ω_n , it will vibrate. This is called relaxation and f_n is called the relaxation frequency. Electrically, the solution of hydration shells has a minimum impedance at that frequency, due to its complex permittivity.

A frequency sweep across the liquid can be performed with a network analyzer connected to an appropriate set of electrodes to detect the impedance minima. This information can sometimes be used to estimate the chemical composition and/or contaminant concentration of the aqueous solution. This is called Electrochemical Impedance Spectroscopy (EIS).

In aqueous solutions, the relaxation frequency can be quite low, in the 5 MHz to 10 MHz range.

2-Point and 4-Point Resistance Measurements

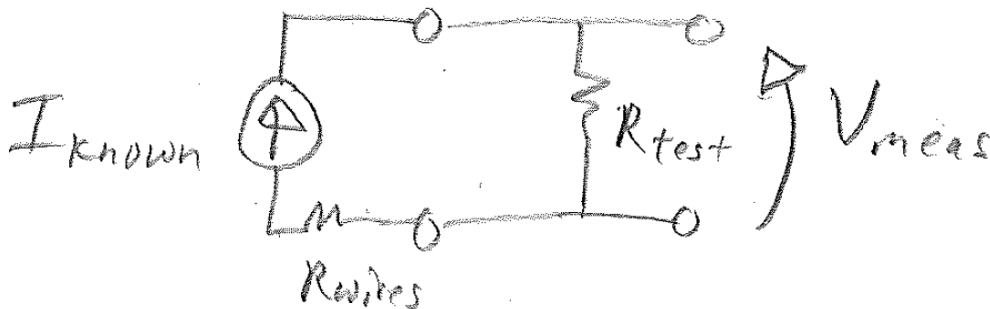
1. 2-Point Resistance Measurement



$R_{wires} \sim \text{few } \Omega$. If $R_{test} \gg R_{wires}$, then $R_{meas} = \frac{v}{i} \approx R_{test}$

However, if $R_{test} \approx R_{wires}$, then $R_{meas} = \frac{v}{i} = R_{test} + R_{wires}$, and measuring R_{meas} does not yield a good estimate for R_{test} .

2. 4-Point Resistance Measurement



Apply a known current to the resistance under test, I_{known} . Measure the voltage across R_{test} , V_{meas} , with a high impedance voltmeter. Then compute R_{meas} to determine R_{test} :

$$R_{meas} = \frac{V_{meas}}{I_{known}} = R_{test}$$

This is a more precise resistance measurement technique, but it is also more complicated.