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# Mathematical Modeling: Kohlrausch-Onsager Law and Debye-Hückel Theory in the Measurement of Specific and Molar Conductivities of NaCl(Aq)

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***ABSTRACT :*** *In this work, we present the mathematical modeling applied to the measurement of the specific and molar conductivities of aqueous NaCl electrolytic solutions at 23.5°C using the Kohlrausch-Onsager Law and the Debye-Hückel theory of electrolytic dissociation. We explain in detail the deviation in conductivity behavior at high concentrations. Furthermore, we demonstrate the relevance and application of mathematical modeling in university-level chemistry education.*

***KEYWORDS:*** *Debye-Hückel theory, Kohlrausch-Onsager Law, electrolytic dissociation*

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## I. INTRODUCTION

Historically, abstract sciences like mathematics and experimental sciences like physics and chemistry have developed and strengthened each other through their inevitable interrelationships. Subdisciplines such as mathematical analysis (including differential and integral calculus as well as differential equations), statistics, electromagnetism, electromagnetic theory, and inorganic and organic chemistry, among many others, have formed what we know as basic sciences, which have been fundamental to the development of science, technology, and engineering. Equally important has been didactics, serving as a means of bridging the gap between theory and practice in the teaching and learning process of science and new technologies, and as a means of disseminating their advancements. The main objective of this research work is to corroborate the validity of the *Kohlrausch-Onsager law* in the determination of the specific and molar conductivity of a NaCl solution at low concentrations and the explanation of the deviation of these from ideality at high concentrations, through the *Debye-Hückel theory*.

## II. THEORETICAL FRAMEWORK

Mathematical modeling has been, for centuries, one of the most important tools enabling the refinement of techniques and the development of science and technology in general. In particular, the foundations of Physics and Chemistry have been greatly enriched in this regard. One of the revolutionary theories of its time was the potential theory, which originated with the contributions of Marquis and Dr. **Pierre Simon de Laplace** (1749-1827) of the University of Caen, as exemplified by the most famous and studied equation that bears his name[1]:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=0 \tag{1}$$

Where ψ is a harmonic potential function. In the mid-19th century, the Irish mathematician and physicist Sir **William Rowan Hamilton** (1805-1865) of Trinity College of Dublin, who introduced the concepts of vectors and quaternions, rewrote equation (1) more compactly in 1853[2]. In 1880 the English physicist and mathematician, Dr. **Oliver Heavisde** (1850-1925) of the University of Göttingen, (who developed the operational calculus) and in 1884[3], the American physicist and chemist Dr. **Joshia Willard Gibbs** (1839-1903) of Yale University, (who introduced the important concept of free energy in thermodynamics and developed the modern vector calculus)[4], symbolized equation (1) using $\nabla^2\psi=0$. The symbol $\nabla^2(\ )$ is now known as the Laplacian operator. Laplace's equation had many repercussions in various areas of Physics such as electromagnetism and classical mechanics. A generalization of Laplace's equation was given in 1823 by a student of Dr. Laplace, the French physicist and mathematician Dr. **Siméon Denis Poisson** (1781-1840) of the ÉcolePolytechnique in Paris. Poisson's equation originally had the form:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\nabla^2\psi=-\frac{4\pi\rho}{\varepsilon_0} \tag{2}$$

This is an elliptic partial differential equation, which represents the electrostatic potential variation of a point charge with a charge density distribution (ρ) in the vacuum. The solution is the scalar function of electrostatic potential that can be observed in a basic course of electromagnetism[5,6].

$$\psi(r)=\frac{q}{4\pi\varepsilon_o r} \tag{3}$$

a) b) c) d) e)

Fig. 1. a) Dr. Pierre Simon de Laplace; b) Sir William R. Hamilton; c) Dr. Oliver Heaviside; d) Dr. Joshia W. Gibbs ande) Dr. Simeon D. Poisson

The *Boltzmann distribution* is a fundamental concept in statistical mechanics. It describes the probability of a system being in a particular state, as a function of the energy of that state and the system's temperature. Simply put, it states that lower energy states are more probable than higher energy states, and this probability changes with temperature. The probability of a particle being in an energy state ($E_i$) is proportional to the *Boltzmann factor*$e^{-\frac{E_i}{k_B T}}$, where: ($E_i$) is the state energy ($i$), ($k_B$) is the Boltzmann's constant and ($T$) is the system absolute temperature in Kelvin. The German mathematician and theoretical physicist Dr. **Ludwig Eduard Boltzmann** (1844-1906) of the University of Vienna published in his article "*On the Nature of Gas Molecules*" of 1877, this important principle. His theory contributed greatly to the theory of gases and in general to the development of thermodynamics[7,8].

Fig. 2. Dr. Ludwig E.Boltzmann

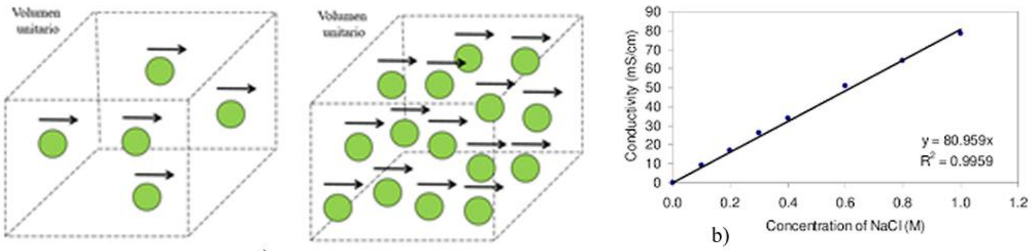
It was truly decisive for the purposes of scientific research and at the same time for the teaching of basic sciences, that improvisation carried out in 1825 by the German scientist Dr. **Justus von Liebig** (1803-1873) to use a disused military barracks of the German army as a chemistry laboratory.Dr. Liebig considered one of the greatest chemistry professors of all time, having dedicated his life to perfecting the design of school laboratories, as we know them today. Dr. Liebig's contributions served as a model and led to the creation of advanced research centers in his time. Illustrious scientists in these types of laboratories developed many established laws and theories in physics and chemistry. The following section presents the theoretical context surrounding the theory of electrolytic dissociation, developed in the early decades of the 19th century[9].


a) b) c)

Fig.3. a) Dr. Justus von Liebig; b) First university Chemistry laboratory (1825); c) Modern Chemistry laboratory (2025)

An **electrolyte** is a substance capable of being dissociated it by the action of a solvent (*for example, the electrolyte NaCl dissolved in water, which is a polar solvent*). An **electrolytic solution**, on the other hand, is a solution whose solute is an electrolyte directly responsible for conducting electricity due to the mobility of its ions within the solvent. Electrolytes are widely used in electrolytic cells, for example, in industrial processes such as galvanizing and chrome plating, and in electrochemical cells, such as galvanic cells (*commonly known as batteries*), for example, lithium-ion batteries. Electrolytes have two fundamental properties, which are often confused due to the mathematical relationship between them: specific conductivity (κ) and molar conductivity ($\Lambda_m$). These properties, which will be defined below, are strongly associated with the concentration of ions in the electrolytic solution.

***Specific conductivity*** (κ).- Is a measure of a solution's overall *ability to conduct electricity per unit volume*. It is measured directly with a conductivity meter and is expressed in Siemens per centimeter (**S/cm**). As the concentration of electrolytes increases, the number of ions per unit volume also increases, causing the specific conductivity to rise.




a) b)

Fig. 4. a) Higher concentration means higher electrical conductivity per unit volume; b) Variation of the specific conductivity of an electrolytic solution of NaCl at different concentrations.

***Molar conductivity*** ($\Lambda_m$). Molar conductivity measures the conductivity of a solution per mole of dissolved electrolyte. In other words, *it is a measure of the efficiency with which one mole of ions transports electrical charge*. It is calculated by dividing the specific conductivity (κ) by the molar concentration (c) measured in moles/cm³. It expressed in units of Siemens square centimeters per mole (**Scm²/mol**). As the concentration of electrolytes increases, molar conductivity decreases slightly in strong electrolytes. This is because, even though there are more ions, the interactions between them become stronger and "*slow down*" their individual movement, reducing the efficiency of each ion in transporting charge. Molar conductivity and specific conductivity are related them by the equation:

$$\Lambda_m = \frac{\kappa}{c} \tag{4}$$

Although this may seem counterintuitive, it is important to note that the physical measurement of conductivity is performed it with a conductivity meter, which actually measures specific conductivity, not molar conductivity. To clarify the physical meaning of the decrease in molar conductivity, consider two electrolytic solutions with concentrations of 1M and 2M. In a 1M solution, one mole of ions will have a certain efficiency in conducting electricity, even though there are factors that affect the mobility of its ions. However, if we now consider a 2M solution, one mole of that solution will have lower efficiency because there are more ions affecting the mobility of the ions in that mole compared to the mole in the 1M solution. This is why molar conductivity decreases with concentration, while specific conductivity increases. It is also important to clarify that, in reality, specific and molar conductivity do not vary linearly. A young German scientist discovered this in the 19th century[10].

Years after the Italian professor and Count Dr. **Alessandro Giuseppe Antonio Anastasio Volta** (1745-1827) of the University of Pavia invented his electric battery in 1799[11]; the theory of electrolytic solutions was born in 1806 with the earlier research of Lieutenant **Christian Johann Dietrich Theodor von Grotthuss** (1785-1822) of the ÉcolePolytechnique[12]. He formulated in 1806 the first law of photochemistry and a theory of electrolysis, which is now known as the *Grotthuss mechanism*. And the 1834 research of the British scientist Dr. **Michael Faraday** (1791-1867), who was the first to introduce the term electrolyte and state that acids, bases, and salts dissolved in water dissociate into charged particles (or ions) that can conduct electric current[13]. For his many contributions to electricity and chemistry, Faraday is considered a pioneer in the field of electrochemistry. In 1874, the German scientist Dr. **Friedrich Wilhelm Georg Kohlrausch** (1840-1910) of the University of Göttingen demonstrated that an electrolyte has a defined and constant coefficient of electrical resistance[14].

a) b) c) d)

Fig. 5. a) Tte. Christian J.D.T. von Grotthuss; b) Dr. Alessandro G.A.A.Volta; c) Dr. Michael Faraday ans d) Dr. Friedrich W.G. Kohlrausch.

By observing the dependence of conductivity on dilution, Kohlrausch was able to determine the transfer rates of ions (charged atoms or molecules) in solution. Considered one of the great pioneering researchers in the field of electrochemistry, his experiments and studies allowed him to establish, in 1875, *the law of independent migration of ions*, also known as **Kohlrausch's law**. He demonstrated that molar conductivity did not vary linearly but rather with respect to the square root of the concentration. Many of his studies and data served as the basis for the development of the *theory of ionic dissociation*.

**Kohlrausch's Law**.- Also known as the ***Law of Independent Migration of Ions***, it states that in an electrolytic solution, the molar conductivity at infinite dilution is the sum of the individual ionic contributions of the cation and anion. This occurs when the electrolyte concentration is so low that the interactions between the ions become negligible.

*Remark*: The law is valid at the limit of infinite dilution, that is, when the electrolyte concentration approaches zero. Under these conditions, the ions are sufficiently separated that they do not interact with each other, allowing them to move completely independently. On the other hand, each ion (cation and anion) contributes to the total conductivity of the solution with a specific value that depends on its own nature, such as its charge and mobility.

Kohlrausch's law can be expressed with the following formula:

$$\Lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0 \tag{5}$$

Where $\Lambda_m^0$ is the limiting molar conductivity (at infinite dilution) of the electrolyte, $v_+$ y $v_-$ are the number of moles of the cation and anion, respectively, per mole of electrolyte, $\lambda_+^0$ y $\lambda_-^0$ are the limiting molar ionic conductivities of the cation and anion, respectively. Kohlrausch also observed experimentally that the molar conductivity ($\Lambda_m$) of a strong electrolyte in dilute solutions decreases linearly with the square root of the concentration (c). An alternative empirical equation to this was:

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c} \tag{6}$$

This relationship (6) is known as Kohlrausch's square root law. He determined the value of K experimentally, but could not explain why this relationship existed[15].

Theory of ionic dissociation it strengthened with the important contributions, such as that of the German chemist Dr. **August Wilhelm von Hofmann** (1818-1892) of the University of Göttingen, who introduced the term molar in 1865[16], and especially the 1884 research on ion-dipole forces, by the Swedish scientist Dr. **Svante August Arrhenius** (1859-1927) of Uppsala University, Nobel Prize winner in Chemistry. This theory explained how compounds dissociate into ions in solution, which was crucial for understanding the solubility of ionic substances. Arrhenius discovered the reversible nature of the dissociation process[17].

On the other hand, and no less important, was the contribution of the German chemist and philosopher Dr. **Wilhelm Friedrich Ostwald** (1853–1932), Nobel Prize winner in Chemistry (1909), regarding his concept of the mole and his theory of weak electrolytes of 1888[18]. The ***theory of ionic dissociation*** was studied and expanded around 1922 by the Dutch scientist Dr. **Petrus (Peter) Josephus Wilhelmus Debye** (1884–1966) of the University of Munich, Nobel Prize winner in Chemistry (1936), and by his student, the German scientist Dr. **Erich Armand Arthur Joseph Hückel** (1896–1980) of the University of Göttingen. The *Debye-Hückel theory* theoretically explains the deviations from ideality in electrolyte solutions and plasmas[19,20].

a) b) c) d) e)

Fig. 6. a) Dr. August Wilhelm von Hofmann; b) Dr. Svante A. Arrhenius; Dr. Wilhelm Friedrich Ostwald c) Dr. Petrus J.W. Debye and d) Dr. Erich A.A.J. Hückel.

Doctors Debye and Hückel assumed that for a central ion with an electric potential ($\psi$) and a charge density ($\rho$), with a perfect spherical shape immersed in an electrolytic solution whose solvent has a permittivity ($\varepsilon$), its electric potential should satisfy Poisson's equation:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\nabla^2\psi=-\frac{4\pi\rho}{\varepsilon} \tag{7}$$

On the other hand, Debye and Hückel considered that the description of the local charge density ($\rho$) around a central ion ($z_i e$) followed the Boltzmann distribution, that is:

$$\rho(r)=\sum_i n_{i,0}\cdot e\cdot z_i\cdot e^{-\frac{e\cdot z_i\cdot\psi(r)}{k_B\cdot T}} \tag{8}$$

Where ($e$) is the electron charge ($|e|$ =1.602×10$^{-19}$C), ($n_{i,0}$), the ions concentration of ionic species $i$, ($e\cdot z_i$) its charge, ($z_i$) is the ion valence, ($k_B$) is the Bolzmann's constant y ($T$) is the temperature (in $K$). Debye and Hückel considered that for dilute solutions they assumed that the electrical potential is small, that is ($|e\cdot z_i\cdot\psi(r)|\ll k_BT$) and that the first-order approximation of the exponential function $e^{-\frac{e\cdot z_i\cdot\psi(r)}{k_B\cdot T}}$ that was enough[10]. Thanks to the power series expansions (polynomial functions) of the Scottish mathematician Dr. **Colin Maclaurin** (1698-1746) of the University of Glasgow, published in 1742[21], this approximation is achieved by expanding the exponential function into a Maclaurin series truncated to the first two terms, for example, the Maclaurin series expansion for the exponential function $e^x$ is:

$$e^x\approx 1+\frac{x}{1!}+\frac{x^2}{2!}+\frac{x^2}{3!}+\cdots+\frac{x^n}{n!} \tag{9}$$

Therefore, a truncated approximation to the first two terms would be: $e^x\approx 1+x$. Similarly:

$$e^{-\frac{e\cdot z_i\cdot\psi(r)}{k_B\cdot T}}\approx 1-\frac{e\cdot z_i}{k_B\cdot T}\psi(r) \tag{10}$$

Then,

$$\rho(r)=\sum_i n_{i,0}\cdot e\cdot z_i\left[1-\frac{e\cdot z_i}{k_B\cdot T}\psi(r)\right]=\sum_i n_{i,0}\cdot e\cdot z_i-\frac{\psi(r)}{k_B\cdot T}\sum_i n_{i,0}(e\cdot z_i)^2 \tag{11}$$

Since electrolytic solutions are generally neutral: $\sum_i n_{i,0} \cdot e \cdot z_i = 0$, Therefore, the charge density $\rho(r)$ simplifies to:

$$\rho(r) = -\frac{e^2\psi(r)}{k_B \cdot T}\sum_i n_{i,0} z_i^2 \tag{12}$$

Substituting this charge density into the Poisson equation, we obtain the linearized Poisson-Boltzmann equation:

$$\nabla^2\psi(r) = \left(\frac{4\pi e^2}{\varepsilon k_B \cdot T}\sum_i n_{i,0} z_i^2\right)\psi(r) \tag{13}$$

$$\nabla^2\psi(r) - \left(\frac{4\pi e^2}{\varepsilon k_B \cdot T}\sum_i n_{i,0} z_i^2\right)\psi(r) = 0 \tag{14}$$

This has the form of the homogeneous Helmholtz equation $\nabla^2\psi - \eta^2\psi = 0$, donde:

$$\eta^2 = \frac{4\pi e^2}{\varepsilon k_B \cdot T}\sum_i n_{i,0} z_i^2 \tag{15}$$

The factor $\eta = \sqrt{\frac{4\pi e^2}{\varepsilon k_B \cdot T}\sum_i n_{i,0} z_i^2}$ is known as the Debye-Hückel shielding factor and its inverse $(\xi = \eta^{-1})$, **Debye-Hückel length,** concepts that we will explain in detail later.

Since the distribution of the ionic atmosphere around a central ion is assumed spherically symmetric (*angle-independent*), the Laplacian operator in *spherical coordinates* simplifies considerably[22]. For a function that depends only on the distance ($r$) from the center, the equation becomes:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \eta^2\psi \tag{16}$$

Making the variable change $\psi(r) = \frac{u(r)}{r}$ and deriving this expression:

$$\frac{d\psi}{dr} = \frac{1}{r}\frac{du}{dr} - \frac{u}{r^2} \tag{17}$$

Substituting into the simplified Helmholtz equation:

$$\frac{d}{dr}\left(r^2\left(\frac{1}{r}\frac{du}{dr} - \frac{u}{r^2}\right)\right) = \eta^2 r u \tag{18}$$

$$\frac{d}{dr}\left(r\frac{du}{dr} - u\right) = \eta^2 r u \tag{19}$$

Deriving the terms:

$$\left(r\frac{d^2u}{dr^2} + \frac{du}{dr}\right) - \frac{du}{dr} = \eta^2 r u \tag{20}$$

Simplifying, we obtain a second-order, homogeneous differential equation with constant coefficients:

$$\frac{d^2u}{dr^2} - \eta^2 u = 0 \tag{21}$$

Using the usual procedure for solving differential equations of this type and as the roots of the characteristic polynomial $m^2 - \eta^2 = 0$, they are real and different $m_{1,2} = \pm\eta$, the general solution to this differential equation has the form:

$$u(r) = Ae^{-\eta r} + Be^{\eta r} \tag{22}$$

To evaluate the constants A y B, the potential function $\psi(r) = \frac{u(r)}{r}$ It must meet certain conditions:

1.-***Condition at large distances***: The potential must tend to zero when the distance $r \to \infty$. This is because the ionic atmosphere neutralizes the charge of the central ion. Therefore $\psi(r) \to 0$, the exponentially increasing term $e^{\eta r}$ must be zero. This implies that B = 0.

2.-***Short-range condition***: Near the central ion (when $r \to 0$), The potential should resemble the Coulomb potential, which diverges as 1/r, es decir $\psi(r) \to \frac{e \cdot z_i}{4\pi\varepsilon r}$. This means that ψ(r) must be of the form $\psi(r) = \frac{Ae^{-\eta r}}{r}$.

When comparing asymptotic behavior to $r \to 0$ (where $e^{-\eta r} \approx 1$)[23], it is obtained that $A = \frac{e \cdot z_i}{4\pi\varepsilon}$. Substituting the values of A and B into the general solution, we obtain the Debye-Hückel potential given by the expression:

$$\psi(r) = \frac{e \cdot z_i}{4\pi\varepsilon r} e^{-\eta r} \tag{23}$$

This electric potential, known as the **Debye-Hückel potential**, is exponential in nature. It differs from the classical electric potential given by equation (3), which decreases hyperbolically with distance. *This means that the actual potential of a central ion in an electrolytic solution decays more rapidly with distance compared to the electric potential given by classical electrostatics*. However, simply understanding the resulting mathematical difference is insufficient. To grasp why this potential decays more rapidly, it is necessary to visualize what actually happens near a central ion both with and without an external electric field. This will allow us to understand the implications of the Debye-Hückel shielding parameter, which plays a crucial role in the behavior of the Debye-Hückel potential. The notion of the "*ionic atmosphere*" that forms around a central ion (*isolated ion within the electrolytic solution*) deduced by Debye and Hückel provides compelling explanations in this regard.

***Ionic atmosphere (without the presence of an electric field (E))***.- The ionic atmosphere is a "*cloud*" of oppositely charged ions surrounding a central ion in an electrolytic solution. It forms due to electrostatic interactions between the ions and the solvent molecules. Its formation is a dynamic process and can be understood as follows:

1. *The central ion and electrostatic attraction*.- When an electrolyte is dissolved in a solvent (*such as NaCl in water*), it dissociates into ions($Na^+$) y ($Cl^-$). Each individual ion, for example, a sodium cation ($Na^+$), it has a positive electric charge. This charge creates an electric field that attracts ions of opposite charge and repels ions of the same charge..

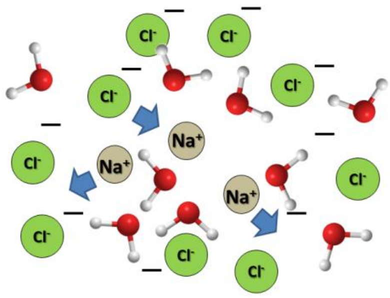



Fig.7. Migration of sodium ions by attracting counterions and repelling ions of the same type.

2. *Initial Solvation*.- Before the ionic atmosphere forms, each ion is first surrounded by solvent molecules (*hydration in the case of water*). Water molecules, being polar, orient their negative end (*the oxygen atom*) towards the cation.($Na^+$) and its positive end (the hydrogen atoms) towards the anion ($Cl^-$). This stabilizes the ions in the solution.

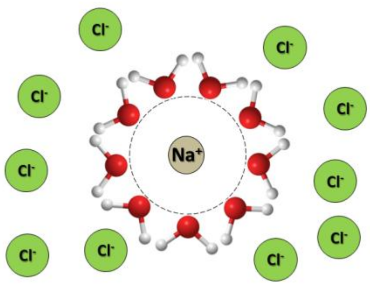



Fig. 8. Formation of the hydration layer.

3. *Theorigin of the ionic atmosphere*.- Due to electrostatic attraction, the central ion ($Na^+$) attracts the anions ($Cl^-$) in the vicinity of the solution. At the same time, it repels the other cations ($Na^+$) that approach. The result is that, on average, there is a higher concentration of anions ($Cl^-$) in the immediate vicinity of the cation ($Na^+$) than there would be in the rest of the solution. This "*cloud*" of counter-ions that accumulates around the solvation layer and the central ion is known as the ionic atmosphere.

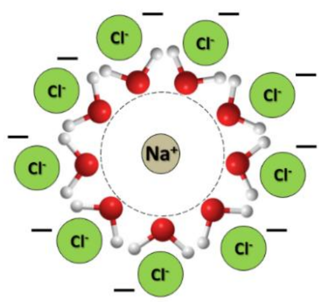



Fig. 9. Formation of the ionic atmosphere for $Na^+$ ion.

***Key characteristics of the ionic atmosphere***

*Charge neutrality*: The total charge of the ionic atmosphere is equal in magnitude but opposite in sign to the charge of the central ion. This ensures that the combination of the central ion and its ionic atmosphere is, on average, electrically neutral.

*Diffuse nature*: The ionic atmosphere is not a rigid, static structure, but rather a statistical distribution of ions within a volume of solution (*Boltzmann distribution*). The ions are constantly moving, entering and leaving the sphere of influence of the central ion.

*Concentration dependence*: As the concentration of ions in the solution increases, the ionic atmosphere becomes denser and more compact. This intensifies the shielding effect and is the basis of the Debye-Hückel theory, which explains why the molar conductivity of a solution decreases with increasing concentration.

**Debye shielding parameter** ($\eta$).-This parameter, deduced above, is directly related to the ionic strength of the solution and other factors such as the permittivity (or dielectric constant) of the solvent ($\varepsilon$), the temperature ($T$), and the Boltzmann constant. ($k_B$ =1.38 × $10^{-23}$ J/K), the ions concentration ($n_{i,0}$) the ionic charge (valence, $z_i$). As the concentration of ions increases, the ionic strength also increases, causing the neutralizing effect of the central ion to become stronger. Dr. Debye called this effect "*shielding*." The expression for the shielding factor, already derived, is:

$$\eta = \sqrt{\frac{4\pi e^2}{\varepsilon k_B \cdot T} \sum_i n_{i,0} z_i^2} \tag{24}$$

In accordance with this expression:

1.- When ($n_{i,0}$) increases, the value of ($\eta$) also increases. This makes sense, since as the number of ions increases, so does the number of counter-ions surrounding the central ion, contributing to the shielding effect.

2.- It can be observed that the ion charge appears squared in the summation, which contributes to the increase of ($\eta$) due to its direct proportionality (*this term is found in the denominator of the fraction*).

3.- Conversely, the dielectric constant contributes to the decrease of the values of ($\eta$) since a high dielectric constant decreases the intensity of ionic interactions and is also found in the denominator of the fraction (*the higher the value of ε, the lower the value of η*).

4.- The absolute temperature ($T$) is in the denominator of the formula. This means that an increase in temperature, by raising the kinetic energy of the ions, reduces electrostatic shielding and therefore reduces the value of ($\eta$). A higher temperature also increases the thermal energy that tends to disperse the ionic atmosphere.

**Debye-Hückel Length** ($\xi$) – Denoted as $\xi$, this is the characteristic distance at which the electrostatic potential of a central ion decreases significantly (to approximately 1/e) of its initial value) due to the presence of the ionic atmosphere. In simpler terms, it is the average distance at which an ion "*senses*" the presence of other ions in the solution. Beyond this distance, the charge of the central ion is effectively "*shielded*" or neutralized by the surrounding cloud of oppositely charged ions. In **dilute solutions**, the ion concentration is low. The ionic atmosphere is more diffuse and dispersed. As a result, the Debye-Hückel length ($\xi$) is large, meaning that the potential of an ion influences a larger area of the solution. In **concentrated solutions**, the ion density is high.

The ionic atmosphere is dense and very close to the central ion. The Debye-Hückel length ($\xi$) is short, indicating that the ion potential is neutralized over a very small distance. Regarding the relationship between ($\eta$) and ($\xi$), the following can be summarized:

A large value of ($\eta$) (small $\xi$) means that the shielding is very effective, and the electric potential of an ion decays rapidly. Conversely, a small value of ($\eta$) (large $\xi$) indicates weak shielding, and the ion's potential extends over a greater distance in the solution[24,25].

***Ionic atmosphere (with the presence of an electric field (E))***.- In this case, the presence of an external electric field (*produced by a circuit with a direct or alternating current source*) significantly alters the ionic atmosphere, since the central ion will tend to move towards the oppositely charged electrode, but the ionic cloud will resist this movement, moving in the opposite direction due to the external charge, which has the opposite sign to the central ion. It was the Norwegian scientist Dr. **Lars Onsager** (1903-1976), Nobel Prize winner in Chemistry (1968), who deduced the main causes of the reduction in ion mobility in an electrolytic solution, based on the Debye-Hückel theory. These causes are the electrophoretic and relaxation effects, which are explained in detail below:

Fig. 10. Dr. Lars Onsager

***Electrophoretic effect***.- This effect occurs because each ion in an electrolytic solution is surrounded by an "*ionic atmosphere*" of polar solvent molecules (*which act as dipoles*) creating a first layer of solvation and oppositely charged ions (for example, the $Na^+$cation, surrounded by $H_2O$ molecules and ($Cl^-$) anions). When an electric field is applied, the central ion and its ionic atmosphere move in opposite directions. The movement of the ionic atmosphere drags solvent molecules along with it, creating a flow of liquid that acts as a viscous drag (*a kind of "wind"*) in the opposite direction to the movement of the central ion. This drag slows the movement of the central ion, reducing its speed and, therefore, its mobility. The higher the concentration of ions, the stronger this effect will be, since there will be more ionic interactions. This effect is modeled as an additional drag force, which, according to fluid mechanics, is the Stokes drag force on a sphere in a viscous medium. $F = 6\pi \cdot \mu \cdot r \cdot v$ . In this case, the "*drag*" is due to the movement of the solvent, and its flow rate depends on the electric field and the ionic atmosphere. From the Debye-Hückel electric potential, Dr. Onsager deduces the force that the ionic atmosphere exerts on the solvent. This results in an additional frictional force. The term that represents this effect is:

$$F_{electroforetic} = \frac{z_i e_0}{6\pi\mu} \cdot \eta \tag{25}$$

This term decreases mobility. The factor ($1/(6\pi\mu)$) comes from **Stokes' law**, which relates drag force to viscosity ($\mu$). The Debye-Hückel shielding factor ($\eta$) is directly related to ionic strength, which determines the density of the ionic atmosphere. As the concentration increases (*higher* ($\eta$)), this effect becomes stronger. It is important to emphasize that viscosity ($\mu$) directly influences electrophoretic drag. A more viscous solvent slows the movement of ions, reducing their conductivity.

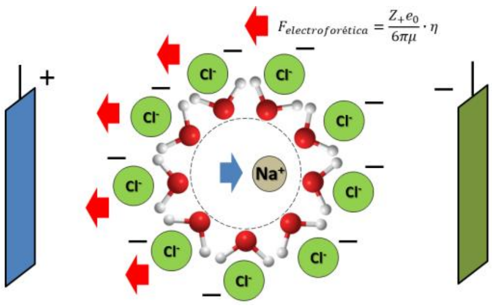



Fig. 11. Illustration showing how the electrophoretic force acts on a central ion in an electrolytic solution under the influence of an external electric field (***E***).

***Relaxing effect***.- This effect, also known as the asymmetry effect, arises from the lack of symmetry in the ionic atmosphere. In the absence of an electric field, the ionic atmosphere is spherically symmetric around a central ion. However, when the central ion moves due to the electric field, the ionic atmosphere takes a finite amount of time to reorganize itself around the ion's new position.

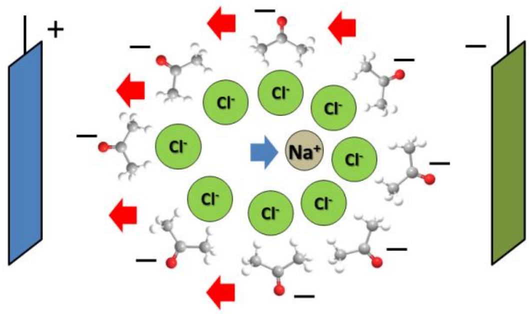



Fig.12. Illustration showing how the ionic atmosphere is distorted by the influence of the electric field (**E**).

The result is that the central ion is always "*ahead*" of its ionic atmosphere, which is behind it. This unbalanced ionic atmosphere, which has an opposite net charge, exerts an electrostatic braking force on the central ion, reducing its speed and mobility. The time it takes for the ionic atmosphere to relax and readjust is called the *relaxation time*. Dr. Onsager derived this relaxation force. Using an electrodynamics treatment for a charged sphere moving in a conductive medium, he determined the retarding force. The resulting term includes the ion's speed ($u$), charge ($e$), the dielectric constant of the medium or permittivity of the solvent ($\varepsilon$), the temperature ($T$), and, crucially, the factor (η). It is worth mentioning that the factor (ε) affects the strength of the interactions between the ions. *A high dielectric constant decreases the strength of the ionic interactions, which in turn minimizes the distortion of the ionic atmosphere and the relaxation effect*. The relaxation force then takes the form:

$$F_{relaxation} = \frac{e^2\omega}{6\varepsilon k_B T} \cdot \eta u_i^0 \tag{26}$$

Where the term (ω) is a geometric factor defined by:

$$\omega = \frac{z_+ z_- (2q)}{1+\sqrt{q}} \tag{27}$$

Where

$$q = \left(\frac{z_+ z_-}{z_+ + z_-}\right)\left(\frac{\lambda_+ + \lambda_-}{z_+\lambda_+ + z_-\lambda_-}\right) \tag{28}$$

The relaxation force is proportional to the ion mobility $u_+^0$, that is, the faster the ion moves, the more pronounced the lag of the ionic atmosphere. Regarding the parameters ($\omega$) and ($q$), the following applies:

In Onsager's conductivity theory, (ω) is known as the **Onsager factor**. This term represents ***the contribution of the ionic atmosphere to the movement of the central ion***. It arises from modeling the electrophoretic interaction (the movement of the solvent in the opposite direction) and relaxation (the asymmetry of the ionic atmosphere). The parameter ($q$), known as the ***valence-conductance factor***, is crucial for calculating the Onsager factor. It combines the charge of the ions and their mobility (represented by their equivalent ionic conductivities) to describe the strength of the ionic atmosphere. Finally, ($q$) depends on an important factor related to the conductivity of the electrolytic solution[20].

***Limiting equivalent ionic conductivity***(λ).- It is the contribution of a specific type of ion (e.g., $Na^+$ and $Cl^-$) to the total conductivity of the solution. Each ion has a different capacity to carry electrical charge, which depends on its size, charge, and the degree to which it is solvated (surrounded by solvent molecules). The ionic conductivity λ is limiting because the value refers to infinite dilution ($c \rightarrow 0$). At infinite dilution, the ions are so far apart that interactions between them are negligible. Therefore, the conductivity of each ion is at its maximum, and the total molar conductivity of the solution ($\Lambda_m$) is simply the sum of the limiting ionic conductivities of the individual ions. This was the basis of **Kohlrausch's Law** of Independent Migration of Ions, which is valid in ideal cases[26,27].

In summary, the (λ) values represent the conductivity of each ion in solution when there is no interaction with other ions. In Onsager theory, these are used to model how ions move in the ionic atmosphere and are therefore a key component in calculating the ($q$) factor and, consequently, the Onsager factor (ω). For the specific case of an electrolytic solution of NaCl in water: The limiting equivalent ionic conductivity $\lambda_+$ of the ($Na^+$) cation is approximately **50.10 S·cm²·mol⁻¹** and the value of $\lambda_-$of the anion ($Cl^-$) is approximately **76.3 S·cm²·mol⁻¹**.

**Modelo de Kohlrausch-Onsager**

The following shows the development of the **Kohlrausch-Onsager model** that predicts the behavior of molar conductivity ($\Lambda_m$). In an electrolytic solution where cations and anions are affected by an electric field ($E$) due to an electric current ($I$) (direct or alternating), there are two quantities strongly related to molar conductivity:

*Ionic mobility* ($u_i$): It measures the speed of an ion per unit electric field. It represents the ease with which an ion can move through the solution. It is measured in SI units in **(m/s)/(V/m)**.

*Faraday constant* ($F$): It represents the electric charge carried by one mole of electrons. Its value is approximately **96,485 C/mol**.

Within the electrolytic solution, the current ($I$) carried by an ionic species $i$ depends on its numerical concentration ($n_i$), its charge ($z_i \cdot e$), its drift velocity ($v_i$), and the cross-sectional area ($A$) through which it moves.

$$I_i = n_i \cdot z_i e \cdot v_i \cdot A \tag{29}$$

On the other hand, the drift velocity ($v_i$) of an ion is the product of its mobility ($u_i$) and the magnitude of the electric field ($E$), such that:

$$v_i = u_i \cdot E \tag{30}$$

According to the basic principles of electrodynamics, the current density $J_i$ would be:

$$J_i = n_i \cdot z_i e \cdot u_i \cdot E \tag{31}$$

According to microscopic **Ohm's law**, specific conductivity ($\kappa$) is related to current density ($J$) and electric field ($E$) as follows:

$$\kappa = \frac{J}{E} = \sum_i \frac{J_i}{E} = \sum_i n_i \cdot z_i e \cdot u_i \tag{32}$$

The sum is performed over all ionic species present (*for example, in the case of NaCl in aqueous solution, i =* 1,2). Now, remembering that the numerical concentration $n_i$ is related to the molar concentration $c_i$ through Avogadro's number $N_A$ as: $n_i = c_i \cdot N_A$ and that Faraday's constant ($F$) can be expressed as: $F = N_A \cdot e$; then the specific conductivity ($\kappa$) is now:

$$\kappa = \sum_i c_i \cdot (z_i N_A) u_i e \tag{33}$$

For an electrolyte that dissociates into cations (+) y anions (–), the total specific conductivity is:

$$\kappa = c(z_+ F u_+ + z_- F u_-) \tag{34}$$

If we divide the above expression by the molar concentration ($c$), we obtain a relationship for the molar conductivity $\Lambda_m$:

$$\Lambda_m = \frac{\kappa}{c} = z_+ F u_+ + z_- F u_- \tag{35}$$

In other words the molar conductivity ($\Lambda_m$) it expressed as the sum of the cations and anions contributions:

$$\Lambda_m = F(z_+ u_+ + z_- u_-) \tag{36}$$

Each term in the sum$z_i F u_i$, represents the molar ionic conductivity of species $i$, which is the contribution of the ions of that species to the total molar conductivity of the electrolyte. This expression demonstrates that the conductivity of an electrolyte depends directly on the charge of its ions and the ease with which they move in the solution. For a symmetric electrolyte, we can assume that $z_+ = z_- = 1$, so ($\Lambda_m$) would be expressed in terms of Faraday's constant and the ion mobilities:

$$\Lambda_m = F(u_+ + u_-) \tag{37}$$

However, the mobilities u_+ and u_- in the presence of an electric field will vary depending on the electrophoretic and relaxation effects as follows:

For the cation:

$$u_+ = u_+^0 - \left(F_{electroforetic} + F_{relaxation}\right) \tag{38}$$

Replacing the equations (25) and (26):

$$u_+ = u_+^0 - \frac{z_+ e}{6\pi\mu} \cdot \eta - \frac{e^2\omega}{6\varepsilon k_B T} \cdot \eta u_+^0 \tag{39}$$

$$u_+ = u_+^0 - \eta\left(\frac{z_+ e}{6\pi\mu} + \frac{e^2\omega}{6\varepsilon k_B T} u_+^0\right) \tag{40}$$

Similarly for the anion:

$$u_- = u_-^0 - \eta\left(\frac{z_- e}{6\pi\mu} + \frac{e^2\omega}{6\varepsilon k_B T} u_-^0\right) \tag{41}$$

Considering the charges symmetry $z_+ = z_- = z$. replacing (40) and (41) in the equatioon (37):

$$\Lambda_m = F\left(u_+^0 - \eta\left(\frac{ze}{6\pi\mu} + \frac{e^2\omega}{6\varepsilon k_B T} u_+^0\right) + u_-^0 - \eta\left(\frac{ze}{6\pi\mu} + \frac{e^2\omega}{6\varepsilon k_B T} u_-^0\right)\right) \tag{42}$$

Simplificando:

$$\Lambda_m = F(u_+^0 + u_-^0) - \left[\frac{Fz\eta e}{3\pi\mu} + \frac{e^2\omega\eta}{3\varepsilon k_B T} F(u_+^0 + u_-^0)\right] \tag{43}$$

Given that $\Lambda_m^0 = F(u_+^0 + u_-^0)$, then:

$$\Lambda_m = \Lambda_m^0 - \left[\frac{Fz\eta e}{3\pi\mu} + \frac{e^2\omega\eta}{3\varepsilon k_B T} \Lambda_m^0\right] \tag{44}$$

Remembering that the Debye-Hückel shielding factor is

$$\eta = \sqrt{\frac{4\pi e^2}{\varepsilon k_B \cdot T} \sum_i n_{i,0} z_i^2} = \sqrt{\frac{4\pi z^2 e^2 c N_A}{1000 \varepsilon k_B \cdot T}} \tag{45}$$

Replacing (45) in (44):

$$\Lambda_m = \Lambda_m^0 - \left[\frac{Fze}{3\pi\mu}\sqrt{\frac{8\pi z^2 e^2 N_A}{1000\varepsilon k_B \cdot T}} + \frac{e^2\omega}{6\varepsilon k_B T}\sqrt{\frac{8\pi z^2 e^2 N_A}{1000\varepsilon k_B \cdot T}} \Lambda_m^0\right]\sqrt{c} \tag{46}$$

If

$$\mathrm{A} = \frac{Fze}{3\pi\mu}\sqrt{\frac{8\pi z^2 e^2 N_A}{1000\varepsilon k_B \cdot T}} \tag{47}$$

and

$$\mathrm{B} = \frac{e^2\omega}{6\varepsilon k_B T}\sqrt{\frac{8\pi z^2 e^2 N_A}{1000\varepsilon k_B \cdot T}} \tag{48}$$

Then, **molar conductivity** is:

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c} \tag{49}$$

Since A, B y $\Lambda_m^0$ are constants that depend on the nature of the electrolyte and the solvent, equation (49) would have exactly the form of equation (6) described above, which is Kohlrausch'slaw $\Lambda_m = \Lambda_m^0 - K\sqrt{c}$ . The equation given by expression (49) is known as the **Kohlrausch-Onsager Law**. Dr. Kohlrausch's merit lay in having arrived at this form even without knowing the nature of the constant K, which Dr. Onsager aptly clarified. Now, from this mathematical model and relating it to equation $\Lambda_m = \frac{\kappa}{c}$, this is for the specific conductivity:

$$\frac{\kappa}{c} = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c}$$

$$\kappa = (\Lambda_m^0)c - (A + B\Lambda_m^0)c\sqrt{c} \tag{50}$$

Equations (49) and (50) represent the general mathematical model for the behavior of the molar ($\Lambda_m$) and specific ($\kappa$) conductivities, respectively, of an electrolytic solution where the solute is capable of dissociating into ions and conducting electricity. These equations represent the **Kohlrausch-Onsager Law** and are valid for low concentrations[28].

## III. EXPERIMENTAL

Ten electrolytic solutions were prepared with different concentrations (mol/cm$^3$) of the NaCl electrolyte in sterile medical-grade water ($\kappa$ = 1.4 μS/cm) by measuring the specific conductivity at a temperature of 23.5°C with a laboratory conductivity meter.

## IV. RESULTS AND DISCUSSIONS

Equation (4) was applied with experimental data of ($\kappa$) to determine the experimental data for molar conductivity ($\Lambda_m$). Equations (47) and (48) were applied to evaluate the Kohlraush-Onsager law constants A and B using the following values: *F* (*Faraday constant*) = 96485 C/mol, *e* (*elemental charge*) = 1.602 $\times 10^{-19}$ C, $N_A$ (*Avogadro number*) = 6.022 $\times 10^{23}$/mol, $k_B$ (*Boltzmann constant*) = 1.380 $\times 10^{-23}$ J/K and the solvent properties: *T* (*temperature*) = 296.7 K, $\varepsilon$ (*dielectric constant*) ≈ 6.946 $\times 10^{-10}$ C$^2$/Nm$^2$, $\mu$ (dynamic *viscosity*) ≈ 8.91 × $10^{-4}$ Pa·s, |z|=1, $\lambda_{+(Na)}$ = 50.10 S·cm²·mol$^{-1}$ , $\lambda_{-(Cl)}$ = 76.3 S·cm²·mol$^{-1}$, ω = 0.58 which were: A ≈ 215.34 S·cm$^2$/mol·(mol/cm$^3$)$^{-1/2}$ and B ≈ 10.2 (mol/cm$^3$)$^{-1/2}$. On the other hand, the value $\Lambda_m^0$ ≈ 3792.8 S·cm$^2$/mol @23.5°C was obtained. With this data the theoretical models for specific conductivity ($\kappa$) and molar conductivity ($\Lambda_m$) were obtained:$\Lambda_m = 3792.8 - 38901.9\sqrt{c}$and $\kappa = 3792.8c - 38901.9c\sqrt{c}$. The values of the solute concentrations and the theoretical and experimental values of the specific and molar conductivities can be observed in the following table:

Table 1. Theoretical and experimental data for molar ($\Lambda_m$) and specific ($\kappa$) conductivities for the dissolution of NaCl in pure water @23.5°C

| | Concentration | TheoreticalData | | Experimental Data | |
|---|---|---|---|---|---|
| g disolved in 100ml | *c* (mol/cm$^3$) | $\Lambda_m$ (S·cm$^2$/mol) | κ S/cm | $\Lambda_m$ (S·cm$^2$/mol) | κ S/cm |
| 0 | 0 | 3792.8 | 0 | 3792.8 | 0 |
| 0.002 | 3.42231E-07 | 3770.042177 | 0.001290227 | 2810.964 | 0.000962 |
| 0.003 | 5.13347E-07 | 3764.927474 | 0.001932714 | 3609.644 | 0.001853 |
| 0.005 | 8.55578E-07 | 3756.816723 | 0.003214251 | 3573.0216 | 0.003057 |
| 0.01 | 1.71116E-06 | 3741.911962 | 0.006402998 | 3696.33 | 0.006325 |
| 0.03 | 5.13347E-06 | 3704.659332 | 0.019017758 | 3038.88 | 0.0156 |
| 0.08 | 1.36893E-05 | 3648.866892 | 0.049950265 | 3345.69 | 0.0458 |
| 0.1 | 1.71116E-05 | 3631.877893 | 0.062147123 | 3132.384 | 0.0536 |
| 0.4 | 6.84463E-05 | 3470.955787 | 0.237573976 | 1132.275 | 0.0775 |
| 0.7 | 0.000119781 | 3367.040125 | 0.403307339 | 695.436 | 0.0833 |

The following graphs show the behavior oftheoretical and experimental values of the specific and molar conductivities

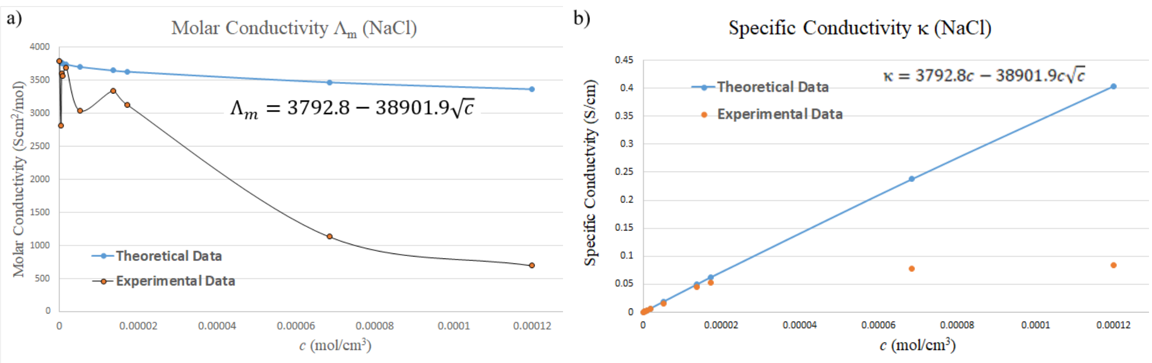



Fig. 13. For NaCl dissolution @25°C, a) Comparison of theoretical and experimental molar conductivity curves and b) Comparison of theoretical and experimental specific conductivity.

Figure 14 clearly shows that the experimental values are very similar to the theoretical values of the specific conductivity, while at higher concentrations the experimental data of k deviate from the ideal theoretical data and this can be explained by the electrophoretic and relaxation effects due mainly to the viscosity and permittivity of the solvent which distort the ionic atmosphere decreasing the mobility of the ions to conduct the electric current.

## V. CONCLUSIONS

The foregoing demonstrates the extraordinary synergy of the contributions of Drs. Friedrich Kohlrausch, Svante Arrhenius, Peter Debye, Erich Hückel, and Lars Onsager, which ultimately yields a law that can predict the electrical conductivity of a strong electrolytic solution, such as the typical case of NaCl in pure water. In general, the importance of mathematical modeling is evident, as it allows for the comparison of theoretical and experimental data, enabling us to understand why the physical quantities involved in a given phenomenon behave as they do. These findings pave the way for future research in the field of electrolytic solutions.

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