

“Impedance Spectroscopy Measurement of Ionic Solutions in order to Distinguish between Different Ions”

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Abstract: In this work simulation and experimental results of the frequency response of ionic solutions are presented. The used technique known as Electrical Impedance Spectroscopy (EIS) can be used for electrical characterization of chemical solutions regarding their ionic concentration. This technique may be used in several fields, e.g. for measurement of biological cells and tissues and for food quality control.

I. Purpose

The objective of this work is the development of a procedure for distinguishing between different ions dissolved in electrolyte, in this case water. By means of Electrical Impedance Spectroscopy (EIS) which later may be used for characterization of biological cells [1-6]. Therefore, experiments were performed with ionic solutions of different salts *NaCl* (sodium chloride), *KCl* (potassium chloride) and *CaCl₂* (calcium chloride) in different concentrations in order to characterize the behavior of the solutions in the frequency range 100mHz – 1MHz.

II. The Electrode-Electrolyte Circuit Model

Strong salts like *NaCl*, *KCl* and *CaCl₂* when added to water dissociate into ions to form electrolytes. When metals are placed in an electrolyte chemical reactions occur exchanging electrons between the solution and the electrode causing the accumulation of charge close to electrode surface, the so-called double layer [7]. Gouy-Champman-Stern theory [7] models the accumulation of charge in this layer by the so-called double layer capacitance (C_{DL} – see Fig 1).

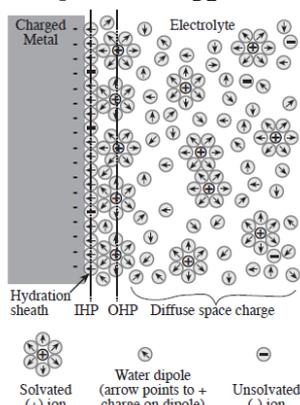


FIGURE 1: Illustration of the double layer showing its composing parts: Inner Helmholtz Plane (IHP), Outer Helmholtz Plane (OHP) and diffuse Space charge [7].

This interfacial capacitance C_{DL} is simply a circuit element which is able to model the complex physical phenomena occurring due to electrode/electrolyte contact in experiments. According to [7, 10] the C_{DL} is composed of

the Inner Helmholtz Plane (IHP), Outer Helmholtz Plane (OHP) and Diffuse Space Charge. Still according to the same authors, in the experimental situation here described the IHP can be neglected¹. The other two layers of charge, OHP and Diffuse Space Charge are also modelled by two capacitances in series: C_{OHP} and $C_{diffuse}$. In the Helmholtz space, potential is maximum at the electrode interface and decays linearly until the boundary between OHP and diffuse layer; this boundary also separates immobile from mobile charges. In the diffuse space charge the potential drop is exponential and the charges although being able to move partially do not have the same mobility as the charges in the bulk electrolyte. Figure 2 shows the potential profile drop from the double layer and equations [1-4] how C_{DL} is calculated.

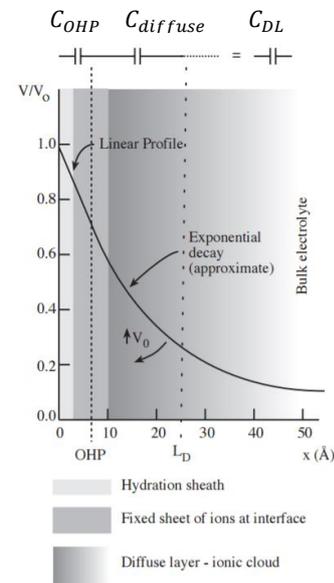


FIGURE 2: Potential profile distribution close to electrode surface. The closest layer to the electrode is known as hydration sheet and is composed of fixed oriented water dipoles. The second layer (starting at OHP) is composed of immobile hydrated ions² and the third layer of partially mobile hydrated ions (diffuse layer). The bulk electrolyte (after LD) is composed of completely free (mobile) hydrated ions. [7].

$$C_{OHP} = \frac{\epsilon_0 \cdot \epsilon_r}{d_{OHP}} [F/m^2] \quad (1)$$

$$C_{diffuse} = \frac{\epsilon_0 \cdot \epsilon_r}{L_D} \cosh\left(\frac{zV_0q}{2K_B T}\right) [F/m^2] \quad (2)$$

¹ A metal surface in contact with an electrolyte solution. For other interfaces, for instance, a biological cell in contact with an electrolyte solution IHP cannot be neglected.

² Ions surrounded by oriented water dipoles.

$$L_D = \sqrt{\frac{\epsilon_0 \epsilon_r V_t}{2n_0 z^2 q}} \quad [m] \quad (3)$$

$$C_{DL} = \frac{1}{\frac{1}{C_{OHP}} + \frac{1}{C_{diffuse}}} [F/m^2] \quad (4)$$

Where the value and explanation of each parameter is given in Table I.

Variable	Value	Explanation
ϵ_0	$8.854 \times 10^{-12} [F/m]$	Vacuum permittivity
ϵ_r	6 for OHP 1 for diffuse layer	Medium relative permittivity
d_{OHP}	0.5nm	OHP length
L_D	Varies according to the ionic concentration and temperature.	Debye length
z	± 1 for $NaCl / KCl$ and ± 2 for $CaCl_2$	Ion valence
V_0	10mV	Applied electrode potential
q	$1.602 \times 10^{-19} C$	Electron charge
K_B	$1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$	Boltzmann constant
T	293.15K (20°C)	Experimental temperature in Kelvin
n_0	Varies according to the ionic concentration	Bulk number concentration of ions in the electrolyte (ions/liter)
V_t	Equals $K_B T / q$	Thermal voltage

TABLE I: Parameters to calculate C_{DL}

The other electrical elements that must be considered in the circuit when simulating the electrode/electrolyte interface are the solution resistance (R_s) modelling the movement of ions and the electric current (charge) carried by them. The charge transfer resistance (R_{CT}) modelling the faradaic current transfer between the electrode and electrolyte. The Constant Phase Element (CPE or Z_{CPE}) that is a replacement of C_{DL} nevertheless taking into account electrode surface imperfections. In reality, the majority of the experimental data cannot be completely fitted by pure C_{DL} , but instead of by a CPE which impedance varies with frequency not to the power of -1, but to the power of some exponent between 0 and -1 (see equations [8-9]). By last, in the case of a large gradient of concentration between the electrode proximity and the bulk electrolyte a diffusion current will be observed (ions diffuse from high to low concentration) and the Warburg element (Z_W) is used to represent this physic phenomena.

For each salt and each concentration all the elements of the circuit were calculated with Matlab and later on fitted with software fitting tool Gamry Echem Analyst.

$$R_s = \frac{\rho l}{A} = \frac{l}{\sigma A} \quad (5)$$

$$R_{CT} = \frac{V_t}{J_0 z} \quad (6)$$

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^\alpha} \quad (7)$$

$$Z_W(\omega) = \frac{\sigma_D(1-j)}{\sqrt{\omega}} = \frac{R_W}{\sqrt{j\omega}} \quad (8)$$

$$\sigma_D = \frac{R_G T}{z^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{ox}^* \sqrt{D_{ox}}} + \frac{1}{C_{red}^* \sqrt{D_{red}}} \right) \quad (9)$$

Variable	Value	Explanation
R_s	Varies according to the ionic concentration	Solution resistance
ρ	Electrolyte resistivity	Characteristic of each electrolyte. Varies according to ionic concentration, temperature and ions present in the solution
σ	Electrolyte conductivity; the inverse of resistivity	Same for resistivity
l	1cm	Electrode separation distance
A	$1cm^2$	Electrode area
V_t	Thermal voltage	As explained in Table I
J_0	Exchange current density. Experimentally measured by fitting or by Cyclic Voltammetry.	Exchange current density between electrode and electrolyte. Function of electrode material (type of metal), its valence and temperature.
Z_{CPE}	Constant phase element impedance. Value varies according to ionic concentration.	In our experiments it was used as a replacement for C_{DL} . Therefore the value of Y_0 was simply assumed to be C_{DL} .
Y_0	Equals C_{DL} to our experimental fitting.	
ω	Equals $2\pi f$	Angular frequency. f is simply the simulation frequency range. In our experimental setup starting in 10mHz until 1MHz
α	Value between 0 and 1. Obtained by fitting of experimental data.	Exponent to account for electrode irregularities.
j	Imaginary number	
Z_W	Value varies according to ionic concentration, temperature, type of ions dissolved in the electrolyte and their diffusion coefficients	Warburg element impedance
R_G	$8.31 J mol^{-1} K^{-1}$	Gas constant
F	$96500 C mol^{-1}$	Faraday's constant
D_{ox}, D_{red}	Varies according to the type of ion. For instance for NaCl: $D_{ox(Na^+)} = 1.334 \times 10^{-5} cm^2 s^{-1}$ $D_{red(Cl^-)} = 2.032 \times 10^{-5} cm^2 s^{-1}$	Diffusion coefficient of oxidant and reductant respectively.
C_{ox}^*, C_{red}^*	Varies according to ionic concentration	Bulk concentration of diffusing species (reduced and oxidized) in moles/cm ³

TABLE II: Parameters to calculate the other circuit elements that characterize the electrode/electrolyte interface.

III. Methodology

Experiments consisted on adding three salts in very precise quantities to deionized water in order to obtain the necessary molar concentration. For each salt 20 different concentrations ranging from 6M – 25 μM ³ were measured. Solutions were then filled to a chamber consisting of parallel plates electrodes made of stainless steel with $1cm^2$ area each separated by 1cm distance (Fig. 3). Following, impedance spectrum of each solution was measured using

³ 1M: 1Molar or 1 mol/Liter

the Electrical Impedance Spectroscopy *Analyzer Gamry Interface 1000* in the frequency range 100mHz – 1MHz at 10mV excitation voltage. Experimental results were post processed and fitted to three circuit models (Fig. 4) to explain the physical behavior of the solutions.

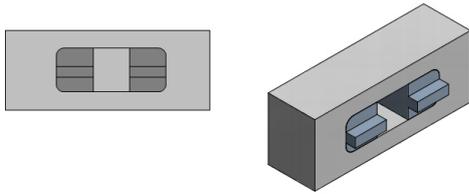


FIGURE 3: Top and 3D view of the measurement chamber used in the experiments.

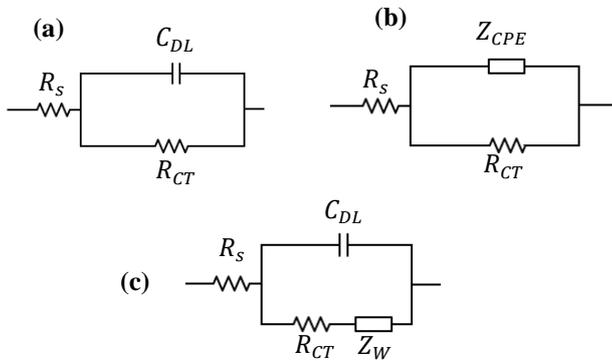


FIGURE 4: Equivalent circuit models for the electrode-electrolyte interface. (a) Randles, (b) Randles with CPE and (c) Randles with Warburg.

IV. RESULTS

Figure 5 shows the results for the measurements of *KCl* salt solution in the molar concentrations ranging from $25\mu M$ until $4M$. Clearly can be seen that the impedance spectrum shows a strong dependence on ionic concentration. From the top curve until the bottom, the concentration starts at $25\mu M$ and increases for each curve until $4M$. The impedance clearly follows the concentration: higher impedances for lower ionic concentrations and low impedances for higher concentrations. Specially in the high frequencies where the double layer is not present anymore because ions cannot follow the electric field frequency and the only visible parameter is the solution resistance R_s . The decrease in solution resistance with the increase in ionic concentration is easily explained by the fact that, more ions dissolved in the electrolyte (in this case water) will conduct more current therefore decreasing the electrolyte resistance and increasing electrolyte conductive (see equation 5) to the current passage. Nevertheless, for very high ionic concentrations the solution is so crowded that the resistance increases again⁴.

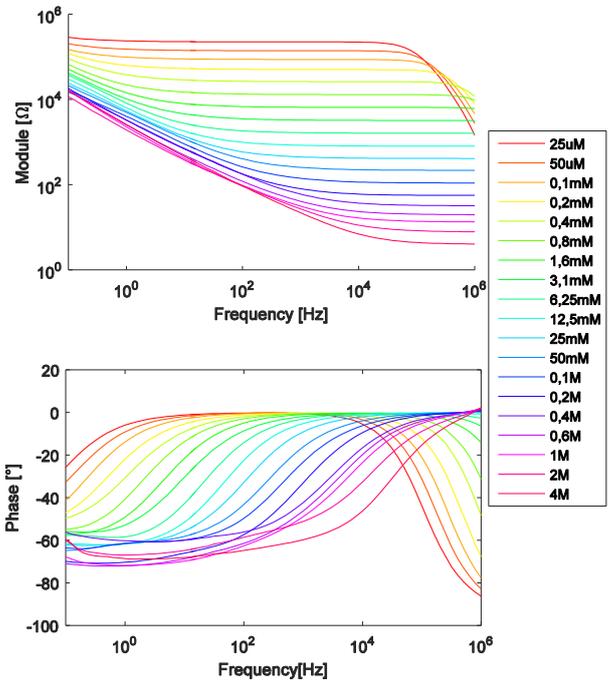


FIGURE 5: Module of impedance (top) and phase of impedance (bottom) plot of *KCl* solution salt dissolved in water for concentrations ranging from $25\mu M$ until $4M$.

Figure 6 shows the results of the macro conductivity extracted from the fitting of impedance measurement data with circuit 4b⁵. From the figure it can be concluded that from the macroscopic point of view at high concentrations it is possible to distinguish the salts by their conductivities, while at lower concentrations it is hard. One reason for that, can be because conductivity measurements at low concentrations are really hard to be performed precisely, therefore any small error will lead to a large deviation in the final value. Even a small variation in temperature, at low concentrations, will affect significantly the final conductivity value measured, while at high concentrations the effect will be less pronounced.

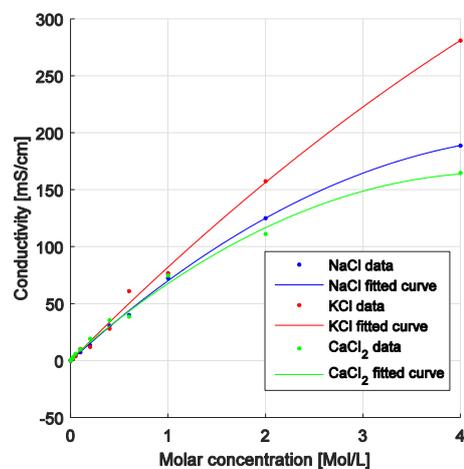


FIGURE 6: Experimentally measured conductivities fitted from impedance curves with circuit 4b. At high concentrations it is easy to distinguish the salts by their conductivities; nevertheless, at low concentrations it is not possible.

⁴ The ion cloud disturbs the passage of current, because ions are interacting and interfering with each other.

⁵ The circuit is used to fit R_s and from R_s the conductivity is extracted.

Going to the microscopic view, if an electrical field is applied to an electrolyte (a liquid with ions dissolved on it) the ions will move following the field. When a spherical charged particle is moving into a conducting liquid there are four forces acting on it: the electric field force (F_{el}), a frictional force against the particle movement (F_{fric}), a retardation force due to ionic atmosphere around the particle (F_{ret}) and a relaxation force (F_{rel}) that is related to the surrounding ions rebuilding the ionic atmosphere which is disturbed after the passage of the charged particle. The first two forces are always present (at high and low concentrations) while the last two are observed in high electrolyte concentrations only and can be neglected at low concentrations⁶ [9]. Graphically:

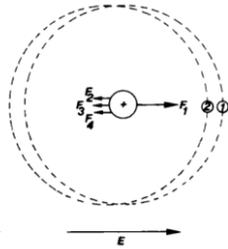


FIGURE 7: Forces acting on a charged particle moving through a charged electrolyte (F_1 or F_{el} , F_2 or F_{fric} , F_3 or F_{ret} and F_4 or F_{rel}). Source [9].

Just as a first approximation, neglecting F_{ret} and F_{rel} , at stationary state, the electric field force will be in equilibrium with the frictional force, therefore the following will be observed:

$$F_{el} - F_{fric} = 0$$

$$qE = 6\pi\eta rv$$

Where q is the electric charge of the particle, E is the electric field strength applied, η is the viscosity of the liquid where the particle is moving, r is the particle (in our case ion) radius and v is the particle speed. Figure 8 shows the results of solving the equation and calculating the drift speed of the three ions in our simulations.

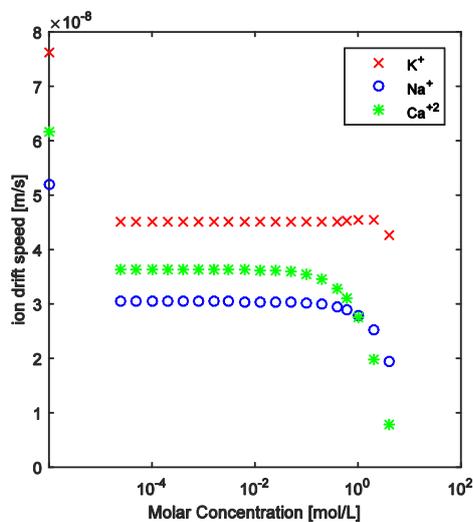


FIGURE 8: Ion drift speed in liquid for our experimental setup. For concentrations below 0.01M the calculation is accurate; above that the error increases (a lower speed would be expected) because of

⁶ Concentrations smaller than 0.01M.

the effect of relaxation and retardation forces, here not considered in the calculation. At zero concentration (directly in the y-axis) is plotted the ionic mobility at infinite dilution (from literature).

By last, Table I shows the results of the fitting for 154mM solution of the three salts with the three circuit models of figure 4. The circuit which gives the best fit for all the concentrations is 4b.

Parameter	NaCl	KCl	CaCl ₂
Circuit Model (a)			
R_s	85Ω	65Ω	74Ω
R_{CT}	18kΩ	34k	26kΩ
C_{DL}	9μF	4.9μF	6μF
Circuit Model (b)			
R_s	74 Ω	63 Ω	70 Ω
R_{CT}	28kΩ	45kΩ	32kΩ
Z_{CPE}	24μF	11e-6μF	19μF
A	0.7	0,8	0.7
Circuit Model (c)			
R_s	76Ω	65Ω	74Ω
R_{CT}	28kΩ	45kΩ	32kΩ
C_{DL}	4μF	9μF	6μF
Z_w	0.002 Ω(s) ^{-1/2}	0.486Ω(s) ^{-1/2}	20e-6Ω(s) ^{-1/2}
A	0.013	0.4	0.9

TABLE III: Result of the fitting for 154mM of the three salt solutions (NaCl, KCl and CaCl₂).

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