

Bachelor's thesis

*Electrical impedance spectroscopy
of the water/nitrobenzene interface*

Kristian van Berlo

Supervisors:
Mark Vis, Msc
Dr. Ben H. Ern 

Van't Hoff Laboratory for Physical and Colloid Chemistry
Debye Institute for Nanomaterials Science
Utrecht University

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Abstract

The electrical impedance spectrum of the water/nitrobenzene interface was studied using a specially designed impedance cell. The main goal of the project was to determine the capacitance of the double layer that exist at the interface between water and nitrobenzene. The interfacial capacitance of the water/nitrobenzene interface is the ability to store electrical charge. The interface will be described by the Gouy-Chapman theory for a flat double layer. During the experiments the interfacial capacitance will be examined as a function of the area of contact between the phases and as an applied DC potential. To extract data from the impedance spectrum an equivalent circuit is fitted to the measured data. From our results, there are two clear indications that the impedance spectrum of the water/nitrobenzene was measured. First, the Warburg coefficient scales with the neck of the center part of the impedance cell. The Warburg coefficient gives information about the diffusion of the ions in the electrolyte, with an increase in area of the neck, more diffusion is possible to the interface. Second, the interfacial capacitance scale with the area of the neck and is in the same order of magnitude as expected from the theory of Gouy-Chapman, the characteristic shape however is not observed.

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1. Introduction

Emulsions are important in everyday products: milk, detergents and paint to name a few. Emulsions usually consist of a mixture of two immiscible liquids. This means that one liquid, in the form of little droplets, is dispersed in a continuous phase of the other and vice versa. When two immiscible liquids contact each other a liquid/liquid interface emerges. Usually these emulsions consist of an oil and water phase. There are indications that it is also possible to make stable emulsions without the use of oil. For example, with biopolymers such as dextran and gelatin. These biopolymers dissolve well in water, but they do not mix when they are dissolved. Figure 1 is a picture of two separated phases of dextran and gelatin [1], with in one phase a high concentration of dextran and in the other gelatin.

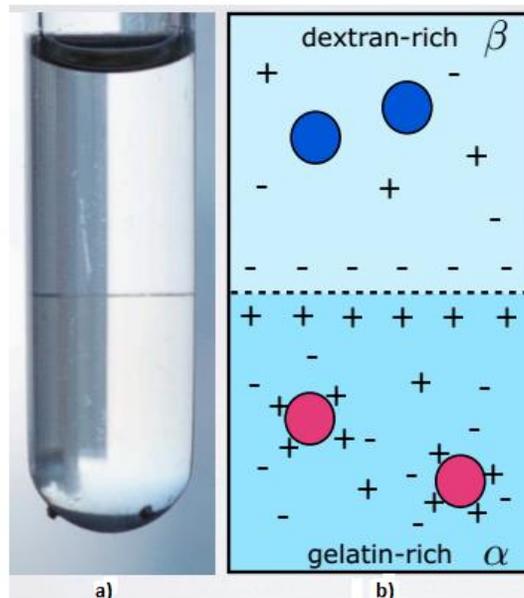


Figure 1: a) Photograph of a capillary containing a dextran-rich and gelatin-rich phase. In the center of the capillary, the interface between the two phases can be observed. In both phases the solvent is water. b) A schematic drawing of the interface and portion of the bulk. Both phases contain biopolymers (big circles) and small ions (plus and minus signs). The interface is shown as the dotted line with on both sides on the interface an accumulation of charges.

Our interest is in the electrostatic properties of such liquid/liquid interfaces. The Donnan potential is the electrical potential that arises between the interface of two immiscible liquids due to the distribution of ions [2]. Very close related to the Donnan potential is the capacitance of the interface. The capacitance of an interface is the ability to store electrical charge.

In this report we are going to explore how to measure and interpret the impedance spectrum of a liquid/liquid interface with impedance spectroscopy. The main focus is to determine the capacitance of the interface.

The system under study will consist of water/nitrobenzene. In the water phase: sodium and chloride ions are dissolved and in the nitrobenzene phase: tetraphenylarsonium (TPA) and tetraphenylborate (TPB) ions, see Figure 2.

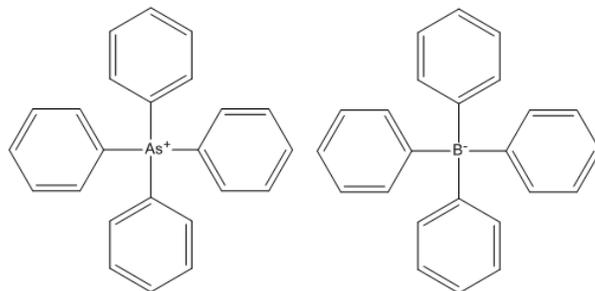


Figure 2: Structure formula of respectively tetraphenylarsonium and tetraphenylborate. These ions consists of four benzene rings with in the center respectively arsonium and borate.

In this thesis a description of the interface will be given. In addition, the concept of electrical impedance will be explained. To extract data from the impedance spectra, the data must be modeled with an equivalent circuit. The circuit elements of such an equivalent circuit will be discussed. The experimental setup will be explained and the results will be discussed and finally a conclusion and outlook will be given.

2. Liquid/liquid interface and electrolyte properties

Interfaces are places where charge can accumulate. An electrical double layer is a certain structure that appears when an interface is in contact with an electrolyte. A simplified drawing of such a structure at a liquid/liquid interface is shown in Figure 3.

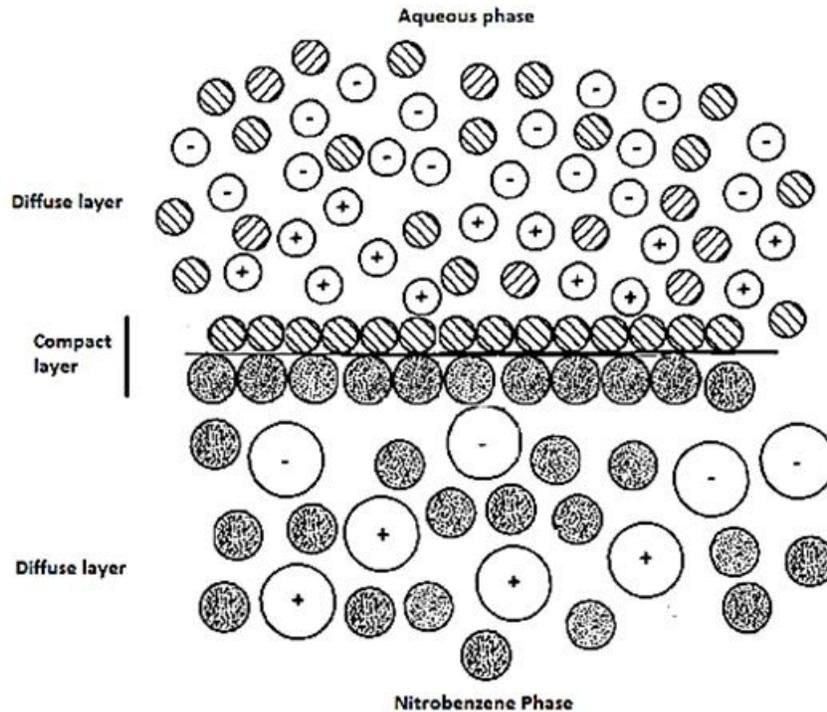


Figure 3: A schematic drawing of the interface between an aqueous and nitrobenzene phase. The shaded circles represent solvent molecules and the circles with positive or negative sign are ions. The interface consists out of two different layers: diffuse and compact layer. The diffuse layer has a parallel cloud of positive and negative ions. The compact layer consists solely out of solvent molecules.

Figure 3 shows two phases, an aqueous and nitrobenzene phase. In each phase ions are solvated, represented as circles with a positive or negative signs. The shaded circles represent solvent molecules. In our assumption of the interface, there is on each site of the interface a compact and a diffuse layer[3]. The compact layer consists purely out of solvent molecules and it is assumed to be blocked. By blocked, it is meant that there is no ion transfer from one phase to the other. In the diffuse layer there is an accumulation of charges. For example, when looking at the aqueous phase, an accumulation of positive ions is observed near the compact layer and after that a cloud of negative ions. The electrical double layer refers to the two parallel layers of ions near the interface. The capacitance of the double layer is the ability of the interface to store electrical charge [4].

The capacitance of a double layer can't be measured directly [5]. The differential capacitance however is a measurable quantity. The differential capacitance is defined as the ability to store charge in response to a perturbation in potential, see equation (2.1).

$$C = \frac{d\sigma}{d\varphi} \quad (2.1)$$

in which C is the capacitance, $d\sigma$ the change in charge density on the interface and $d\varphi$ the change of the interfacial potential.

In the next sections the theory relevant for describing the interface and the electrolyte will be discussed.

I. Gouy-Chapman theory for a flat double layer

The Gouy-Chapman theory for a flat double layer[6-7] was developed to describe the double layer at an electrode/electrolyte interface, but in literature it is shown that it describes a blocked interface rather well[8].

The basic ideas of the Gouy-Chapman theory are that the solution is modeled as point ions embedded in a dielectric continuum representing the solvent. The metal electrode is considered as a perfect conductor. This means that there is no charge transfer resistance from the electrode to the electrolyte. The distribution of the ions is calculated from electrostatic interactions and statistical mechanics. The capacitance of the double layer per area is given by equation (2.2); a derivation is given in appendix A.

$$\frac{C_{dl}}{A} = \epsilon\epsilon_0\kappa \cosh\left(\frac{F(\varphi - \varphi_{pzc})}{2RT}\right), \quad \kappa = \sqrt{\frac{\epsilon\epsilon_0 RT}{2F^2 c_0}} \quad (2.2)$$

In which C_{dl} is the capacitance of the double layer, A the area of the interface, ϵ the permittivity of the solvent, ϵ_0 the permittivity of vacuum, κ is the ion strength, F the Faradays constant, R the gas constant, T the temperature, C_0 concentration of the salt in the bulk and $(\varphi - \varphi_{pzc})$ is the potential difference between the applied potential and the potential of zero charge (pzc). The potential of zero charge is a characteristic potential for an interface and defined as the potential in which the charge density is lowest.

The Gouy-Chapman theory predicts a characteristic shape for the capacitance as function of the applied potential: a parabola that opens upward. The lowest capacitance per area is found at the potential of zero charge. At different potentials there is more charge accumulation at the interface, this results in a higher capacitance.

II. Electrolyte resistance

The electrolyte resistance is the opposition that the electrolyte presents to a current. The electrolyte resistance is defined as

$$R_{\text{electrolyte}} = \rho \frac{L}{A} \quad (2.3)$$

In equation (2.3), ρ is the specific resistance of a substance, L the length the current has to flow and A the area the current flows through. The specific resistance is heavily influence by the temperature. A one degree temperature difference can have a 5% conductance difference for KCl and NaCl solutions[9]. The conductance is defined as one over the resistance, with units in Siemens (S) which is equal to $1/\Omega$.

III. Diffusion

Diffusion is a form of mass transfer within the system. Thermodynamic forces are responsible for the spontaneous tendency of ions to disperse[10]. At constant temperature and pressure, the maximum work that can be done when an ion moves from a location with chemical potential μ to a location where the chemical potential is $\mu + d\mu$ is $dw = d\mu$. Assuming a system that only depends on x :

$$dw = d\mu = \left(\frac{\partial\mu}{\partial x}\right) \cdot dx \quad (2.4)$$

Work can always be expressed in terms of an opposing force F , so that

$$dw = -F \cdot dx \quad (2.5)$$

From equation (2.4) and (2.5) follows

$$F = -\left(\frac{\partial\mu}{\partial x}\right) \quad (2.6)$$

Equation 2.6 gives an expression for the thermodynamic force. This force can be explained as the tendency of the system to achieve maximum entropy.

In our experiments, an external potential will be applied. So, there will not only be a thermodynamic force but also an electrical force. Assuming that the potential difference $\Delta\phi$ between two electrodes a distance d , then the ions in the solutions experience an electrical field (E) of

$$E = \frac{\Delta\phi}{d} \quad (2.7)$$

In such a field, an ion of charge z experience a force of magnitude

$$\mathbf{F} = \frac{z \cdot e \cdot \Delta \phi}{d} \quad (2.8)$$

in which e is the elementary charge. When an electrical field is present, the ions in the solutions experience a force. This force can be attractive or repulsive, depending on the charge of the ions (positive or negative). The result of this electrical force is that a cation will accelerate to the negative electrode and vice versa. The magnitude of this behavior depends on the concentration, diffusion coefficients of the ions in the solvent and the applied potential.

3. Electrical impedance spectroscopy

With electrical impedance spectroscopy one studies the response of a system when a sinusoidal potential is applied[11]. These sinusoidal potential are send through the system at different AC frequencies. Electrical impedance is the opposition that a circuit presents to a current. It is a generalization of the concept of resistance to include a frequency-dependent phase and amplitude. For comparison Ohm's Law is given in equation (3.1), the resistance is defined as the ratio between the applied potential and the current through the system.

$$R = \frac{V}{I} \quad (3.1)$$

In equation (3.2) the impedance is defined as the complex ratio between the applied potential and current but as a function of the frequency. This means that the impedance can be a complex number.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} \quad (3.2)$$

In the next section the impedance of selected circuit elements will be discussed.

I. Resistor in an AC circuit

An ideal resistor is a device whose current and voltage are proportional[12]. In Figure 4 the voltage-current relation can be observed, in which $V_p \sin(\omega t)$ is the applied voltage and $I_p \sin(\omega t)$ the current response. V_p and I_p are the amplitude, ω is the angular frequency($2\pi f$) with f the frequency and t is the time.

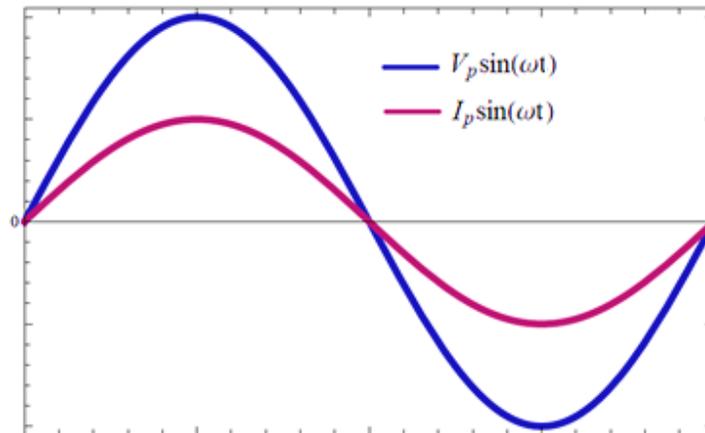


Figure 4: The voltage-current relation for a resistor in an AC circuit. The vertical axis shows the amplitude and the horizontal axis the time. When a certain potential is applied $V_p \sin(\omega t)$ the current response is given by $I_p \sin(\omega t)$.

The current has the same phase as the voltage. The impedance for a resistor is given in equation (3.3).

$$\mathbf{Z}_R(\omega) = \frac{V_p \cdot \sin(\omega \cdot t)}{I_p \cdot \sin(\omega \cdot t)} = \frac{V_p}{I_p} \quad (3.3)$$

It follows that the impedance of a resistance is independent of the frequency.

$$\mathbf{Z}_R = \frac{V_p}{I_p} = \mathbf{R} \quad (3.4)$$

II. Capacitors in AC circuits

Before an expression for the impedance can be obtained, the voltage-current relation must be known. A starting point for this is the relation between charge and voltage in a capacitor, which is given as

$$\mathbf{Q} = \mathbf{C} \cdot \mathbf{V} \quad (3.5)$$

In which the Q is the charge in coulomb, C the capacitance in Farad and V the voltage. The current is the flow of electrical charges. So, differentiation of equation (3.5) with respect to time gives

$$\mathbf{I}(t) = \mathbf{C} \cdot \frac{dV}{dt} \quad (3.6)$$

the current is shown as I(t) and the voltage is also a function of time. When a sinusoidal voltage is applied in the form of

$$\mathbf{V}(\omega) = \mathbf{V}_p \cdot \sin(\omega \cdot t) \quad (3.7)$$

in which V_p is the amplitude, ω the angular frequency and t the time. The current is then equal to

$$\begin{aligned} \mathbf{I}(t) &= \mathbf{C} \cdot \omega \cdot \mathbf{V}_p \cdot \cos(\omega \cdot t) \\ &= \mathbf{C} \cdot \omega \cdot \mathbf{V}_p \cdot \sin(\omega \cdot t + \theta_i), \quad \theta_i = \frac{1}{2}\pi \end{aligned} \quad (3.8)$$

With the expression of the current found in equation (3.8), the voltage-current relation can be shown, see Figure 5. (In Figure 5, $I_p = C \cdot \omega \cdot V_p$ and θ_i the phase difference($\frac{1}{2}\pi$))

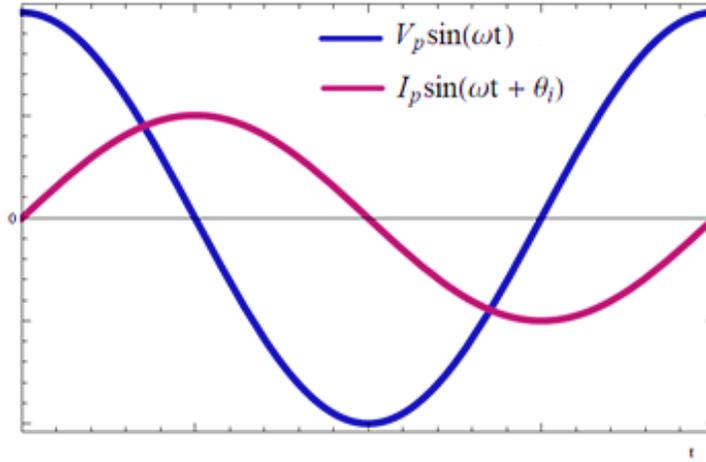


Figure 5: Voltage-current relation of a capacitor in an AC circuit. The vertical axis shows the amplitude and the horizontal axis the time. When a certain potential is applied $V_p \cdot \sin(\omega \cdot t)$ the current response is given by $I_p \cdot \sin(\omega \cdot t + \theta_i)$. The current is $\frac{1}{2} \pi$ out of phase with the voltage.

The impedance is defined as the ratio between voltage and the current, see equation (3.2). So for a capacitor:

$$Z_C(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_p \cdot \sin(\omega \cdot t)}{C \cdot \omega \cdot V_p \cdot \sin(\omega \cdot t + \frac{\pi}{2})} \quad (3.9)$$

To find a useful form of the impedance, the sinus function is rewritten as a complex exponential function [12]. The result is shown in equation (3.10). A more extended derivation is given in appendix B.

$$Z_C(\omega) = \frac{-j}{C \cdot \omega} = \frac{1}{j \cdot C \cdot \omega}, \quad j = \sqrt{-1} \quad (3.10)$$

In equation 3.10, j is the imaginary unit. The impedance of a capacitor is a function of the capacitance C and the frequency ω . From this result it can be seen that the impedance of a capacitor is low when the frequency is high and vice versa.

III. Constant phase and Warburg element

The constant phase element is a circuit element that was introduced while looking at the response of real-world systems [11]. In our case it is used to model diffusion. Equation (3.11) gives the impedance of a constant phase element.

$$Z_Q(\omega) = \frac{Q_c}{(j \omega)^n} \quad (3.11)$$

with Q_c the constant phase element coefficient, j the imaginary unit, ω the angular frequency and n an exponent between $0 \leq n \leq 1$.

The Warburg impedance is seen as a special kind of constant phase element, equation (3.11).

$$\mathbf{Z}_w(\omega) = \frac{Q_w}{\sqrt{j} \omega} \quad (3.12)$$

in which Q_w is the Warburg coefficient. For the case of the Warburg the exponent $n = 0.5$. The constant phase element and Warburg element describe the same behavior. If possible our preference will go to the Warburg element because it contains one less variable.

The constant phase element and Warburg element are difficult concepts. The basic idea is that: at high frequencies diffusion of the ions to and from the electrodes is not so important, because the currents are small and changing sign continuously. Diffusion contributes significantly at lower frequencies, then ions have the time to diffuse and this diffusion gives rise to an impedance.

IV. Impedance elements in a circuit

Impedance elements can be arranged in series or parallel. The total impedance in series is given by the sum of the impedance values of each individual element, equation (3.13).

$$\mathbf{Z}_{\text{total}} = \mathbf{Z}_1 + \mathbf{Z}_2 \quad (3.13)$$

The total impedance in parallel is given by the fraction of the sum of the impedance values of each element, equation (3.14).

$$\frac{1}{\mathbf{Z}_{\text{total}}} = \frac{1}{\mathbf{Z}_1} + \frac{1}{\mathbf{Z}_2} \quad (3.14)$$

V. Plotting the impedance spectrum

There are several ways to plot the impedance spectrum. A Nyquist-plot is a plot of minus the imaginary part of Z ($-\text{Im}(Z)$) against the Real part of Z ($\text{Re}(Z)$)[13]. It is a useful plot for diagnostic purposes, since certain arrangements of circuit elements give characteristic shapes. The main drawback of a Nyquist-plot is that it gives no direct information about the frequency. The frequency is hidden within the data points.

Figure 6 gives the equivalent circuit a) which is used to calculate the impedance spectrum b).

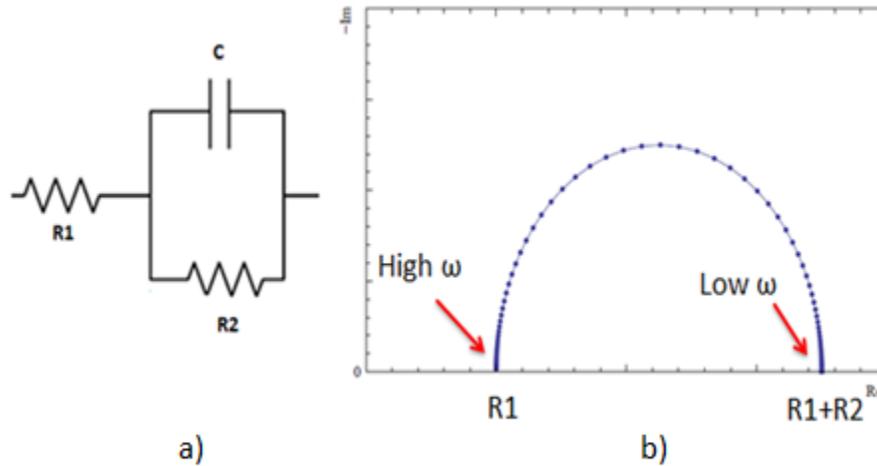


Figure 6: a) Electrical circuit used to calculate the impedance spectrum of b), consisting of a resistor and a resistor in parallel with a capacitor. b) The impedance spectrum on the vertical axis the $-Im$ and on the horizontal axis the Real part of the impedance. At high frequencies the impedance of the capacitor is very small, only R_1 will be observed. At low frequencies the impedance of the capacitor is high, R_1+R_2 will be observed. The semi-circle is due to frequency values between high and low.

With equations (3.4, 3.10, 3.13 and 3.14) an expression for the circuit in Figure 6a can be found as

$$\mathbf{Z}(\omega) = \mathbf{R}_1 + \frac{\mathbf{R}_2}{1+(\omega \cdot \mathbf{R}_2 \cdot \mathbf{C}_1)^2} + \mathbf{j} \frac{\omega \cdot \mathbf{R}_2^2 \cdot \mathbf{C}_1}{1+(\omega \cdot \mathbf{R}_2 \cdot \mathbf{C}_1)^2} \quad (3.15)$$

Closer examination of equation (3.15) shows that at high frequencies the second and third terms in the fraction will go to zero and only R_1 is observed. When the frequency decreases, the impedance of the capacitance will be in the same order of R_2 . That means that some of the current is flowing through the resistor and some through the capacitor. The peak of the semi-circle is observed when the value for the frequency is equal to $\frac{1}{R_2 \cdot C_1}$, equation (3.15) then reduces to

$$\mathbf{Z}(\omega) = \mathbf{R}_1 + \frac{\mathbf{R}_2}{2} + \mathbf{j} \frac{\mathbf{R}_2}{2} \quad (3.16)$$

When the frequency is decreased even further the denominator will go to a value of one and the imaginary part will be infinitely small, only R_1+R_2 will then be observed.

Figure 7 shows another example of two equivalent circuits a), which are used to calculate the two impedance spectra in b).

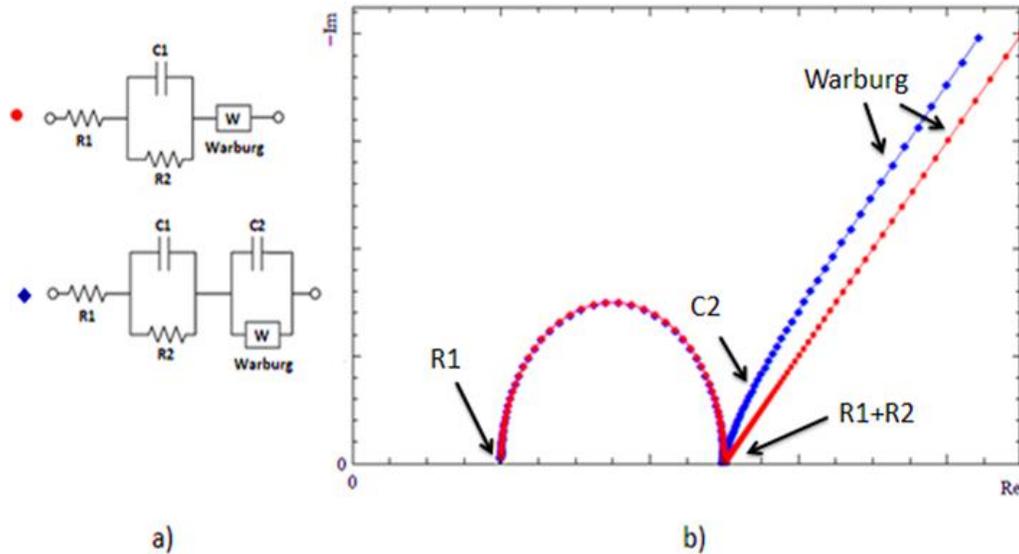


Figure 7: a) Two electrical circuits used to calculate the impedance spectrum shown in b). b) The calculated impedance spectrum of the two circuits. The curve with the diamonds shapes differs from the curve with the circles after the semi-circle reaches zero, the diamond shape curve has a little bend which is due to the capacitor in parallel with the Warburg element.

In Figure 7a, two different circuits are shown with their corresponding spectra in b). The semi-circle in the first part of the spectrum is due to $R1$ and in parallel $C1$ and $R2$, as shown in Figure 5. In the second part, for the circuit with the circle, only a Warburg element (W) is present. This Warburg element is responsible for the straight line observed in the spectrum. In the circuit of the diamond figure, there is a capacitor ($C2$) in parallel with a Warburg element (W). In the spectrum, there is a little bend at the beginning of the second part, due to the capacitor; it goes over in the straight line of the Warburg element.

The impedance spectrum of the diamond shape circuit, shown in Figure 7, is later used to fit to the measured data.

4. Experimental methods

In this section the experimental setup and methods will be discussed.

I. The impedance cell

The impedance cell consists of five glass plates stacked on top of each other, with four ceramic screws combining them. The complete cell is drawn in Figure 8.

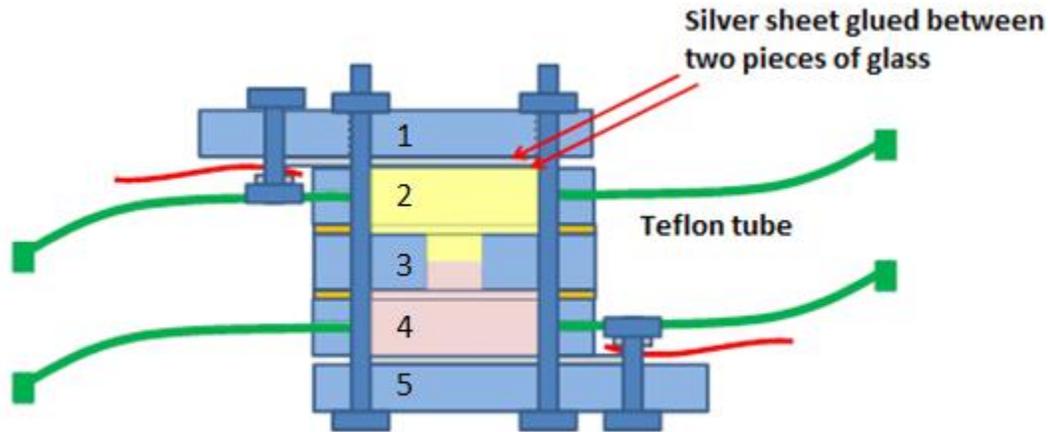


Figure 8: Schematic drawing of the impedance cell. The cell consists out of five glass plates hold together with ceramic screws and glue. A silver sheet is glued on glass plate 1 and 5, the silver functions as the electrode. Glass plate 2 and 4 consist of two compartments and tube holes. The tube holes are for filling the cell. Glass plate 3 is referred to as the center part of the cell. With this plate the contact area between the liquids can be modified.

Now each glass piece will be discussed:

Glass plate 1 and 5 are identical, see Figure 9. A sheet of silver is glued on the glass plate. The silver sheet functions as the electrode. Also, there is a contact present which connects the silver to a wire. The four holes in the corner are the screw holes and are present in each glass plate.

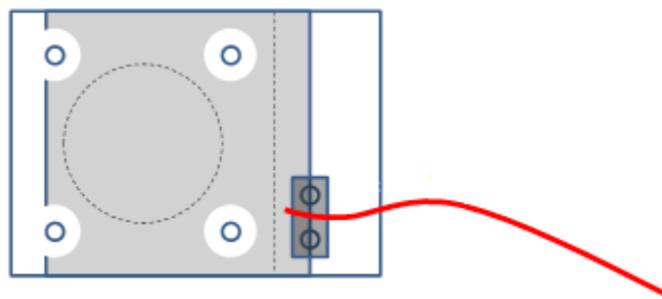


Figure 9: Schematic drawing of glass plate 1 and 5. A Sheet of silver is glued on top of the glass plate. The silver sheet has a contact which connects the silver to a wire.

On top of the silver electrode an another piece of glass is glued (2 and 4), shown in Figure 10. These glass plate have two tube openings for filling the compartments with a liquid. The dimensions of the glass plate is 50-50mm and the thickness is 10mm. The diameter of the circle in the center is 30mm.

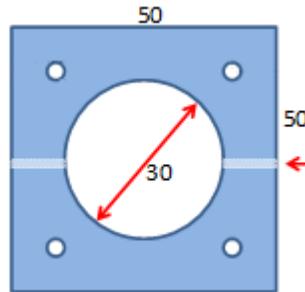


Figure 10: A schematic drawing of glass plate 2 and 4. These glass plates are 10 mm thick, the circle has a diameter of 30 mm and the outer dimensions are 50-50mm. Two holes in the side of are used to fill the cell with a liquid.

The glass plate from Figure 11 is laid on top of that, shown as 3 in Figure 8. A thin Teflon layer is laid between the glass piece (2,4) and 3 to make sure that no fluid can escape between the glass plates.

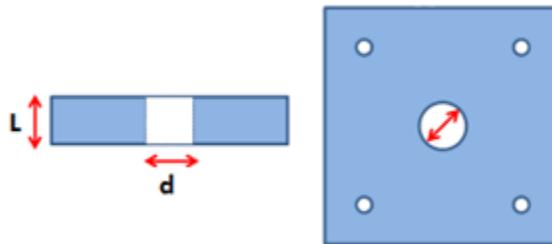


Figure 11: A schematic drawing of glass plate 3. We have multiple shapes of this glass plate with different diameters d and lengths L .

This glass plate will be referred to as the center part of the cell and the hole in the center part will be called the neck. There are multiple shapes of this glass plate with different diameters d and lengths L .

II. Cage of Faraday

The measurements are performed in a Faraday cage. A Faraday cage consists of an enclosure formed of a mesh of conducting material and is grounded. Especially during our measurements at lower frequencies it is important to shield any external electrical fields.

III. Chemicals

Table 1 gives a list of chemicals used during the experiments.

Table 1: An overview of the used chemicals.

Chemical	Brand	Quality
potassium chloride	Acros organics	99%+
sodium chloride	Emsure	for analytic use
tetraphenylarsonium chloride monohydrate	Acros organics	97%
sodium tetraphenylborate	Acros organics	99%
nitrobenzene	Sigma-Aldrich	99%+

IV. Preparation of ± 0.05 M nitrobenzene solutions with tetraphenylarsonium and tetraphenylborate (TPATPB) salt

Preparation of two solutions of nitrobenzene with two batches of TPATPB salt were made by dissolving TPATPB in nitrobenzene. Table 2 gives the amount of each batch

Table 2: Amount of TPATPB used to make ± 0.05 M nitrobenzene solution

	Amount (g)
Batch	TPATPB
#1	0.18290
#2	0.17560

Each batch was transferred quantitatively to a volumetric flask of 50 mL and nitrobenzene was added to make the total volume of 50 mL.

The TPATPB salt was prepared from sodium tetraphenylborate and tetraphenylarsonium chloride. Two different batches of TPATPB were made. Table 3 gives the amount of each batch:

Table 3: Amount of precursors used to make TPATPB salt

	Amount (g)	
Batch	NaTPB	TPACl
#1	0.16332	0.20871
#2	0.33833	0.42739

First, addition of NaTPB and TPACl to two separate 20 mL sample vials. Next 10 mL of a 50/50 mixture of acetone and water was added. After that, the two sample vials were combined and a white sediment was observed. After centrifugation for 20 min at 300g, the supernatant was removed. About 650 mL of acetone was added to dissolve the sediment. Then 400 mL deionized

water was added to precipitate the salt again. The solution was then set overnight to sediment. The next day the supernatant was removed. The salt was transferred to plastic 20 ml sample vials and dried at 65°C under a nitrogen flow.

V. Preparation of $\pm 0.1\text{M}$ aqueous solution of KCl

The KCl solution was made by addition of 18.66 g KCl salt to a 250 mL volumetric flask. Deionized water was added to make the total volume 250 mL. From this solution 0.250 mL was transferred quantitatively to a 250 mL volumetric flask. Deionized water was added again to make to volume 250 mL.

VI. Preparation of salt bridge composing of agar gel and potassium chloride

A salt bridge composed of agar gel and potassium chloride was prepared by adding 6.09 g of agar to a beaker with 200 mL deionized water. The solution was heated and stirred until most of the agar was dissolved. The solution had a light brownish color. After that, 1.66g of potassium chloride was added. After the potassium chloride was dissolved, the solution was poured in a plastic tube and was set to cool.

VII. Cleaning of the silver electrode

At first there was a white substance visible on the electrode. The electrode was placed in a beaker with 200 mL concentrated ammonia under stirring. The white substance could not be removed this way, it was removed by gentle mechanical scraping. After removal of the most of the white substance, the electrode was placed in a 3 M nitric acid for 1 min. To wash away the remaining nitric acid the electrode was placed in a beaker with deionized water for a couple of minutes.

VIII. Anodic treatment of the electrode

In Figure 12, a schematic drawing of the anodic treatment setup is shown. The silver electrode was placed in a beaker containing a solution of 0.01 M KCl. The counter electrode, made of platinum, was placed in another beaker with 0.01 M KCl solution. The two beakers were connected by a salt bridge. The electrodes were linked to a power source.

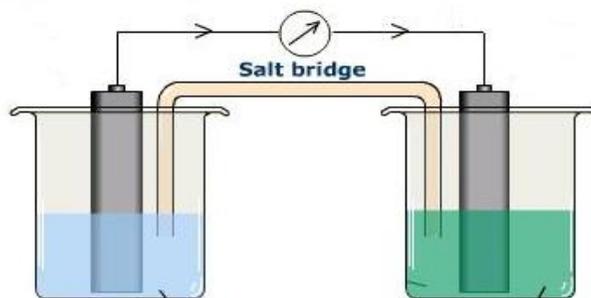
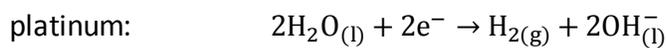
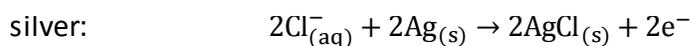
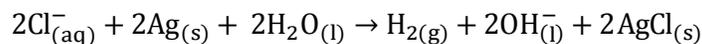


Figure 12: A schematic drawing of the anodic treatment setup. The silver electrode is placed in a beaker containing a solution of 0.01 M KCl. For the counter electrode platinum was used. (Source: chem-guide.blogspot.nl/2010/04/electrochemical-cell.html)



Total reaction in the setup is given as



In Figure 13, a photograph of the electrode is shown before and after anodic treatment and ageing. The electrode was aged for a couple of hours in a 0.01 M KCl solution.

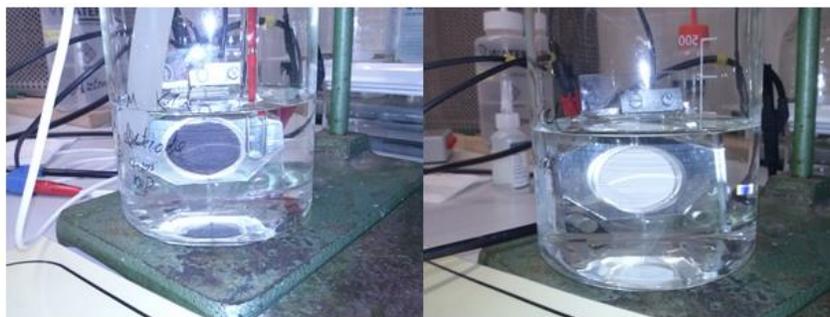


Figure 13: Photograph of electrode before and after ageing. A color change from black to white was observed. Before the treatment the silver has a black color due to etching. The white color after the treatment comes from Ag/AgCl.

Before the treatment the silver has a black color due to etching with 3M nitric acid. The white color after the treatment comes from Ag/AgCl.

IX. Equilibration of the water/nitrobenzene solutions

Before any measurements were done, the aqueous and nitrobenzene solutions were equilibrated. Some water will dissolve in the nitrobenzene and the other way around (see appendix C) [14]. The two solutions were equilibrated by combining the solutions in a flask and

shaking. The two solutions were later separated again with use of a syringe. A color change was observed for the water phase to a slightly more yellow color.

X. Filling the impedance cell

There are two different systems under study. In one case the impedance cell is filled with one solution and in the other the cell is filled with two solutions which do not mix. For the case with two solutions an interface is present. Later on, we want to change the area of contact between the two phases, this means that the interface must lie within the neck of the center part, see Figure 8. The way of filling the cell with a single solution is straight forward. The solution is injected with use of a syringe into the bottom compartment. It is important to remove all the air bubbles from the cell, therefore the cell was tilted to make sure that all the air could escape from one of the tube openings in the top compartment. With an interface present, in our case with nitrobenzene and water, the bottom compartment and the center part were filled with nitrobenzene with the use of syringe. Then the aqueous solution was added in the top compartment. When the two liquids made contact, the nitrobenzene solution was sucked out a little to position the interface in the middle of the center part. Figure 14 is an example of a filled cell with a solution of nitrobenzene and water.

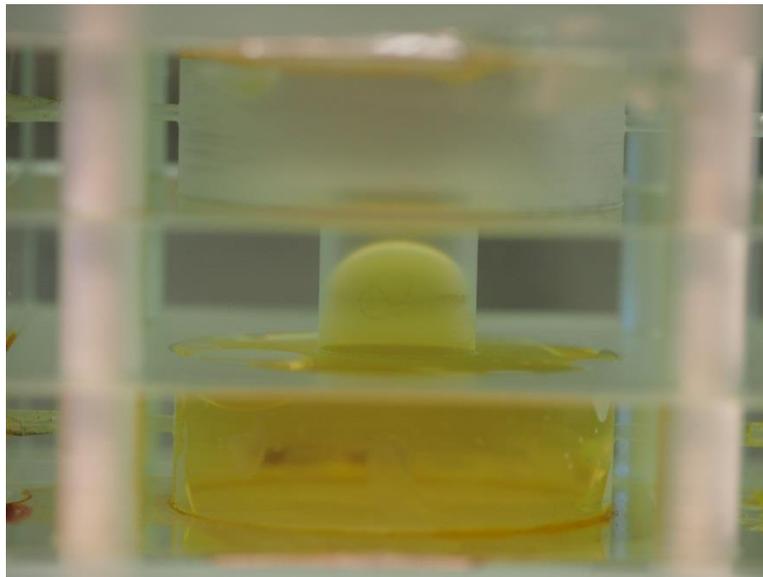


Figure 14: Photograph of the interface between water and nitrobenzene in the impedance cell.

The curved interface between the water/nitrobenzene interface is due to wetting effects of the glass[14].

XI. Autolab Settings

In this section the hardware setup will be discussed

Instrument used: Autolab PGSTAT100

Software used: Nova 1.10

Two procedures were used:

- FRA impedance potentiostatic
- FRA potential scan

Table 4 gives an overview of the settings during both procedures

Table 4: overview of Autolab settings during FRA impedance potentiostatic and FRA potential scan.

Wait time (between measurements)	5 seconds
Amplitude	0.35 mV TOP
Frequency step	Logarithmic 100.000 Hz to 0.1 Hz in 61 steps
Wave type	single wave
Integration time	0.125 seconds
integrate = 3	3

Table 5 gives an overview about the settings of the fit software.

Table 5: Overview of fit and simulate settings in Autolab

Max number of iteration	300
Max change in x^2 (scaled)	0.001
Max iterations without improvement	50
Weight factor	Yes

5. Results & Discussion

In this section two results will be discussed, first the interpretation of the impedance spectrum and second the potential dependence of the interfacial capacitance. During the measurement two different solutions of nitrobenzene were used, see table 2. We assume that these concentrations are the same.

A. Impedance spectrum

I. Typical impedance spectrum

Figure 15 is an example of a typical impedance spectrum of a water/nitrobenzene interface. For this particular measurement the configuration of the center part was 10 mm in diameter of the neck and 10 mm in length.

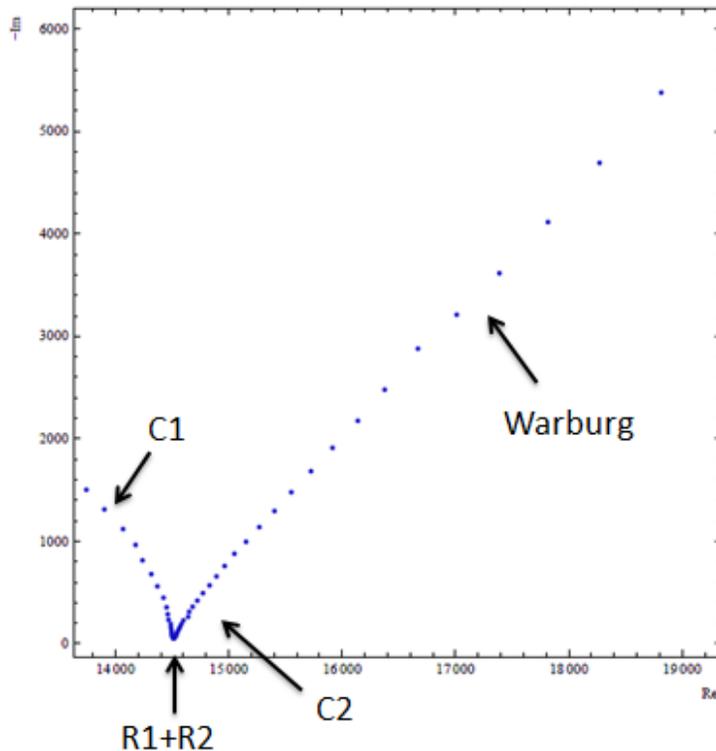


Figure 15: typical Nyquist plot of impedance spectrum of water/nitrobenzene

There are four main parts of interest in this impedance spectrum. The part of the semi-circle (C1), the point where the semi-circle goes to zero on the Real axis (R1+R2), the little bend that follows when the imaginary part increases again (C2) and the straight line (Warburg).

II. Extracting data from the impedance spectrum

To extract data from the impedance spectrum an equivalent circuit is fitted to the measured data. The equivalent circuit used is shown in Figure 16.

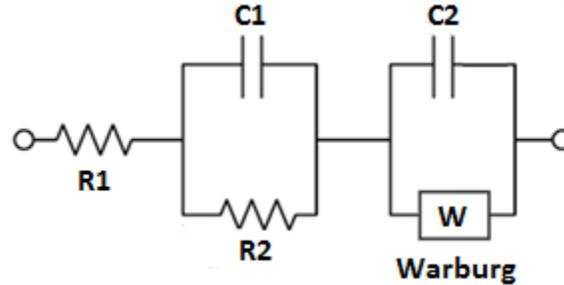


Figure 16: Equivalent circuit used to fit the measured data. R1 and R2 are resistors, C1 and C2 are capacitors and W is a Warburg element.

The resistors R1 and R2 account for the electrolyte resistance. R2 is the main electrolyte resistance, R1 possibly includes some other effects, such as charge transfer resistance from the electrode with the electrolyte. The capacitor C1 is used to model the geometric capacitance. With our current cell setup, there are two plates (electrodes) parallel to each other and a dielectric medium in between. So the cell as a whole can be seen as a plate capacitor. The electrical double layer at the liquid/liquid interface is modeled as capacitor C2. The Warburg element models the diffusion of the ions in the solution.

The fit was carried out by the Autolab Nova 1.10 software. In the measured spectrum, there is big difference between the lowest and the highest value of the real and imaginary part. Therefore, the fit software uses a weight factor. For example the software finds a fit with in each point an error of 10%. At the high values this could be for instance 1% of their value. But for small values this could be for example 90%. With the use of a weight factor this problem is solved and the lower values count heavier in the fit. For the weight factor the inverse of the square of the modulus to each point was used. The modulus ($|Z|$) is the length of a vector that can be drawn from the origin to a measured point, see equation (5.2).

$$\text{Weight factor} = \frac{1}{|Z|^2} \quad (5.1)$$

With

$$|Z| = \sqrt{Z_{\text{real}}^2 + Z_{\text{imaginary}}^2} \quad (5.2)$$

In the next sections the different areas of the impedance spectrum will be discussed together with the measurements. The error bars in the graphs are the estimated errors for the parameters obtained by the fit.

III. The geometric capacitance

The geometric capacitance can be estimated from the equation for a plate capacitor. Equation (5.3) gives the capacitance for a plate capacitor.

$$C = \left(\frac{\epsilon_W}{3} + \frac{\epsilon_N}{3} + \frac{\epsilon_G}{3} \right) \epsilon_0 \frac{A}{d} \quad (5.3)$$

In which $\epsilon_{W,N,G}$ are respectively the electric permittivity of water (80), nitrobenzene (35) and glass (4), ϵ_0 electric permittivity of vacuum, A the area of the overlap and d the distance between the plates. The area of the electrode was used for the area of overlap. An estimate of the geometric capacitance for the water and nitrobenzene solution is $8 \cdot 10^{-12}$ F.

Figure 17 is a plot of the measured geometric capacitance against the area of the center part.

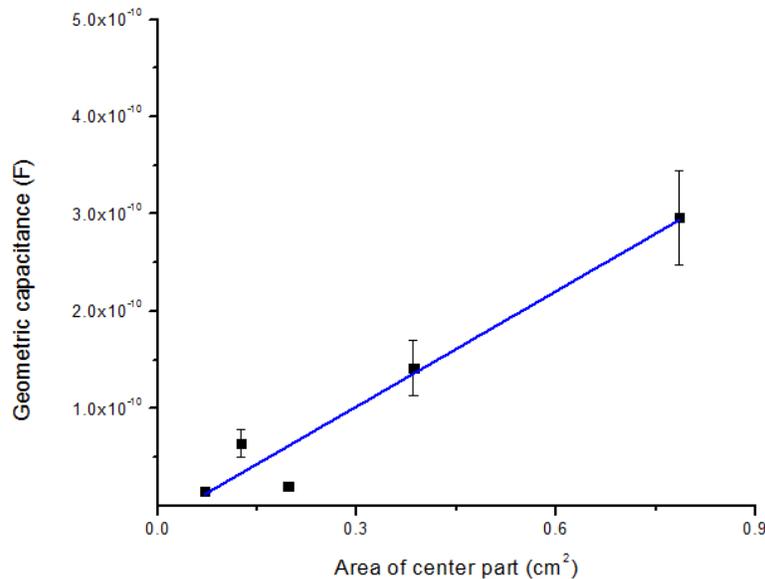


Figure 17: The geometric capacitance is plotted against the area of the center part.

The geometric capacitance increases with an increase of the area of the center part. Our expectation is that the geometric capacitance is almost independent of the neck of the center part. A possible explanation for the slight increase of the geometric capacitance could be that the ratio between the permittivity's of dielectrics changes. The capacitance was averaged for each measurement and was found to be $1 \cdot 10^{-10}$ F. Which is about 12 times higher than we would expect. I would say it is a reasonable estimate for such a crude model.

IV. Electrolyte conductance

Impedance measurements were done to find the contribution of the electrolyte conductance due to neck of the center part. The conductance is defined as one over the resistance. The electrolyte resistance is given by equation (5.4).

$$R_{\text{electrolyte}} = \rho \frac{L}{A} \quad (5.4)$$

In which ρ is the specific resistance, L and A are respectively the length and area in which the current has to flow. In our case that is the 2 compartments and the narrowing in the center part, see Figure 8. When looking at the geometry of the cell, the total resistance can be defined as

$$R_{\text{total}} = 2 R_{\text{compartment}} + R_{\text{middle part}} \quad (5.5)$$

The resistance of the two compartments can be measured by leaving out the center part. The resistance of the two compartments will be called R_0 . Rewriting equation (5.6) can give us the relation between the electrolyte conductance and area

$$\frac{1}{R_{\text{middle part}} - R_0} = \frac{A}{\rho L} \quad (5.6)$$

The impedance spectrum of a 0.01 M KCl solution is shown in Figure 18.

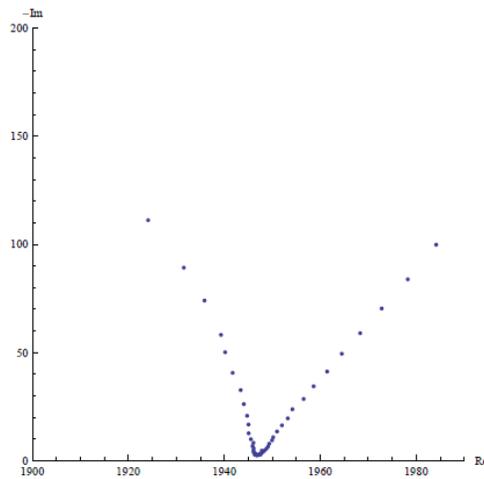


Figure 18: Nyquist plot of the impedance spectrum of 0.01 M KCl

The semi-circle observed at the left of the figure is due to the geometric capacitance. In the right of the spectrum a linear area can be observed, this is due to diffusion to the electrode. To find the electrolyte resistance we extrapolated the linear part of the spectrum. This was done by removing the lower frequency data (semi-circle) and fit the data with a linear function. The point where the linear function intersected the Re-axis was taken as the electrolyte resistance.

By measuring the conductance of a KCl solution with different area of the neck, the contribution of the neck can be found. For the measurements, a 0.01M KCl solution was used. The center part of the measuring cell was varied, the diameter of the neck was change to: 10, 7, 5, 3mm and one with no center part. This is shown in Figure 19. The fit is done with a linear function.

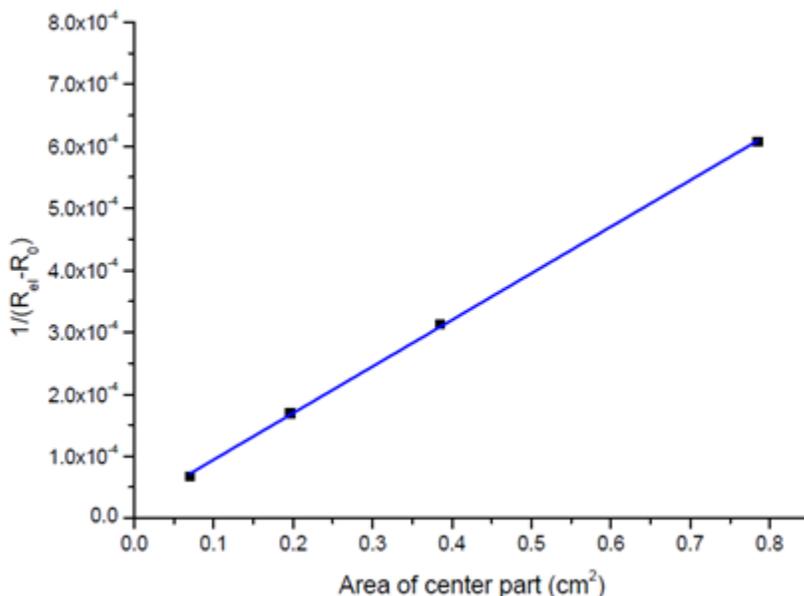


Figure 19: Electrolyte conductance against the area of the center part, the area refers to the area of the neck of the center part.

One can see that the electrolyte conductance is a function of the area of the center part. This result is as expected. The position of R₁+R₂ in the spectrum is given by the conductance of the two compartments and that of the narrowing in the center part. In each measurement the two compartments are the same. This means that the exact position of R₁+R₂ is only determined by the neck of the center part. This result can be extended to the case where there is an interface present. In that case, two compartments are present with a certain conductance, which are probably now not the same. The conductance in the center part is now due to the neck, the specific resistance of the two solvents and charge transfer resistance of the interface.

V. Warburg coefficient

In this section the Warburg coefficient between KCl and water/nitrobenzene measurements will be compared. The most important difference between the two measurements is that in the case of KCl no interface is present. To fit the data, two different circuits are used. For water/nitrobenzene the equivalent circuit is shown in Figure 16, for KCl it is shown in Figure 20.

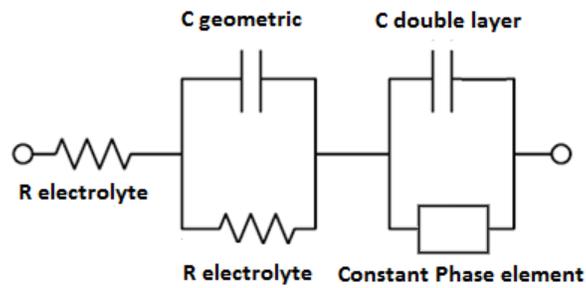


Figure 20: Equivalent circuit used to fit the impedance data for the measurement of a KCl solution

A different equivalent circuit was used for the KCl measurement because the fit was better, instead of a Warburg element a constant phase element was used. The exponent in a constant phase element is a variable, see equation (3.11). For the KCl solution, the value of the exponent was found to be 0.77 in every measurement. In the case of water/nitrobenzene the value of the exponent was found to be 0.5, which is the same as the fixed value in the Warburg element. So the choice was made to fit the data with a Warburg element because it is one less variable. We assume that the two different coefficients are comparable. The Warburg and constant phase element describe very similar behavior, the diffusion of the ions in the electrolyte.

In the case of KCl, where there is no interface present, there will only be diffusion to and from the electrode. The surface area of the electrode does not change and a change in the area of the center part should not matter. So our expectation is that the Warburg coefficient is a constant. The center part was changed during the different measurements, the area of the neck changed to: 10,7,5, 3 mm and one without the center part, the length was held constant at 10 mm. Figure 21 gives the result of the measurements. The measurement without the center part is shown at 7 cm², which is the area of the electrode. The data was fitted using a constant (γ =constant).

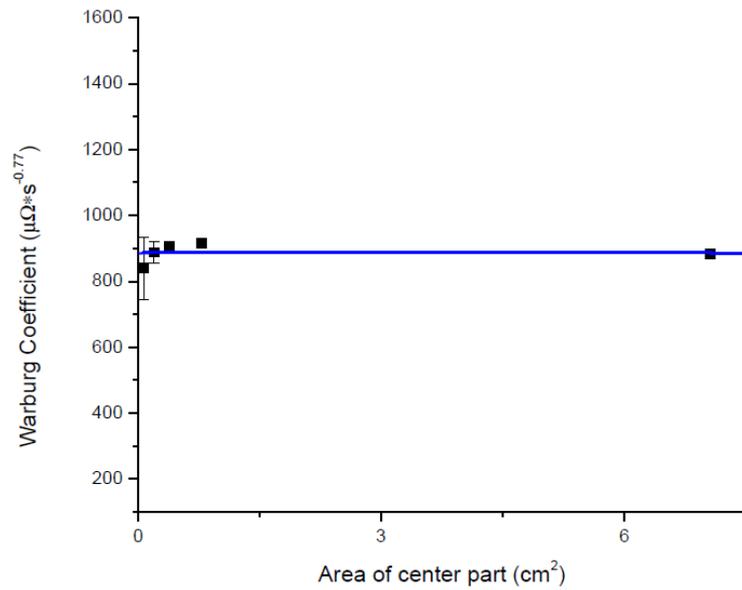


Figure 21: Warburg coefficient against the area of the center part for KCl solution

From this, it can be observed that the coefficient, in the case of a single solutions, is a constant and not a function of the area of the center part.

Now let's look at the Warburg coefficient when there is a water/nitrobenzene interface present, see Figure 22. The diameter of the neck of the center part was changed to: 10,7,5,4 and 3 mm. The length was held constant at 10 mm. The data point near 0.3 cm² area, with the big error bars, is left out of the fit. This is probably a poor measurement. The used fit is linear.

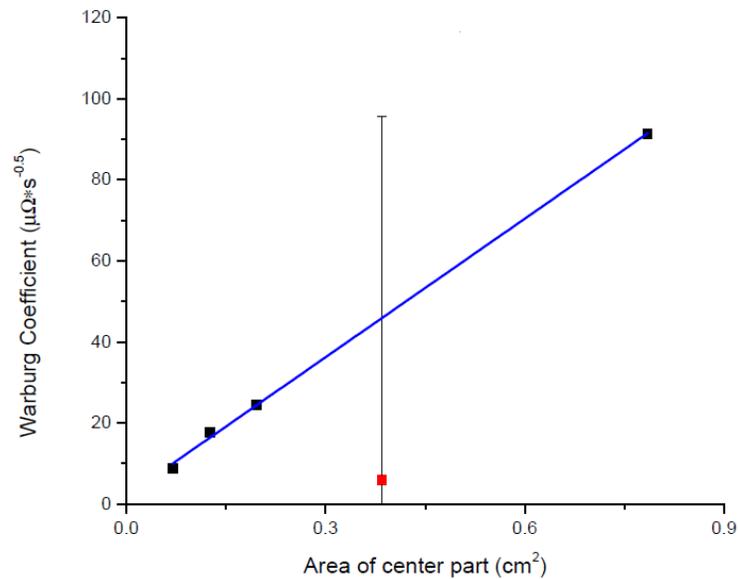


Figure 22: Warburg coefficient against area of center part of water/nitrobenzene solution

A clear increase can be observed with increasing area of the interface. Comparing Figure 21 and 22, one could say that when there is an interface present, the coefficient scales with the area of the interface.

VI. Capacitance of the double layer at the water/nitrobenzene interface

The main goal of this project was to determine the capacitance of the double layer at the water/nitrobenzene interface. In Figure 23, the capacitance is shown versus the area of the neck of the center part. The used fit is linear.

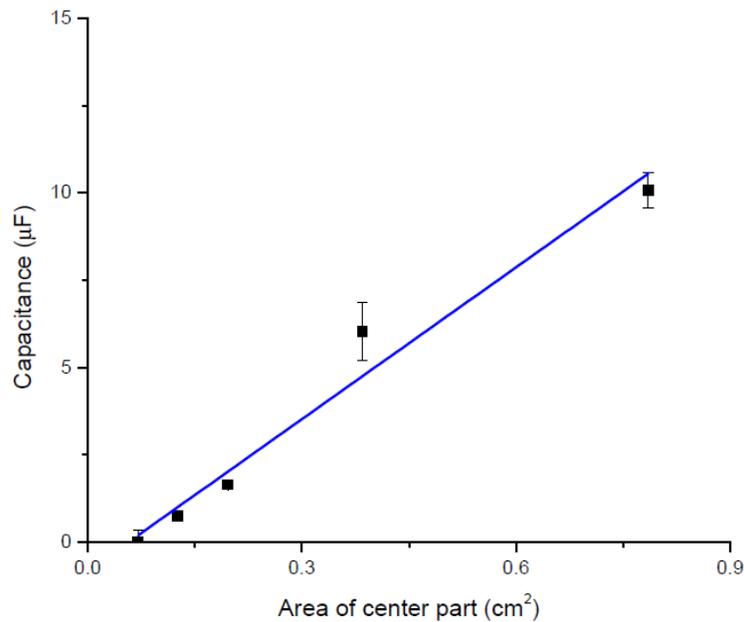


Figure 23: Capacitance of the double layer against area of center part

Our expectation is that the capacitance of the double layer should increase with an increase of area of the interface. From Figure 23, one could observe that this is indeed the case. However, there is an unexpected result as the trend line does not go through the origin as expected. When there is no interface, there is no double layer, so the capacitance should be zero and not negative. This needs further research.

B. Potential dependence of the interfacial capacitance

The Gouy-Chapman theory predicts that the capacitance is a function of an applied potential. In this section an external potential will be applied from typically -0.3 to 0.3 V in steps of 0.1 V between the two electrodes. The capacitance measured is from the liquid/liquid interface. First the reproducibility of the measurements will be discussed.

I. Reproducibility of the measurements

In Figure 24, almost the same measurements are performed twice on the same setup. The difference between the measurement is that there is a delay of 180 seconds between measuring each point in measurement 1 (blocks). These measurements are done with a diameter of the neck of 5 mm and length of 1mm.

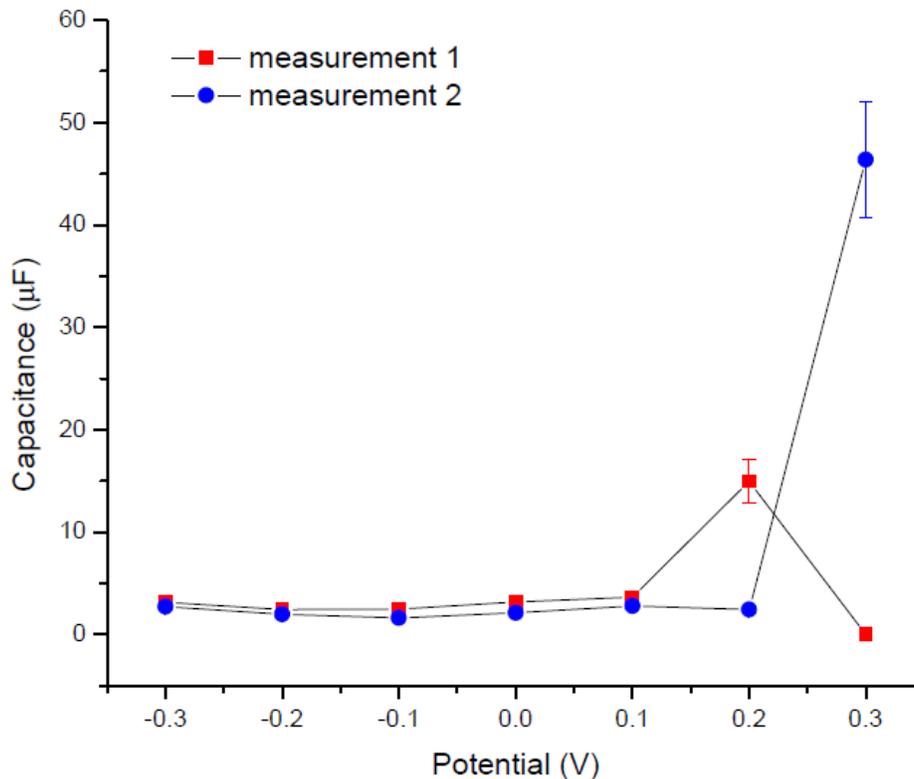


Figure 24: Capacitance of the interface as function of external applied potential of two almost identical measurements.

We observe that for a applied potential higher than 0.1, the measurements become unreliable. An explanation for this is that the ions get so much potential energy to transfer the interface. So the interface is no longer blocked. More research is needed to verify this.

II. Capacitance as function of potential with different d in center part

When an external potential is applied, more charge accumulation at the interface is expected and hence a higher capacitance. The potential range is -0.3 V to +0.3 V with steps of 0.1 V. After each potential scan, the diameter of the neck was changed: D=10, 7, 5, 4 and 3 mm and the length was held constant at 10 mm. The result is shown in Figure 25.

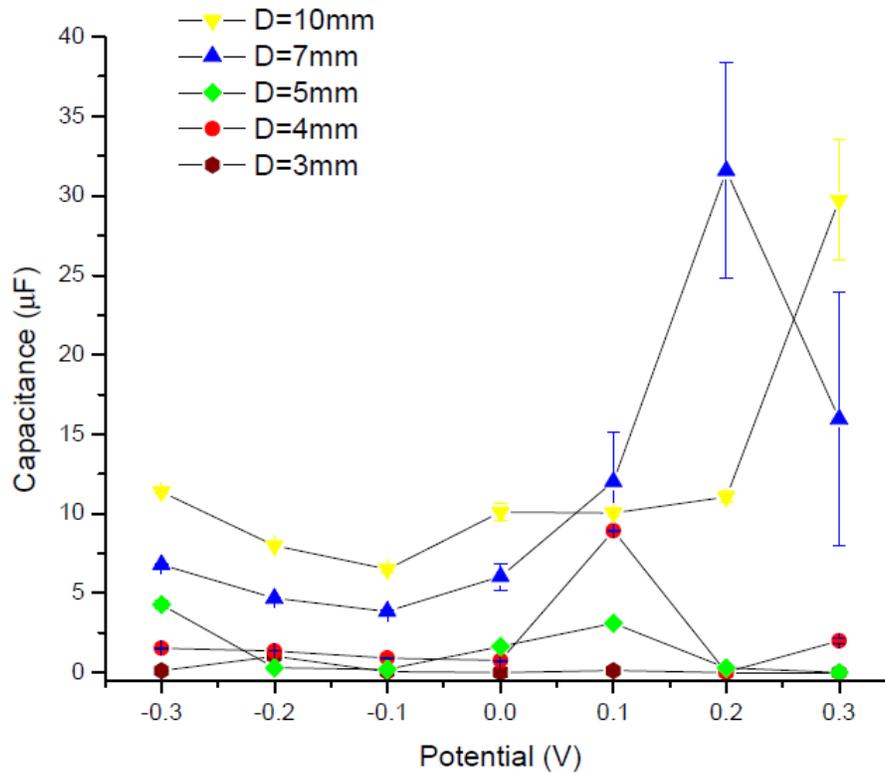


Figure 25: Capacitance of the interface against an external applied potential. Five different center parts are used for the measurement, see legend. The length of the center part is held constant at 10 mm.

To make the graph a bit more clear, the error bars for the D=5, 4 and 3mm have been removed for the potentials higher than 0.2 V because they were very big and overlapped with each other. For the same reasons given earlier, above a potential of 0.1 V the measurements are unreliable. The measurement of D=5mm is probably poor. For the most part, the capacitance changes accordingly with a change in area of the neck.

III. Comparison of our measured interfacial capacitance to theory

The Gouy-Chapman theory predicts that the capacitance is a function of an external applied potential. In equation (2.2) the capacitance per area of the double layer is shown. In Figure 26 the predicted behavior by Gouy-Chapman is shown as a parabola that opens upward.

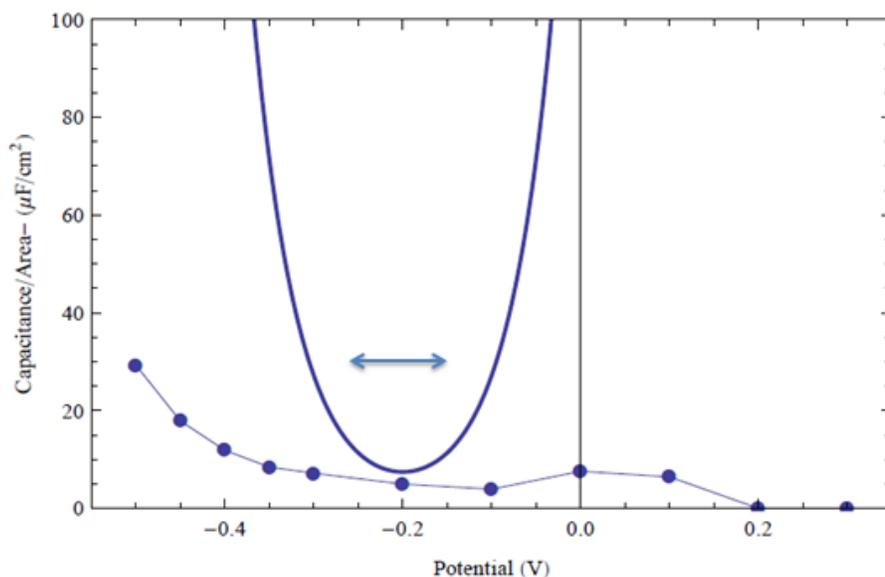


Figure 26: Calculated capacitance following the Gouy-Chapman theory (parabola that opens upwards) and the measured capacitance of the liquid/liquid interface, with center part of length of 1mm and diameter of neck 5mm.

The lowest capacitance is found at the potential of zero charge. At this moment it is not clear what that potential exactly is. Therefore a double arrow is shown in the graph. The circles in the Figure 26 are a measurement of the water/nitrobenzene interface. For the center part, a length of 1 mm and a neck of 5 mm was used. The potential range is from -0.5 to 0.3 V. The measurement is in the same order of magnitude as the theory, the shape however is different.

A possible explanation why the shape is different could be that the potential drop over the interface is not the same as over the entire cell. The potential shown in Figure 26 is applied over the entire cell, let's say 0.1 V. There is a potential drop across the bulk phases when the current flows through the first compartment and then through the neck of the center part. So the applied potential across the interface is not 0.1 V but for example 0.01 V. More research is necessary to confirm this.

In Figure 27 is an example of the capacitance of the double layer at the water/nitrobenzene interface found in literature[2].

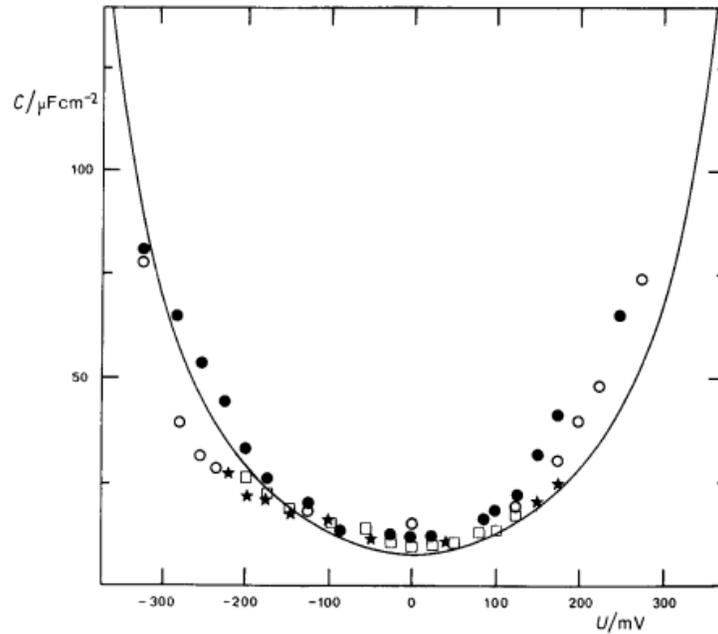


Figure 27: Capacitance according to Gouy-Chapman (parabola) and measurements (dots) found in literature

The measurement are in agreement with the predicted capacitance by Gouy-Chapman. However, we were not able to reproduce the calculated capacitance or the measurements. These particular measurements are done with a four electrode cell. This could possible give us also better results.

6. Conclusion & outlook

The goal of this work was to measure and interpret the impedance spectrum of a water/nitrobenzene interface and to determine the capacitance of the double layer at the liquid/liquid interface. From the result shown, there are clear indications that the impedance spectrum of the interface between water and nitrobenzene was measured. First, the Warburg coefficient scales with the neck of the center part of the impedance cell. The Warburg coefficient gives information about the diffusion of the ions in the electrolyte, with an increase in area of the neck, more diffusion is possible to the interface. Second, the capacitance scale with the area of the neck and is in the same order of magnitude as expected from the theory of Gouy-Chapman. We were not able to produce the characteristic shape of the Gouy-Chapman theory (parabola). A four electrode setup could improve the potential scan measurements. With a four electrode cell two extra electrodes are introduced near each side of the interface, so the potential difference between the interface can be measured.

To take the measurements of the liquid/liquid interface a step further, the impedance spectrum of a phase separated aqueous dextran/ gelatin mixture could be measured. Figure 28 is a schematic drawing of the interface in which there are two phase: α and β , dextran and gelatin respectively. Solvent is depicted by the shaded circles and ions by the circles with positive or negative signs. This measurement would be more challenging than to measure the interface of water/nitrobenzene because the interface wouldn't be blocked, which means that ions can pass relatively easy between the two phases.

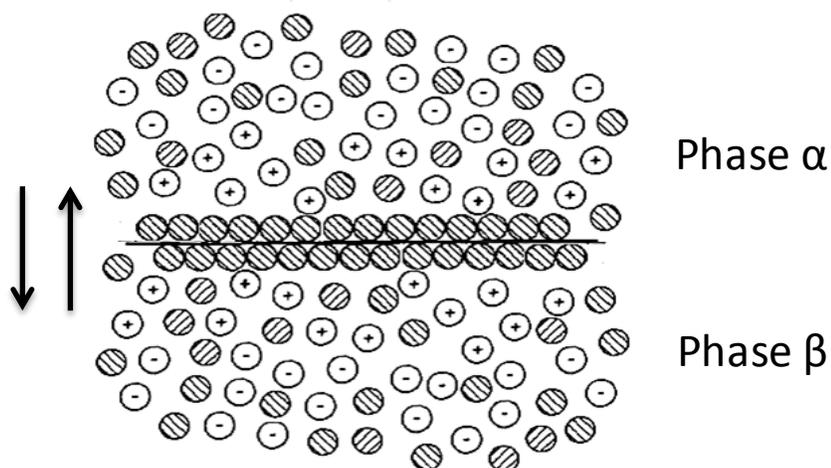


Figure 28: Schematic drawing of the interface between dextran and gelatin

The equivalent circuit of two aqueous phases could be represented by figure 29.

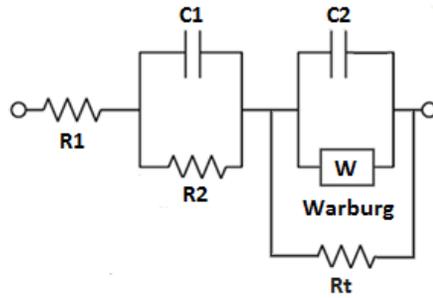


Figure 29: equivalent circuit for the unblocked interface

The circuit looks very similar as before but an extra resistance is introduced R_t . In the case of the blocked interface, the assumption was that this resistance was infinite. For two water/water phases that resistance has to be taken into account.

7. Bibliography

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8. Appendices

A. Derivation of the Gouy-Chapman theory

Considering a planar electrode in contact with a solution of a z-z electrolyte (cations of charge number z and anions of charge number -z) . We choose the coordinate system such that the electrode surface is situated in the plane at x=0[5]. See Figure 30.

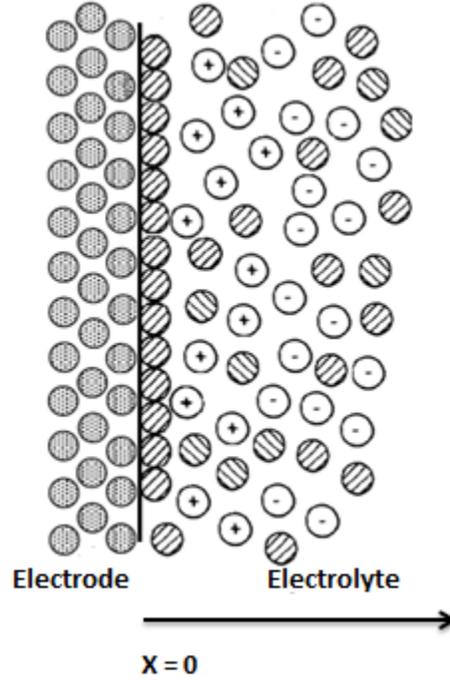


Figure 30: a schematic drawing of the interface between an electrode and electrolyte

The Poisson equation relates the potential to the charge density. For a flat geometry the Poisson equation is given by

$$\nabla^2 \varphi(x) = \frac{d^2 \varphi}{dx^2} = \frac{-\rho(x)}{\varepsilon \varepsilon_0} \quad (\text{A.1})$$

Where we have, ε_0 is the permittivity of free space and ε the dielectric constant of the solvent. The charge density $\rho(x)$ is related to the local electrolyte concentration. The charge density $\rho(x)$ is generally given as

$$\rho(x) = F \sum_j z_j c_j(x) \quad (\text{A.2})$$

For a symmetrical electrolyte with $z_+=1$ and $z_-=-1$ equation (A.2) can be written as

$$\rho(x) = F[c_+(x) - c_-(x)] \quad (\text{A.3})$$

The ionic density depends on the potential $\varphi(x)$ and local concentrations are related to their bulk values. When applying Boltzmann statistics

$$c_+(x) = c_0 e^{\frac{F\varphi(x)}{RT}} \quad (\text{A.4})$$

$$c_-(x) = c_0 e^{\frac{F\varphi(x)}{RT}} \quad (\text{A.5})$$

where $\varphi(x)$ is a potential. Substitution of equation (A.5) and (A.6) into the equation (A.4) gives

$$\frac{d^2\varphi}{dx^2} = \frac{-Fc_0}{\epsilon\epsilon_0} \left(e^{\frac{F\varphi(x)}{RT}} - e^{-\frac{F\varphi(x)}{RT}} \right) \quad (\text{A.6})$$

this relation is called the Poisson-Boltzmann equation. Using the relation in equation (A.8),

$$\sinh x = \frac{1}{2} (e^x - e^{-x}) \quad (\text{A.7})$$

equation (A.7) can be written as

$$\frac{d^2\varphi}{dx^2} = \frac{-2Fc_0}{\epsilon\epsilon_0} \sinh \frac{zF\varphi(x)}{RT} \quad (\text{A.8})$$

With equation (A.9) an expression has been found for the second derivative of the potential with distance from the electrode to the charge density with respect to the position x . Our interest goes to how the potential changes the electrolyte concentration near the electrode. Now some mathematical tricks will follow to solve the second order differential equation.

Multiplication of both sides with $2d\varphi/dx$ using

$$2 \frac{d^2\varphi}{dx^2} \frac{d\varphi}{dx} = \frac{d}{dx} \left(\frac{d\varphi}{dx} \right)^2 \quad (\text{A.9})$$

Integrating both sides

$$2 \int_0^\infty \frac{d^2\varphi}{dx^2} \frac{d\varphi}{dx} dx = \left(\frac{d\varphi}{dx} \right)^2 \Big|_0^\infty \quad (\text{A.10})$$

$$\int_0^\infty \frac{d^2\varphi}{dx^2} \frac{d\varphi}{dx} dx = - \int_0^\infty \frac{4Fc_0}{\epsilon\epsilon_0} \sinh \frac{zF\varphi(x)}{RT} \frac{d\varphi}{dx} dx \quad (\text{A.11})$$

Both the field E and the potential φ vanish at $x = \infty$, so we obtain

$$E(0)^2 = \frac{4RTFc_0}{\epsilon\epsilon_0} \left(\cosh \frac{F\varphi(0)}{RT} - 1 \right) \quad (\text{A.12})$$

According to Gauss's theorem, $E(0) = \sigma / \epsilon\epsilon_0$; using the identity

$$\cosh(x) - 1 = 2 \sinh^2 \frac{x}{2} \quad (\text{A.13})$$

One obtains

$$\sigma = \sqrt{\frac{8RTFc_0}{\epsilon\epsilon_0}} \sinh \frac{zF\varphi(0)}{2RT} \quad (\text{A.14})$$

With equation (A.14) we found an expression for the surface charge density on the electrode. We are interested in the differential capacity, which is a measurable quantity defined as

$$C = \frac{d\sigma}{d\varphi} \quad (\text{A.15})$$

differentiating equation (A.14) with respect to the potential φ gives

$$C = \epsilon\epsilon_0\kappa \cosh\left(\frac{zF\varphi(0)}{2RT}\right), \quad \kappa = \sqrt{\frac{\epsilon\epsilon_0 RT}{2F^2 c_0}} \quad (\text{A.16})$$

B. Derivation of the impedance of a capacitor

Before an expression for the impedance can be obtained, the voltage-current relation must be known[12]. A starting point for this is the relation between charge and voltage in a capacitor

$$\mathbf{Q} = \mathbf{C} \cdot \mathbf{V} \quad (\text{B.1})$$

in which Q represent the charge in coulomb, C the capacitance in Farad and V electrical potential in volt Differentiating this relation with respect to time gives:

$$\frac{dQ}{dt} = \mathbf{C} \cdot \frac{dV}{dt} \quad (\text{B.2})$$

Current is the change of the charge with time. So we have

$$\mathbf{I}(t) = \mathbf{C} \cdot \frac{dV}{dt} \quad (\text{B.3})$$

So when there is an applied sinusoidal voltage $V(t) = V_p \cdot \sin(\omega \cdot t)$ with V_p the amplitude, ω the angular frequency and t the time; we get

$$\mathbf{I}(t) = \mathbf{C} \cdot \frac{d(V_p \cdot \sin(\omega \cdot t))}{dt} \quad (\text{B.4})$$

$$= \mathbf{C} \cdot \omega \cdot V_p \cdot \cos(\omega \cdot t) \quad (\text{B.5})$$

Because the cosine curve is a sine curve shifted by $\pi/2$, equation (B.7) can be written as

$$\mathbf{I}(t) = \mathbf{C} \cdot \omega \cdot V_p \cdot \sin(\omega \cdot t + \frac{\pi}{2}) \quad (\text{B.6})$$

$$\mathbf{I}(t) = \mathbf{I}_p \cdot \sin(\omega \cdot t + \frac{\pi}{2}), \mathbf{I}_p = \mathbf{C} \cdot \omega \cdot V_p \quad (\text{B.7})$$

With an expression for the current, the impedance can defined as

$$\mathbf{Z}_C(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_p \cdot \sin(\omega \cdot t)}{\mathbf{C} \cdot \omega \cdot V_p \cdot \sin(\omega \cdot t + \frac{\pi}{2})} \quad (\text{B.8})$$

Equation (B.8) is very difficult to solve in this form. The function can be rewritten using the relation given in (B.9)

$$\sin(\omega \cdot t + \theta_{V,I}) = \frac{e^{j(\omega \cdot t + \theta_{V,I})} - e^{-j(\omega \cdot t + \theta_{V,I})}}{2j} \quad (\text{B.9})$$

In which $\theta_{V,I}$ is respectively the phase of the voltage and the current. After some manipulation we get

$$\mathbf{Z}_C(\omega) = \frac{1}{\mathbf{C} \cdot \omega} \cdot e^{j(\theta_V - \theta_I)} \quad (\text{B.10})$$

When we fill in the phase of the voltage and current we have

$$\mathbf{Z}_C(\omega) = \frac{1}{C\omega} \cdot e^{j(0-\frac{\pi}{2})} = \frac{1}{C\omega} \cdot e^{-j\frac{\pi}{2}} \quad (\text{B.11})$$

From Euler's formula we know that

$$\mathbf{A}e^{j\varphi} = \mathbf{A}(\cos(\varphi) + j \cdot \sin(\varphi)) \quad (\text{B.12})$$

So

$$\mathbf{Z}_C(\omega) = \frac{-j}{C\omega} = \frac{1}{j \cdot C\omega} \quad (\text{B.13})$$

The impedance of a capacitor is given in equation (B.13)

C. Thermodynamic equilibrium and ion partitioning

With the interpretation of the data we assumed that the interface is blocked. But a completely blocked interface is an invalid assumption. Usually there is some solubility of one solvent in the other. The solubility of nitrobenzene in water is 0.19g/100ml at 20°C [14]. Not only will one of the solvents dissolve in the other, also when a solute is added to one of the phases, it will diffuse into the other. The distribution of the solute between the two phases is known as partitioning. In the liquid/liquid equilibrium it is assumed that the electrochemical potentials of each solute is equal in both phases, see (C.1).

$$\mu_{\alpha} = \mu_{\beta} \quad (\text{C.1})$$

The equilibrium condition for the partitioning of a solute between two immiscible phases introduces a relationship between standard electrochemical potential, the activity and the inner potentials, see(C.2).

$$\mu_{\alpha}^0 + RT \ln a_{\alpha} + zF\phi_{\alpha} = \mu_{\beta}^0 + RT \ln a_{\beta} + zF\phi_{\beta} \quad (\text{C.2})$$

Where μ^0 is the chemical potential at infinite dilution and is mainly determined by the interaction between the solvent and the electrolyte. a is the activity, which is given as the product of the concentration and the activity coefficient. The activity coefficient gives the degree in which the solute deviates from ideal behavior. The indices refer to the two phases. For a charged solute the requirement of equal chemical potential gives the relation

$$\frac{a_{\alpha}}{a_{\beta}} = \exp \frac{(\mu_{\beta}^0 - \mu_{\alpha}^0) + zF(\phi_{\beta} - \phi_{\alpha})}{RT} \quad (\text{C.3})$$

Where ϕ_1 and ϕ_2 are the electrical potentials of the respective phases. The difference in the standard chemical potential is known as the standard Gibbs energy of transfer. It is the Gibbs energy gained when a single particle is transferred from one phase to the other, by the difference in energies of solvation. A real system cannot be described by equation (C.3). The condition of electro-neutrality gives the need of counter ions. So the distribution of one kind of ions does not only depend on the standard Gibbs energy of transfer and the electrical potential of the phase but on all ions in the solution. The concept of the standard Gibbs energies of transfer is however the same.

It is assumed that the standard Gibbs energies of transfer of both the cation and anion of tetraphenylarsonium (TPA⁺) and tetraphenylborate (TPB⁻) are equal in every solvent. This is plausible because both ions are symmetrical, fairly large, and the charge is at the center of the molecule. They have however slightly different sizes.

Standard potentials of transfer for selected individual ions from water (phase α) to nitrobenzene (phase β) is given in table 5.

Table 5: Standard potentials of transfer for selected individual ions from water (phase α) to nitrobenzene (phase β)

Ion	Standard potentials of transfer $\Delta\alpha\beta$, kJ/mole
Na^+	34,2
Cl^-	31.4
TPA^+	-35.9
TPB^-	-35.9