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# The connection between the Debye and Güntelberg Charging Processes and the importance of relative permittivity: the Ionic Cloud Charging Process

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## Abstract

The Debye and Güntelberg Charging Processes are essential tools for deriving electrolyte solutions' activity coefficient models. The Debye-Hückel, Born, and Mean Spherical Approximation are among some famous theories derived via charging processes. How they relate to each other, or if both charging processes are equivalent, or even if both are consistent, is a matter of discussion in the literature for many years. In this work, we evaluate the results from both charging processes using the Debye-Hückel and the Born equations, using different dependencies of the relative permittivity concerning salt concentration, temperature, and partial charging variable. Our results show that both charging processes are connected through a charging process here called the Ionic Cloud Charging Process. We show how these three charging processes relate to each other, verifying the magnitude of the derivatives of relative permittivity on the final models and their origin from the Ionic Cloud Charging Process.

# 1 Introduction

This paper is part of the Special Issue in Honor of Gabriele Sadowski. Prof. Sadowski's group was the first to use the full Debye-Hückel equation with electrolytes equations state, namely, the ePC-SAFT, in 2005<sup>1</sup>, while most uses of the Debye-Hückel equation relied on approximate versions of the original equation. After which, many works and developments with this equation have been done<sup>2-12</sup>, with a strong focus on electrolytes in biological systems. Since its origin, further improvements to the model were already suggested, such as including the Born term and concentration-dependent dielectric constant<sup>10,13-15</sup>. In this work, we further discuss the correlation of the full Debye-Hückel and Born equations with the concentration-dependent dielectric constant and charging processes.

The charging process is present at the core derivation of famous electrolyte theories, such as the Debye-Hückel equation<sup>16</sup> (DH), Hückel equation<sup>17</sup>, Born equation<sup>18</sup>, Mean Spherical Approximation<sup>19-23</sup>, Gronwall-LaMer-Sandved<sup>24</sup>. Therefore, it influences derived and extended equations from the previous ones, such as the Pitzer-Debye-Hückel equation<sup>25,26</sup>. These theories are used in electrolyte Equations-of-State<sup>7,10,13-15,27-33</sup> (e-EoS) to account for the electrostatic contributions of the system.

Other electrolyte theories which require numerical solutions, such as those developed for the Poisson-Boltzmann (PB) equation<sup>34-42</sup> and those using its several modifications<sup>43-51</sup> also require the charging processes to calculate thermodynamic properties.

In the aforementioned theories, the Güntelberg<sup>52</sup> and Debye charging processes<sup>53-55</sup> (respectively, GCP and DCP) are the most used approaches for calculating free energies and chemical potentials. The differences between both charging processes are still shrouded in some controversy. Earlier works<sup>56-58</sup> concerned with inconsistencies in the Poisson-Boltzmann equation, studied differences in chemical potential and activity coefficient from both charging processes. In these works, the result for the Linearized Poisson-Boltzmann equation was the same for both processes, while it was different for the non-linearized version. The resulting claim was that this result was a direct influence of the inconsistencies of

the non-linearized Poisson-Boltzmann equation.

In the colloid chemistry area, the electrostatic contributions were explored with different types of charging processes<sup>59-65</sup>, also based on the Güntelberg and Debye Charging processes and some modifications. In ionic solutions, a given ion can be considered to be part of the ionic atmosphere of another ion, and this second ion can be considered part of the first given ion. This symmetry is not present in colloid systems, where the colloids present a specific reference to the rest of the system. Therefore, it is more straightforward to work with respect to this given reference and not a general one, as done for ionic solutions.

Verwey and Overbeek<sup>59</sup> studied two different charging methods to calculate the Free energy of a double-layer system. They have shown that different charging pathways led to the same result of free energy for both systems. However, added to the different reference system of a colloid solution when compared to simple ionic solutions, both methods were derived to calculate the free energy directly, which is a different relation between DCP and GCP. The former calculates the electrical contribution to the Helmholtz Free Energy of the system, and the latter calculates the electrical contribution to a given ion chemical potential.

We have demonstrated in a previous work<sup>66</sup>, considering a constant relative permittivity, how the Linearized version of PB also has different results with GCP versus DCP for the Individual Ionic Activity Coefficient calculated with both methods while maintaining equal Mean Ionic Activity Coefficient results. Another interesting factor observed was that whenever the system was restricted (i.e., all ions have equal sizes), the results were equal with both charging processes. This demonstrates how both charging processes are able to give diverging results for some properties given the necessary conditions, without this implying that there is a fault of either charging processes or the underlying method studied.

In our previous paper<sup>67</sup>, we studied the effect of considering the concentration dependency of relative permittivity on different levels during the derivation of an activity coefficient model. We have compared the results using both the Debye-Hückel and Born equations. The model derived by the Shilov and Lyashchenko<sup>68</sup> (SL), although it introduces the relative per-

mittivity concentration dependency before the charging process, presented different results from our model with the same level of concentration dependency.

Lei et al.<sup>69</sup> and Sun et al.<sup>70</sup> have shown numerically that the activity coefficient of the SL model equals the one calculated with the Extended Debye-Hückel and Born equations (without the derivatives of relative permittivity with respect to the number of ions in solution). Shilov and Lyashchenko<sup>71</sup>, and Valiskó and Boda<sup>72</sup> have shown the same result analytically. It is, therefore, not further explained theoretically why it is so and why different models, at different levels of concentration, dependency of relative permittivity, may be equal, despite the implied derivatives with respect to concentration.

In this work, we start by evaluating the differences between GCP and DCP at three different levels of relative permittivity dependency: (1) constant; (2) concentration and temperature dependent; (3) partial charge variable, concentration, and temperature dependent. Finally, we develop a theory to explain this difference, the Ionic Cloud Charging Process (ICCP), showing how it connects the GCP and DCP physically and thermodynamically at any given level.

## 2 Theory

### 2.1 The Linearized Poisson-Boltzmann Equation

As presented in previous work from our group<sup>66</sup>, the Linearized Poisson-Boltzmann Equation is a common starting point to derive not only the Debye-Hückel equation and many of its variations but also to derive the Born equation. We have demonstrated their derivations considering a constant relative permittivity<sup>66</sup>. However, different relative permittivity concentration-dependent and temperature-dependent models can be considered at different levels during the derivation of Debye-Hückel and Born equations. We divided the relative permittivity models into two categories: (1) charge-dependent, which naturally can be considered before the charging process is used in the derivation; (2) charge-independent, which

needs additional assumptions to be considered before the charging process. Before deriving any specific equation, we highlight the important variables and equations to be used here.

The first quantity of importance is the Debye screening length, which can be defined as

$$\kappa_s = \sqrt{\frac{F^2}{\epsilon_s \epsilon_0 R T V}} \sqrt{\sum_i n_i z_i^2} \quad (1)$$

where  $\epsilon_s$  is a constant relative permittivity of the pure solvent,  $\epsilon_0$  is the vacuum relative permittivity,  $R$  is the ideal gas constant,  $T$  is the temperature,  $V$  is the volume,  $n_i$  and  $z_i$  are respectively the number of moles, and the charge of the  $i$ -th ion, and  $F$  is the Faraday constant, given by  $F = e_0 N_A$ , where  $e_0$  is the elementary charge,  $N_A$  is the Avogadro's constant.

We note that the Debye screening length is a quantity that depends not only on the relative permittivity of the solution but exists because of and depends on the charge of the ions in it. Considering further that the relative permittivity is a function of the concentration of the ions and the temperature of the solution, given by  $\epsilon_r$ , we have that the screening length is represented by:

$$\kappa = \sqrt{\frac{F^2}{\epsilon_r \epsilon_0 R T V}} \sqrt{\sum_i n_i z_i^2} \quad (2)$$

Finally, if we consider that  $\kappa_s$  and  $\kappa$  are quantities related only to the solution with fully charged ions, we have to consider a different Debye screening length during the charging process due to the partial charges of the ion, which is given by:

$$\kappa(\lambda) = \sqrt{\frac{F^2}{\epsilon_r(\lambda) \epsilon_0 R T V}} \sqrt{\sum_i n_i z_i^2 \lambda^2} \quad (3)$$

where  $\lambda$  is the partial charging variable. We highlight that  $\kappa$  considers not only the partial charges but the partial relative permittivity  $\epsilon_r(\lambda)$ . A relation between the previously defined

screening length is:

$$\kappa(\lambda) = \kappa\lambda \sqrt{\frac{\epsilon_r}{\epsilon_r(\lambda)}} = \kappa_s \lambda \sqrt{\frac{\epsilon_s}{\epsilon_r(\lambda)}} \quad (4)$$

Although  $\kappa_s$  also contains the charge of the ions inside its equation, we note that we have defined  $\kappa_s$  as the Debye screening length of an electrolyte solution with fully charged ions. We will also introduce a fourth representation of the inverse screening length, which does not depend on the relative permittivity, given by:

$$\kappa_* = \sqrt{\frac{F^2}{\epsilon_0 RTV}} \sqrt{\sum_i n_i z_i^2} = \kappa_s \sqrt{\epsilon_s} = \kappa \sqrt{\epsilon_r} = \kappa(\lambda) \frac{\sqrt{\epsilon_r(\lambda)}}{\lambda} \quad (5)$$

## 2.2 The Güntelberg and Debye Charging Processes

The Güntelberg charging process<sup>52</sup> (GCP) is characterized by charging the central ion of interest in a solution where all other ions are already charged. This is done from a given considered electrostatic potential  $\psi_i$ , which commonly is derived from the linearized Poisson-Boltzmann equation in the context of Debye-Hückel equations<sup>36</sup>. It calculates the activity coefficient of an individual ion through

$$RT \ln \gamma_i^{el} = N_A z_i e_0 \int_0^1 \psi_i(\lambda) d\lambda \quad (6)$$

Although the GCP calculates the activity coefficient directly (and, therefore, also the chemical potential), we can use the basic thermodynamic relations to find the free energies associated with this activity coefficient. This will be explored in the next section of this work. The Debye charging process<sup>52</sup> is characterized by charging all ions in a solution simultaneously. It calculates the Helmholtz free energy from a given electrostatic potential through

$$A^{el} = N_A \sum_{i=1}^s n_i z_i e_0 \int_0^1 \psi_i(\lambda) d\lambda \quad (7)$$

From the Helmholtz free energy, all other thermodynamic properties of interest can be derived, and this will also be explored in the next section of this work. The previously cited equations are not new in literature, being only fundamental descriptions of what has already been established. Now we move on to discuss what we obtain by applying both processes at three different levels of relative permittivity dependence on important thermodynamic variables.

### 2.3 Thermodynamic properties from both charging processes (DCP and GCP)

In the following cases, all derived properties will have a superscript indicating their derived method (DCP or GCP) followed by a number indicating the level of relative permittivity (0 for constant, 1 for concentration, and temperature dependent, and 2 for partial charge, concentration, and temperature dependent). The following sections will present the derivations for the DH and Born potentials (respectively, the ion-ion and self-energy contributions).

More details on the derivations for all the properties are presented in the Supplementary Material of this work. Also, for brevity purposes, we highlight that a constant relative permittivity is represented by  $\epsilon_s$ , while a concentration and temperature-dependent relative permittivity is represented by  $\epsilon_r$ . Finally, if the relative permittivity also depends on the partial charge variable  $\lambda$ , we represent it by  $\epsilon_r(\lambda)$ . The equations and models derived in this work are summarized in Table 1.

Table 1: Activity coefficient equations and models used in this work.

Model	Equations for $\ln\gamma_i^{DH}$	Equations for $\ln\gamma_i^{Born}$	Comments
$GCP_0$	(19)	-	GCP with $\epsilon_s$
$\Delta\sigma_0$	(20)	-	Only term that differentiates GCP and DCP with $\epsilon_s$
$ICCP_0$	(20)	-	ICCP with $\epsilon_s$ , equal to $\Delta\sigma_0$
$DCP_0$	(18)	-	DCP with $\epsilon_s$



Table 1 continued from previous page

Model	Equations for $\ln\gamma_i^{DH}$	Equations for $\ln\gamma_i^{Born}$	Comments
$GCP_1$	(39)	(40)	GCP with $\varepsilon_r$
$\Delta\sigma_1$	(43)	-	Term that differentiates $GCP_1$ and $DCP_1$ which does not contain the derivative of $\varepsilon_r$ with respect $n_i$
$\Delta\varepsilon_1$	(44)	(45)	Term that differentiates $GCP_1$ and $DCP_1$ which contains the derivative of $\varepsilon_r$ with respect $n_i$
$ICCP_1$	(43)+(44)	(45)	ICCP with $\varepsilon_r$ , equal to $\Delta\sigma_1+\Delta\varepsilon_1$
$DCP_1$	(37)	(38)	DCP with $\varepsilon_r$
$GCP_2$	(63)	(64)	GCP with $\varepsilon_r(\lambda)$ , equal to GCP with $\varepsilon_r$
$\Delta\sigma_2$	(66)	(68)	Term that differentiates $GCP_2$ and $DCP_2$ which does not contain the derivative of $\varepsilon_r$ with respect $n_i$ , when $\varepsilon_r(\lambda)$
$\Delta\varepsilon_2$	(67)	(69)	Term that differentiates $GCP_2$ and $DCP_2$ which contains the derivative of $\varepsilon_r$ with respect $n_i$ , when $\varepsilon_r(\lambda)$
$ICCP_2$	(66)+(67)	(68)+(69)	ICCP with $\varepsilon_r(\lambda)$ , equal to $\Delta\sigma_2+\Delta\varepsilon_2$
$DCP_2$	(61)	(62)	DCP with $\varepsilon_r(\lambda)$

To do the interconversion between the molarity and molality of the solution, we use the correlation of Novotný and Söhnel<sup>73</sup>. The Experimental Correlation and Michelsen-Mollerup-Breil<sup>55</sup> (MMB) models used for the relative permittivity and the models' parameters for the different ions are presented in the Supplementary Material of this work. Further details on how both models are introduced before the charging process are presented in our previous work<sup>67</sup>. In the Results section, instead of presenting the chemical potential calculations, we will present activity coefficient calculations, which are related to the chemical potential equations using the following equation:

$$\ln\gamma_i = \frac{\mu_i}{RT} \quad (8)$$

However, we consider the activity coefficients as the mole fraction rational, unsymmetrical activity coefficient, which has a reference in the infinite dilution case and is therefore calculated by:

$$\ln\gamma_i = \frac{1}{RT} \left[ \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j} - \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n=0} \right] \quad (9)$$

This is an important aspect, as in this case, the Born term is zero at the constant relative permittivity case, for example. However, as we are interested mainly in the impact of the activity coefficient level, which is used in many relevant chemical engineering models as we have previously defined, we choose this analysis method. We will also present results for the Mean Ionic Activity Coefficient, calculated for a single salt via

$$\ln\gamma_{\pm} = \frac{\nu_+ \ln\gamma_+ + \nu_- \ln\gamma_-}{\nu_+ + \nu_-} \quad (10)$$

### 2.3.1 Case 0. Constant relative permittivity

In this section, we remark that all equations are derived considering that the relative permittivity is constant, given by  $\epsilon_s$ . We begin with the basic thermodynamic properties that can be calculated using the DCP. The properties derived by this method in this section will have a superscript  $X, Y_0$ , to indicate that they pertain to case 0 derived using the charging process  $Y$ , for a given potential  $X$ . The Helmholtz free energy is given by:

$$A^{DH,DCP_0} = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{3N_A} \sum_{i=1}^s n_i z_i^2 \chi_{i,0} \quad (11)$$

where  $\chi_{i,0}$  is an auxiliary variable calculated by

$$\chi_{i,0} = \frac{3}{(\kappa_s a_i)^3} \left[ \ln(1 + \kappa_s a_i) - \kappa_s a_i + \frac{1}{2} (\kappa_s a_i)^2 \right] \quad (12)$$

From the Helmholtz free energy, we can derive the electrostatic pressure and electrostatic contribution to the entropy using the relations  $P^{el} = - \left( \frac{\partial A^{el}}{\partial V} \right)_{T,n}$ , and  $S^{el} = - \left( \frac{\partial A^{el}}{\partial T} \right)_{V,n}$ . The results are given by:

$$P^{DH,DCP_0} = - \frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} \frac{1}{V} \sum_{i=1}^s n_i z_i^2 \sigma_{i,0} \quad (13)$$

$$S^{DH,DCP_0} = - \frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} \frac{1}{T} \sum_{i=1}^s n_i z_i^2 \sigma_{i,0} \quad (14)$$

where

$$\sigma_{i,0} = \frac{\partial \kappa_s \chi_{i,0}}{\partial \kappa_s} = \frac{3}{(\kappa a_i)^3} \left[ 1 + \kappa_s a_i - \frac{1}{1 + \kappa_s a_i} - 2 \ln(1 + \kappa_s a_i) \right] \quad (15)$$

From the above properties, we can also calculate the Gibbs free energy, and internal energy, given by:

$$G^{DH,DCP_0} = A^{DH,DCP_0} + P^{DH,DCP_0} V = - \frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} \sum_{i=1}^s n_i z_i^2 (2\chi_{i,0} + \sigma_{i,0}) \quad (16)$$

$$U^{DH,DCP_0} = A^{DH,DCP_0} + S^{DH,DCP_0} T = - \frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} \sum_{i=1}^s n_i z_i^2 (2\chi_{i,0} + \sigma_{i,0}) \quad (17)$$

We can see from the above equations that  $G^{DH,DCP_0} = U^{DH,DCP_0}$  because  $P^{DH,DCP_0} V = S^{DH,DCP_0} T$ . The relative permittivity constant implies no difference between the internal energy and Gibbs energy of the system. The activity coefficient is given by:

$$RT \ln \gamma_i^{DH,DCP_0} = - \frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} z_i^2 \left( 2\chi_{i,0} + \frac{\sum_{k=1}^s n_k z_k^2 \sigma_{k,0}}{\sum_{k=1}^s n_k z_k^2} \right) \quad (18)$$

Equation (18) is most commonly known as the Debye-Hückel equation (also referred to as DHFULL<sup>55,74</sup>, presented in the original paper of Debye and Hückel<sup>16</sup>).

We now turn our attention to the GCP, which derives the activity coefficient/chemical

potential directly, given by:

$$RT \ln \gamma_i^{DH, GCP_0} = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} z_i^2 (2\chi_{i,0} + \sigma_{i,0}) = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{2N_A} z_i^2 \frac{\kappa_s}{1 + \kappa_s a_i} \quad (19)$$

In a previous work<sup>66</sup>, we have shown how both chemical potentials/activity coefficients differ from each other by the following equation:

$$RT \ln \gamma_i^{DH, diff_0} = RT \ln \gamma_i^{DH, DCP_0} - RT \text{ext} \ln \gamma_i^{DH, GCP_0} = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} z_i^2 \left( \frac{\sum_{k=1}^s n_k z_k^2 \sigma_{k,0}}{\sum_{k=1}^s n_k z_k^2} - \sigma_{i,0} \right) \quad (20)$$

It is then easy to see that while the activity coefficient derived using DCP includes the size-asymmetric effects from all the other ions in solution through the  $\frac{\sum_{k=1}^s n_k z_k^2 \sigma_{k,0}}{\sum_{k=1}^s n_k z_k^2}$  term, the GCP does not include any parameters from the other ions into its activity coefficient, substituting this term by only  $\sigma_{i,0}$ . This is the first basic difference between the GCP and DCP and hints that both processes are not equal, considering their derived thermodynamic properties.

Another interesting aspect of this difference is that as the GCP activity coefficient does not consider size-asymmetric effects, the Individual Ionic Activity Coefficient (IIAC) of a given ion, calculated via GCP, is insensible to changing the counterion size (only the charges, which are contained into the screening length), as the sizes of other ions are not used in this equation. This is different from what is expected from simulation and experimental results<sup>75–79</sup>. If the IIAC from GCP was theoretically correct, the only difference between the electrostatic part of the IIAC of a  $Na^+$  ion in a  $NaCl$  and  $KCl$  solution would be due to other contributions.

From Equation (20) we can also demonstrate, as discussed in our previous work<sup>66</sup>, that the MIAC for GCP and DCP is equal (although the IIAC is different). If we consider the

MIAC for a binary salt, using the activity coefficient equation, we have that :

$$\ln\gamma_{\pm}^{DH,diffo} = \frac{\mathbf{v}_+ \ln\gamma_+^{DH,diffo} + \mathbf{v}_- \ln\gamma_-^{DH,diffo}}{\mathbf{v}_+ + \mathbf{v}_-} \quad (21)$$

Considering that  $\Theta = -\frac{F^2}{4\pi\epsilon_s\epsilon_0RT} \frac{\kappa_s}{6N_A}$ , for this case, we also have that:

$$RT\ln\gamma_+^{DH,diffo} = \Theta z_+^2 \left( \frac{n_+ z_+^2 \sigma_{+,0} + n_- z_-^2 \sigma_{-,0}}{n_+ z_+^2 + n_- z_-^2} - \sigma_{+,0} \right) \quad (22)$$

As for a binary salt solution  $z_i^2 = \mathbf{v}_j^2$ , we have that:

$$RT\ln\gamma_+^{DH,diffo} = \Theta \mathbf{v}_-^2 \left( \frac{\mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0}}{\mathbf{v}_+ \mathbf{v}_-^2 + \mathbf{v}_- \mathbf{v}_+^2} - \sigma_{+,0} \right) \quad (23)$$

Substituting Equation (23) and its analogous equation for the anion into Equation (21), we obtain:

$$RT\ln\gamma_{\pm}^{DH,diffo} = \frac{\Theta}{\mathbf{v}_+ + \mathbf{v}_-} \left[ \mathbf{v}_+ \mathbf{v}_-^2 \frac{\mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0}}{\mathbf{v}_+ \mathbf{v}_-^2 + \mathbf{v}_- \mathbf{v}_+^2} - \mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \right. \\ \left. \mathbf{v}_- \mathbf{v}_+^2 \frac{\mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0}}{\mathbf{v}_+ \mathbf{v}_-^2 + \mathbf{v}_- \mathbf{v}_+^2} - \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0} \right] \quad (24)$$

The first and third terms inside the brackets in the above equation contain a common part.

If we join them, we obtain:

$$RT\ln\gamma_{\pm}^{DH,diffo} = \frac{\Theta}{\mathbf{v}_+ + \mathbf{v}_-} \left[ (\mathbf{v}_+ \mathbf{v}_-^2 + \mathbf{v}_- \mathbf{v}_+^2) \frac{\mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0}}{\mathbf{v}_+ \mathbf{v}_-^2 + \mathbf{v}_- \mathbf{v}_+^2} - \mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} - \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0} \right] \quad (25)$$

From the above equation, we can cut out the numerator and denominator of the first term inside the brackets, further obtaining:

$$RT\ln\gamma_{\pm}^{DH,diffo} = \frac{\Theta}{\mathbf{v}_+ + \mathbf{v}_-} [\mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} + \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0} - \mathbf{v}_+ \mathbf{v}_-^2 \sigma_{+,0} - \mathbf{v}_- \mathbf{v}_+^2 \sigma_{-,0}] = 0 \quad (26)$$

As the above equation equals zero, we have demonstrated that although the IIAC calculated from  $diff_0$  is not zero, the MIAC is, and therefore, the MIAC for GCP and DCP is equal.

### 2.3.2 Case 1. Concentration and temperature-dependent relative permittivity

In this case, we consider that the relative permittivity is a function of both the salt concentration and the temperature. As these two variables are kept constant through the charging process, the relative permittivity is also kept constant during the charging process in this specific case. However, after we have gone through the charging process and started the derivation process towards other properties, we can consider such dependencies. Note that we will now use  $\kappa$ ,  $\chi_i$  and  $\sigma_i$  which are the respective versions of  $\kappa_s$ ,  $\chi_{i,0}$  and  $\sigma_{i,0}$  substituting  $\epsilon_s$  by  $\epsilon_r$ , where  $\epsilon_r$  is a function of salt concentration and temperature.

The Helmholtz Free Energy calculated via the DCP is given by:

$$A^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{3N_A} \sum_{i=1}^s n_i z_i^2 \chi_i \quad (27)$$

Now that we consider the concentration dependency of the relative permittivity, we can also derive the equations for the Born term, where the Helmholtz Free Energy is given by:

$$A^{Born,DCP_1} = \frac{F^2}{4\pi\epsilon_r\epsilon_0 N_A} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \quad (28)$$

where  $b_i$  is the Born radius.

For the electrostatic pressure and electrostatic contribution to the entropy, we have:

$$P^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} \frac{1}{V} \sum_{i=1}^s n_i z_i^2 \left[ \sigma_i + (2\chi_i + \sigma_i) \frac{V}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial V} \right)_{T,n} \right] \quad (29)$$

$$S^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} \frac{1}{T} \sum_{i=1}^s n_i z_i^2 \left[ \sigma_i + (2\chi_i + \sigma_i) \frac{T}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial T} \right)_{V,n} \right] \quad (30)$$

$$P^{Born,DCP_1} = -\frac{F^2}{4\pi\epsilon_0 N_A} \frac{1}{\epsilon_r^2} \left( \frac{\partial \epsilon_r}{\partial V} \right)_{T,n} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \quad (31)$$

$$S^{Born,DCP_1} = -\frac{F^2}{4\pi\epsilon_0 N_A} \frac{1}{\epsilon_r^2} \left( \frac{\partial \epsilon_r}{\partial T} \right)_{V,n} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \quad (32)$$

and for the Gibbs free energy and internal energy, we have:

$$G^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} \sum_{i=1}^s n_i z_i^2 (2\chi_i + \sigma_i) \left[ 1 + \frac{V}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial V} \right)_{T,n} \right] \quad (33)$$

$$U^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa_s}{6N_A} \sum_{i=1}^s n_i z_i^2 (2\chi_i + \sigma_i) \left[ 1 + \frac{T}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial T} \right)_{V,n} \right] \quad (34)$$

$$G^{Born,DCP_1} = \frac{F^2}{4\pi\epsilon_r\epsilon_0 N_A} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left[ 1 - \frac{V}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial V} \right)_{T,n} \right] \quad (35)$$

$$U^{Born,DCP_1} = \frac{F^2}{4\pi\epsilon_r\epsilon_0 N_A} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left[ 1 - \frac{T}{\epsilon_r} \left( \frac{\partial \epsilon_r}{\partial T} \right)_{V,n} \right] \quad (36)$$

Now that we consider the concentration and temperature dependency of the relative permittivity, the Gibbs Free Energy and Internal Energy are no longer equal due to the terms containing the derivatives of relative permittivity. Only  $A^{DH}$  is obtained from the previous case by substituting  $\epsilon_s$  by  $\epsilon_r$ , as the other derived properties contain an extra term with a partial derivative of relative permittivity. The derived activity coefficient are

$$RT \ln \gamma_i^{DH,DCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} z_i^2 \left( 2\chi_i + \frac{\sum_{k=1}^s n_k z_k^2 \sigma_k}{\sum_{k=1}^s n_k z_k^2} \right) + \frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} \frac{1}{\epsilon_r} \left[ \sum_{k=1}^s n_k z_k^2 (2\chi_k + \sigma_k) \right] \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T,V,n_j} \quad (37)$$

and

$$RT \ln \gamma_i^{Born,DCP_1} = \frac{F^2}{4\pi\epsilon_0 N_A} \left[ \frac{z_i^2}{2b_i} \left( \frac{1}{\epsilon_r} - \frac{1}{\epsilon_s} \right) - \frac{1}{\epsilon_r^2} \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T,V,n_j} \sum_{j=1}^s \frac{n_j z_j^2}{2b_j} \right] \quad (38)$$

If instead we use the GCP, the activity coefficients are given by:

$$RT \ln \gamma_i^{DH,GCP_1} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} z_i^2 (2\chi_i + \sigma_i) \quad (39)$$

$$RT \ln \gamma_i^{Born,GCP_1} = \frac{F^2}{4\pi\epsilon_0 N_A} \frac{z_i^2}{2b_i} \left( \frac{1}{\epsilon_r} - \frac{1}{\epsilon_s} \right) \quad (40)$$

The only difference in the GCP from the previous case is substituting  $\epsilon_s$  by  $\epsilon_r$  in Equation (19) for the DH equation. The Born term was not derived in the constant relative permittivity case, as we are considering the infinite dilution as a reference. For the DCP, the difference is not only by the substitution of  $\epsilon_s$ , but also by the addition of a new term containing the derivative of relative permittivity with respect to the concentration. The difference between the activity coefficient calculated with the DCP and GCP is now given by:

$$RT \ln \gamma_i^{DH,diff_1} = -\frac{F^2}{4\pi\epsilon_s\epsilon_0} \frac{\kappa}{6N_A} z_i^2 \left( \frac{\sum_{k=1}^s n_k z_k^2 \sigma_k}{\sum_{k=1}^s n_k z_k^2} - \sigma_i \right) + \frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} \frac{1}{\epsilon_r} \left[ \sum_{k=1}^s n_k z_k^2 (2\chi_k + \sigma_k) \right] \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T,V,n_j} \quad (41)$$

$$RT \ln \gamma_i^{Born,diff_1} = -\frac{F^2}{4\pi\epsilon_0 N_A} \frac{1}{\epsilon_r^2} \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T,V,n_j} \sum_{j=1}^s \frac{n_j z_j^2}{2b_j} \quad (42)$$

Where  $\ln \gamma_i^{diff_1} = \ln \gamma_i^{DCP_1} - \ln \gamma_i^{GCP_1}$ .

In order for us to better understand the differences between the DCP and GCP, we introduce two auxiliary activity coefficients: (1)  $\ln \gamma_i^{l,\Delta\sigma}$ , which contains the difference between GCP and DCP activity coefficients without the relative permittivity derivatives; and (2)  $\ln \gamma_i^{l,\Delta\epsilon}$  which contains the difference between GCP and DCP activity coefficients with the relative permittivity derivatives. These terms are given by:



$$RT \ln \gamma_i^{DH, \Delta \sigma_1} = -\frac{F^2}{4\pi \epsilon_s \epsilon_0} \frac{\kappa}{6N_A} z_i^2 \left( \frac{\sum_{k=1}^s n_k z_k^2 \sigma_k}{\sum_{k=1}^s n_k z_k^2} - \sigma_i \right) \quad (43)$$

$$RT \ln \gamma_i^{DH, \Delta \epsilon_1} = \frac{F^2}{4\pi \epsilon_r \epsilon_0} \frac{\kappa}{6N_A} \frac{1}{\epsilon_r} \left[ \sum_{k=1}^s n_k z_k^2 (2\chi_k + \sigma_k) \right] \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T, V, n_j} \quad (44)$$

For the Born equation, we only have the  $\Delta \epsilon_1$  term, given by:

$$RT \ln \gamma_i^{Born, \Delta \epsilon_1} = -\frac{F^2}{4\pi \epsilon_0 N_A} \frac{1}{\epsilon_r^2} \left( \frac{\partial \epsilon_r}{\partial n_i} \right)_{T, V, n_j} \sum_{j=1}^s \frac{n_j z_j^2}{2b_j} \quad (45)$$

Using the above equations, we have as a general case for both the DH and Born equation:

$$\ln \gamma_i^{DCP_1} = \ln \gamma_i^{GCP_1} + \ln \gamma_i^{\Delta \sigma_1} + \ln \gamma_i^{\Delta \epsilon_1} \quad (46)$$

The equation is general in the sense that it applies to both DH and Born equations. However, for the Born equation, we remind that the term  $\Delta \sigma_1$  is zero.

It is easy to see from Equation (20) that only the term  $\ln \gamma_i^{el, \Delta \sigma}$  appears (using  $\epsilon_s$ ), while in Equation (41), both terms appears. We have also shown in previous work<sup>66</sup> that  $\sum_{i=1}^s \ln \gamma_i^{el, \Delta \sigma} = 0$  for a constant relative permittivity, which remains true when we analyze the  $\epsilon_r$  scenario. Analogously, we can also expect from the above reasoning that

$$G^{DCP_1} = G^{GCP_1} + G^{\Delta \sigma} + G^{\Delta \epsilon} \quad (47)$$

and

$$U^{DCP_1} = U^{GCP_1} + U^{\Delta \sigma} + U^{\Delta \epsilon} \quad (48)$$

For the DH and Born equations, the scenario is the same. The only difference is that the Born term does not depend on  $\kappa$ , and therefore the term  $\ln \gamma_i^{el, \Delta \sigma}$  does not appear on the final equation. We note that at the MIAC level, the  $\Delta \sigma_1$  term is also expected to be zero, following the exact same derivation using Equations (21) to (26).

### 2.3.3 Case 2. Partial charging variable, concentration, and temperature-dependent relative permittivity

Here, we start developing the DCP, considering at first a general dependency of  $\epsilon_r(\lambda)$ . For the Helmholtz free energy, considering the linearized Poisson-Boltzmann solution, we have that:

$$A^{DH,DCP_2} = -\frac{F^2}{4\pi\epsilon_0 N_A} \sum_{i=1}^s n_i z_i^2 \int_0^1 \frac{\lambda}{\epsilon_r(\lambda)} \frac{\kappa\lambda}{1 + \kappa a_i \lambda} d\lambda = -\frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s n_i z_i^2 \tau_i \quad (49)$$

$$A^{Born,DCP_2} = \frac{F^2}{4\pi\epsilon_0 N_A} \sum_{i=1}^s n_i z_i^2 \int_0^1 \frac{\lambda}{\epsilon_r(\lambda)} d\lambda = \frac{F^2}{4\pi\epsilon_0 N_A} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \xi \quad (50)$$

where

$$\tau_i = \int_0^1 \frac{\lambda}{\epsilon_r(\lambda)} \frac{\kappa\lambda}{1 + \kappa a_i \lambda} d\lambda \quad (51)$$

$$\xi = 2 \int_0^1 \frac{\lambda}{\epsilon_r(\lambda)} d\lambda \quad (52)$$

In our previous work<sup>67</sup>, we have shown how both charge-dependent and charge-independent relative permittivity models can be used as  $\epsilon_r(\lambda)$ . Charge-dependent models are naturally introduced into the charging process as the partial charge variable appears naturally to the model. On the other hand, charge-independent models need an arbitrary way to be introduced as varying during the charging process. In our previous work<sup>67</sup>, we have considered that  $\epsilon_r(\lambda) = \epsilon_r(c\lambda)$ , upon the idea that the same salt solution upon different total charges of ions would have the same relative permittivity. Shilov and Lyashchenko, in a series of works<sup>68,80–84</sup> have considered that  $\epsilon_r(\lambda) = \epsilon_r(\kappa\lambda)$ . The electrostatic contribution, based on Equations (49) and (50), to the entropy and pressure are:

$$P^{DH,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s n_i z_i^2 \left( \frac{\partial \tau_i}{\partial V} \right)_{T,n} \quad (53)$$

$$S^{DH,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s n_i z_i^2 \left( \frac{\partial \tau_i}{\partial T} \right)_{V,n} \quad (54)$$

$$P^{Born,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left( \frac{\partial \xi}{\partial V} \right)_{T,n} \quad (55)$$

$$S^{Born,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left( \frac{\partial \xi}{\partial T} \right)_{V,n} \quad (56)$$

Consequently, for the Gibbs free energy and internal energy, we have:

$$G^{DH,DCP_2} = -\frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s n_i z_i^2 \left( \tau_i - V \left( \frac{\partial \tau_i}{\partial V} \right)_{T,n} \right) \quad (57)$$

$$U^{DH,DCP_2} = -\frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s n_i z_i^2 \left( \tau_i - T \left( \frac{\partial \tau_i}{\partial T} \right)_{V,n} \right) \quad (58)$$

$$G^{Born,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left( \xi + V \left( \frac{\partial \xi}{\partial V} \right)_{T,n} \right) \quad (59)$$

$$U^{Born,DCP_2} = \frac{F^2}{4\pi\epsilon_0} \sum_{i=1}^s \frac{n_i z_i^2}{2b_i} \left( \xi + T \left( \frac{\partial \xi}{\partial T} \right)_{V,n} \right) \quad (60)$$

The activity coefficients are:

$$RT \ln \gamma_i^{DH,DCP_2} = -\frac{F^2}{4\pi\epsilon_0 N_A} \left[ z_i^2 \tau_i + \sum_{j=1}^s n_j z_j^2 \left( \frac{\partial \tau_j}{\partial n_i} \right)_{V,n} \right] \quad (61)$$

$$RT \ln \gamma_i^{Born,DCP_2} = \frac{F^2}{8\pi\epsilon_0 N_A} \left[ \frac{z_i^2}{b_i} \left( \xi - \frac{1}{\epsilon_s} \right) + \left( \frac{\partial \xi}{\partial n_i} \right)_{V,n} \sum_{j=1}^s n_j \frac{z_j^2}{b_j} \right] \quad (62)$$

For the GCP, we have to consider again that the charging of a single ion is not going to change neither the screening length nor the relative permittivity of the solution, so we have that:

$$RT \ln \gamma_i^{DH, GCP_2} = -\frac{F^2}{4\pi\epsilon_r\epsilon_0} \frac{\kappa}{6N_A} z_i^2 (2\chi_i + \sigma_i) \quad (63)$$

$$RT \ln \gamma_i^{Born, GCP_2} = \frac{F^2}{8\pi\epsilon_0 N_A} \frac{z_i^2}{b_i} \left( \frac{1}{\epsilon_r} - \frac{1}{\epsilon_s} \right) \quad (64)$$

Now, if the reasoning of eq. (46) is correct for this case, we have that:

$$\ln \gamma_i^{DCP_2} = \ln \gamma_i^{GCP_2} + \ln \gamma_i^{\Delta\sigma_2} + \ln \gamma_i^{\Delta\epsilon_2} \quad (65)$$

We have that for the DH equation:

$$RT \ln \gamma_i^{DH, \Delta\sigma_2} = -\frac{F^2}{4\pi\epsilon_0 N_A} \left[ z_i^2 \tau_i - \frac{\kappa}{6N_A} z_i^2 (2\chi_i + \sigma_i) \right] \quad (66)$$

and

$$RT \ln \gamma_i^{DH, \Delta\epsilon_2} = -\frac{F^2}{4\pi\epsilon_0 N_A} \sum_{j=1}^s n_j z_j^2 \left( \frac{\partial \tau_j}{\partial n_i} \right)_{v,n} \quad (67)$$

For the Born equation, we have that:

$$RT \ln \gamma_i^{Born, \Delta\sigma_2} = \frac{F^2}{4\pi\epsilon_0 N_A} \frac{z_i^2}{2b_i} \left( \xi - \frac{1}{\epsilon_r} \right) \quad (68)$$

and

$$RT \ln \gamma_i^{Born, \Delta\epsilon_2} = \frac{F^2}{8\pi\epsilon_0 N_A} \left( \frac{\partial \xi}{\partial n_i} \right)_{v,n} n_j \sum_{j=1}^s \frac{z_j^2}{b_j} \quad (69)$$

The current hypothesis in this work is that both  $\ln \gamma_i^{el, \Delta\epsilon}$  and  $\ln \gamma_i^{el, \Delta\sigma}$  can be generalized, independently of the relative permittivity case, into a separate charging process denominated Ionic Cloud Charging Process. This hypothesis is going to be tested in the Results section. In a previous work<sup>67</sup>, we have derived the so-called DHFULL-2 and Born-2 models using the above equations and considering that  $\epsilon_r(\lambda) = \epsilon_r(c\lambda)$ . We are also going to test the differences of our method against the Shilov-Lyashchenko model, which considers that  $\epsilon_r(\lambda) = \epsilon_r(\kappa_s \lambda)$ .

The reader is referred to the original works of both equations for a complete derivation analysis<sup>67,68</sup>. In Table 2 summarizes the differences between the DHFULL-2 and DH-SL approaches.

Table 2: Different variables in the DHFULL-2 and DH-SL models. The differences are highlighted in red.

Variable	DHFULL-2	DH-SL
$\Psi_i^{DH}$	$\frac{z_i e_0 \lambda}{4\pi \varepsilon_0 \varepsilon_r(c\lambda)} \frac{\kappa \lambda}{1 + \kappa \lambda a_i}$	$\frac{z_i e_0 \lambda}{4\pi \varepsilon_0 \varepsilon_r(\kappa_s \lambda)} \frac{\kappa \lambda}{1 + \kappa \lambda a_i}$
$A^{DH}$	$N_A \sum_{i=1} n_i z_i e_0 \int_0^1 \frac{z_i e_0 \lambda}{4\pi \varepsilon_0 \varepsilon_r(c\lambda)} \frac{\kappa \lambda}{1 + \kappa \lambda a_i} d\lambda$	$N_A \sum_{i=1} n_i z_i e_0 \int_0^1 \frac{z_i e_0 \lambda}{4\pi \varepsilon_0 \varepsilon_r(\kappa_s \lambda)} \frac{\kappa \lambda}{1 + \kappa \lambda a_i} d\lambda$
$\varepsilon_r(c, \lambda)$	$\varepsilon_s + \sum_{j=1}^k a_j (c\lambda)^{j/2}$	$\varepsilon_s + \sum_{j=1}^k b_j (\kappa_s \lambda)^{j/2}$

We note that although it seems possible to include  $\lambda$  inside an experimental correlation of relative permittivity through  $\kappa$ , that is not the case. First, the concentration (which is the natural variable of these correlations) relates to the inverse Debye screening length by

$$c = \frac{\kappa_s^2}{\varepsilon_s} \Omega = \frac{\kappa^2}{\varepsilon_r} \Omega = \frac{\kappa^2(\lambda)}{\varepsilon_r(\lambda) \lambda} \Omega = \kappa_*^2 \Omega \quad (70)$$

where

$$\Omega = \left( \frac{F^2}{\varepsilon_s \varepsilon_0 RT} \sum_i v_i z_i^2 \right)^{-1} \quad (71)$$

From a first analysis, it seems that we can arrive at an equation for concentration where the term  $\lambda$  appears. However, in that case, we are using the  $\kappa(\lambda)$  and  $\varepsilon_r(\lambda)$  terms, and as soon as we substitute Equation (4) to be able to calculate  $\kappa(\lambda)$ , we end up with the other relations, which do not contain  $\lambda$ .

It is, therefore, very important to distinguish the different definitions of  $\kappa$ . During the charging process,  $\kappa_s$  and  $\kappa$  do not contain the  $\lambda$  variable, only the  $\kappa(\lambda)$  variable, as defined. The concentration is a quantity that should also not depend on  $\lambda$  at any moment, as the charging process is a TVN process.

This problem is non-existent in charge-dependent models for relative permittivity. In

these models, the charges are contained in them as natural variables, and when we consider the charging process, they naturally transform from  $z_i e_0$  to partial charges  $z_i e_0 \lambda$ .

### 3 Results

First, to observe the impact of the derivatives of relative permittivity contained in term  $\Delta\epsilon$ , and also the differences in the extra term  $\Delta\sigma$ , we compare them to the *GCP* equation for *NaCl*. We have tested more systems, such as *CaCl<sub>2</sub>*, and the results are presented in the Supplementary Material. The results using the MMB correlation also are presented in the Supplementary Material of this work. The results are presented in Figure 1.

We can see from Figure 1 that the derivative parts of both DH and Born contributions do not cancel out, despite having similar magnitudes and opposite signs for both DH and Born counterparts. This is shown in the results of  $\Delta\epsilon_2$  and  $\Delta\epsilon_1$  of Figure 1(c), as it represents the sum of the  $\Delta\epsilon$  parts of both DH and Born parts. For the  $\Delta\epsilon_1$  case, this sum is monotonically increasing for *NaCl*, while  $\Delta\epsilon_2$  has a minimum. For *CaCl<sub>2</sub>*, both  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  have a maximum, as presented in Figure S.1.

As expected, at the constant relative permittivity case, the superimposed results for the  $\Delta\sigma_0$  and  $\Delta\sigma_1$  terms are zero (as already shown analytically by Equations (21) to (26), as the *diff<sub>0</sub>* term is equal to  $\Delta\sigma_0$ ), and the  $\Delta\sigma_2$  is non-zero because now it considers the integral of  $\epsilon_r(\lambda)$  with respect to  $\lambda$ , as shown in Figure 1. The  $\Delta\epsilon_2$  term is higher in magnitude for the DH equation when compared to  $\Delta\epsilon_1$ , and the inverse is true for the Born term. The  $\Delta\sigma_2$  and  $\Delta\epsilon_2$  have opposite signs both for DH and Born contributions, as shown in Figure 1(a) and (b), being respectively positive and negative for the DH contribution. Despite this, when we sum the terms, as shown in Figure 1, they do not cancel out.

The specific relative permittivity concentration has great impact on both the magnitude and sign of the  $\Delta\sigma$  and  $\Delta\epsilon$  contributions, as seen for the behaviors observed for *CaCl<sub>2</sub>* in the Supplementary Material for *CaCl<sub>2</sub>*, as presented in Figure S.1. Regarding the SL model,

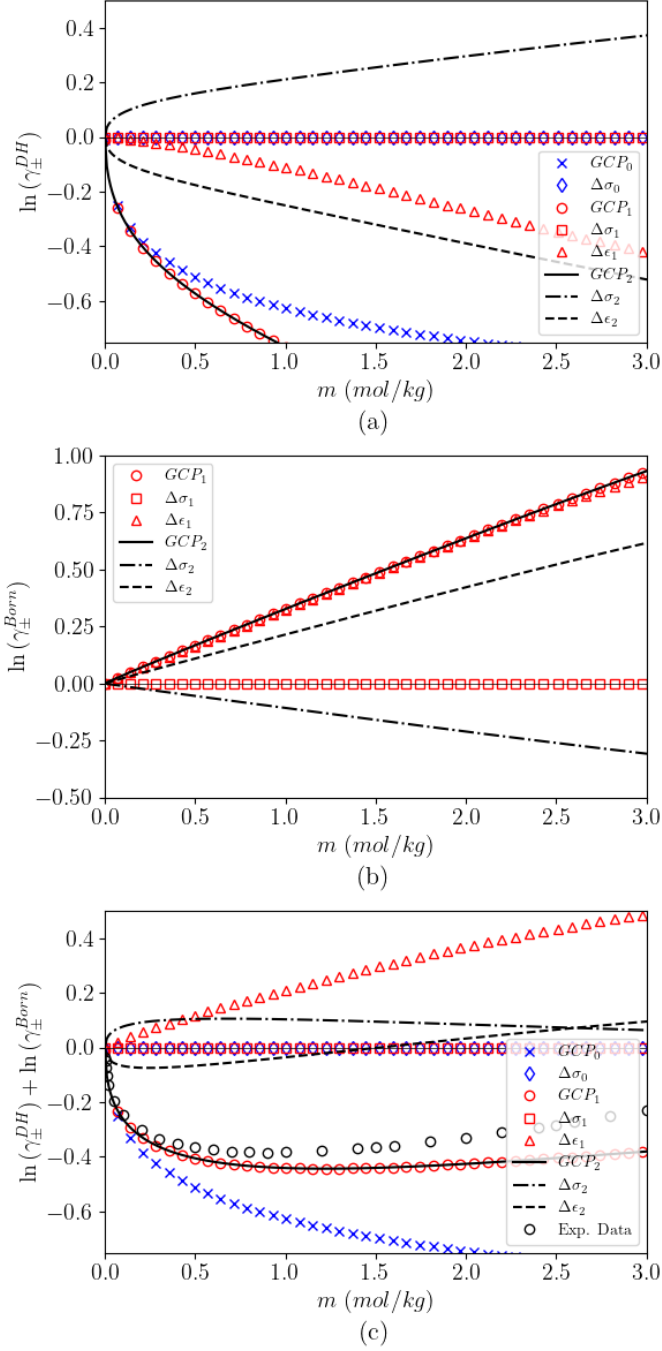


Figure 1: MIAC for  $NaCl - water$  at 298.15K using the Experimental Correlation relative permittivity model at different cases for relative permittivity, separated by the different terms. (a) Results for DH equation. (b) Results for Born equation. (c) Results for DH+Born equation.

we present the results for *NaCl* in Figure 2.

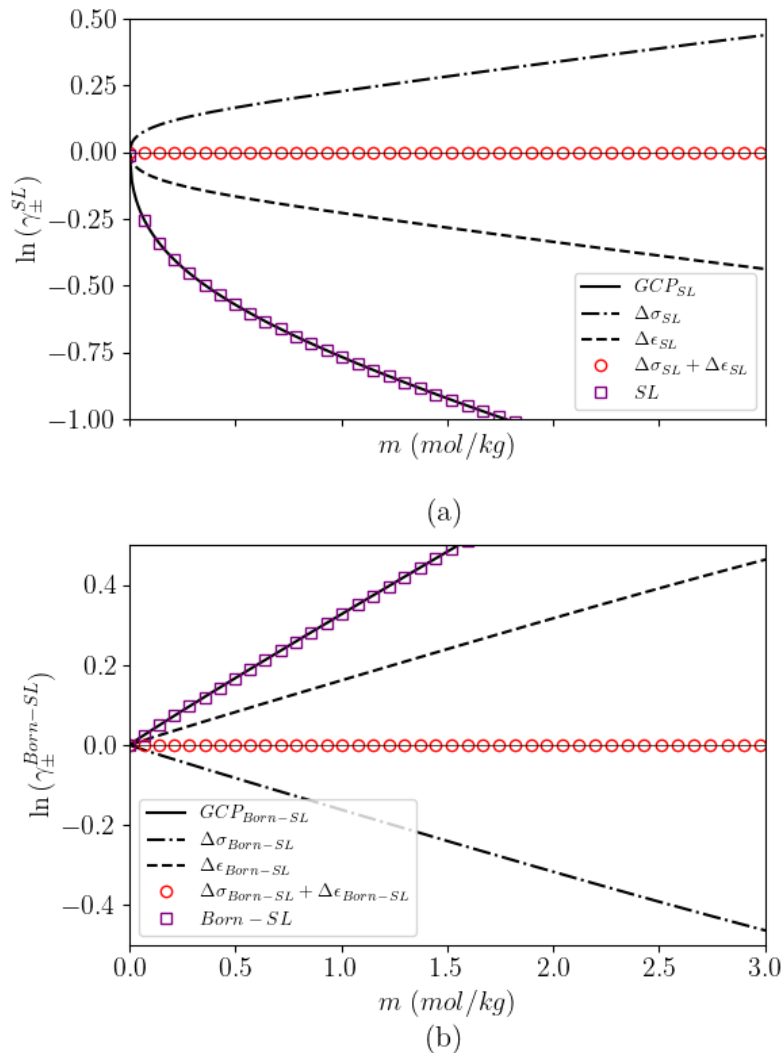


Figure 2: MIAC for *NaCl* – *water* at 298.15K using the Experimental Correlation relative permittivity model at different cases for relative permittivity, separated by the different terms using the SL model. (a) Results for SL equation. (b) Results for Born-SL equation. (c) Results for SL+Born-SL equation.

As it is clear from Figure 2, the SL model does contains at MIAC level non-zero  $\Delta\sigma$  and  $\Delta\epsilon$  contributions, as shown in Figure 2 (a) and (b) for both DH and Born counterparts. However, these contributions are equal in magnitude but of opposite signs, and therefore they cancel out, making the full DH-SL and Born-SL models equal to the equation derived with the GCP, despite being derived using the DCP. This result is achieved before summing the



DH and Born parts of the SL model, as shown in Figure 2. To understand which contributions are canceling out just at the MIAC level, we present results for IIAC in Figure 3.

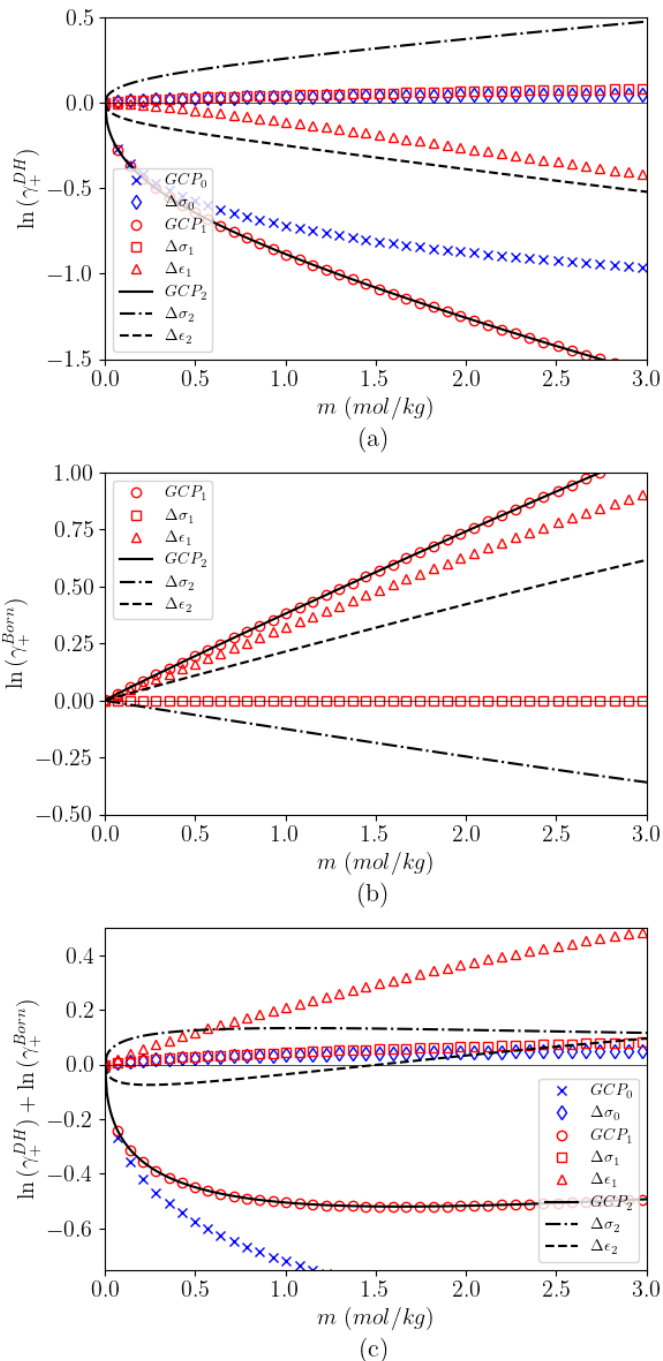


Figure 3: IIAC for  $Na^+$  in the system  $NaCl - water$  at 298.15K using the Experimental Correlation relative permittivity model at different cases for relative permittivity, separated by the different terms. (a) Results for DH equation. (b) Results for Born equation. (c) Results for DH+Born equation.

For the constant relative permittivity case, as shown in Figure 3, both the  $GCP_0$  and  $\Delta\sigma_0$  terms are non-zero, demonstrating that there is a difference already between DCP and GCP at this level of IIAC, as suggested previously for DH only in our previous work<sup>66</sup>, and now shown for both DH and Born equations. This is in contrast to the observed for the MIAC in Figure 1, where the  $\Delta\sigma_0$  term was already zero. Regarding Case 1, when adding the  $\Delta\epsilon$  term, which is also non-zero and negative for the DH term, while positive for the Born term, they also do not cancel when summed, as shown in Figure 3 (c). For Case 2, all terms are non-zero, and  $\Delta\epsilon$  becomes more negative for both the DH and Born terms, while  $\Delta\sigma$  becomes more positive for DH, and negative for the Born term (in Case 1, we do not have this term in the Born term, it is zero).

Little difference is observed in the trends for IIAC when compared to the MIAC. However, we note that all terms are non-zero at the IIAC level, contrary to the observed trends for the MIAC, meaning that they all contribute to the individual ion chemical potential and activity coefficient, but not necessarily to the mean properties of the salt. In our previous work<sup>66</sup>, we have already outlined why the term  $\Delta\sigma_0$  is non-zero at the IIAC level, but zero at the MIAC level.

## 4 Discussion

### 4.1 The Ionic Cloud Charging Process - Connecting the Debye and Güntelberg charging process

The most basic descriptive difference between the Debye and the Güntelberg charging process is that in the former, we charge all ions simultaneously, while in the latter, we charge a single ion in a solution where all ions are already charged. Physically, we must consider that this difference directly influences the thermodynamic properties that depend on the charges of the ions. When we charge all ions simultaneously through the DCP, we expect - at a physical level - that the relative permittivity and the screening length are going to change while the

ions are being charged. Thus, one would expect that all thermodynamic properties linked to the screening length and relative permittivity would also change during the charging process. Meanwhile, for the GCP, charging a single ion does not influence the screening length nor the relative permittivity of the solution, which remains unaltered through the charging process.

It has been debated and even affirmed that both processes would be thermodynamically equivalent<sup>85</sup>. The argument of equivalency has caused confusion for a long time with the discussion of the validity or not of the results calculated by the Poisson-Boltzmann equation. We have shown in a previous work<sup>66</sup> that this is not the case, as even for the Debye-Hückel equation, using constant relative permittivity, both processes can give different results for individual ion activity coefficient and chemical potential, but identical results for MIAC. The confusion in literature has reached a point where some researchers would affirm that if a theory tested through both processes would give different results, the theory might be inconsistent<sup>56,85,86</sup>.

Here we introduce what we call the Ionic Cloud Charging Process (ICCP), which is the first step in the DCP. In the ICCP, we charge all the ions in solution, excluding only the central ion of interest. Then, the next step of the DCP is charging the ion of interest through a GCP. Thus, the DCP can be divided into a two-step process, where the first one is the ICCP, and the second one is the GCP, as the sum of both is actually an alternative thermodynamic pathway to DCP. A schematic representation of the intercorrelation between ICCP, DCP, and GCP is presented in Figure 4.

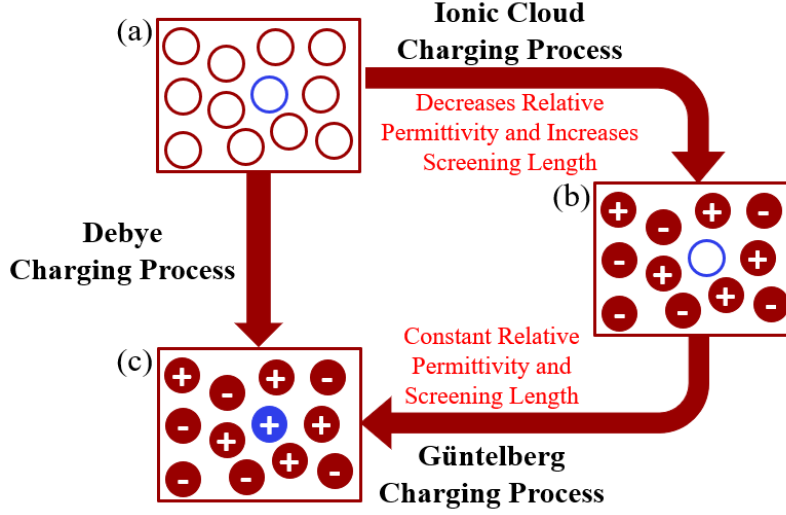


Figure 4: Schematic diagram on how the Ionic Cloud Charging Process and Güntelberg Charging Process connect with the Debye Charging Process as being an alternative thermodynamic pathway. (a) Solution with all the ions uncharged. (b) Solution where all the ions are charged, with the exception of the central observed ion. (c) Solution with all ions fully charged.

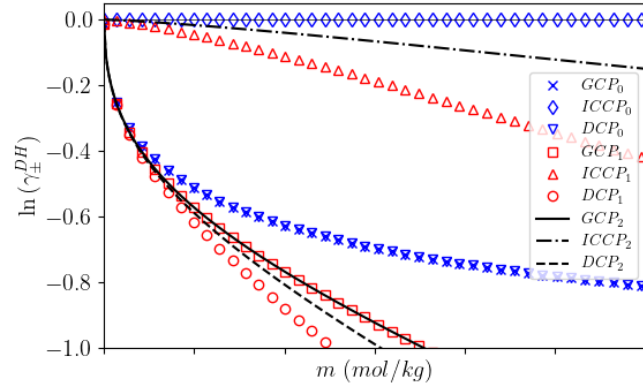
The previous description is only physical. Now we move on to test this possibility through thermodynamics by analyzing the results in this work at the three levels of relative permittivity dependence that we have considered. Furthermore, the results are generally not only to the DH potential (which is related to the ion-ion interaction) but also to the Born potential (which is related to the self-potential), showing that it can be generalized to electrostatic models. From a chemical potential perspective, we have that

$$\mu_i^{DCP} = \mu_i^{GCP} + \mu_i^{ICCP} \quad (72)$$

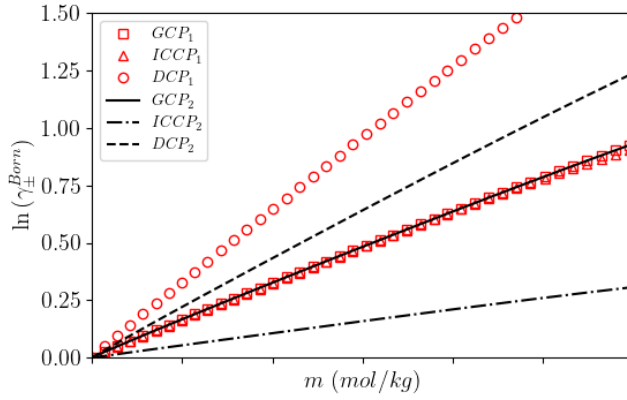
where (see Equations (46) and (65))

$$\mu_i^{ICCP} = \mu_i^{\Delta\sigma} + \mu_i^{\Delta\varepsilon} \quad (73)$$

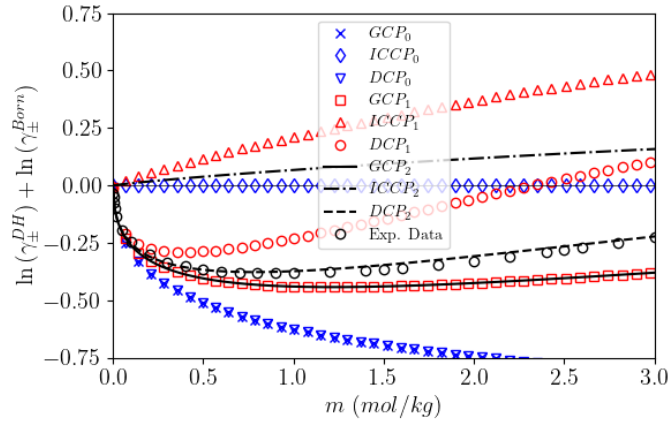
A comparison of how the MIAC of GCP, ICCP, and DCP compare is presented in Figure 5.



(a)



(b)



(c)

Figure 5: MIAC for  $NaCl - water$  at 298.15K using Experimental Correlation relative permittivity model at different cases for relative permittivity, comparing the DCP, GCP, and ICCP results. (a) Results for DH equation. (b) Results for Born equation. (c) Results for DH+Born equation.

Basically, acknowledging that the DCP is actually divided into GCP and ICCP is a recognition that analyzing a system solely by using the GCP gives an incomplete description, as other additions ( $\Delta\sigma + \Delta\epsilon$ ) are necessary to better describe the ion-ion interactions (and also the ion-solvent interactions in the primitive approach). When analyzing derived thermodynamic properties from the free energies, we need to consider all contributions that go into it, and just considering a system where we repeat the GCP up to  $n$  times does not give us all the necessary free energy that we need to analyze the whole system. Regarding the two specific terms of ICCP,  $\Delta\sigma$  and  $\Delta\epsilon$ , we note that the former encloses the size-asymmetric effects between cation and anion and also the effect of charging the relative permittivity during the charging process. The latter encloses the effect of the relative permittivity derivative with respect to the ions' composition.

A schematic comparison of how both ICCP and GCP relate to each other in terms of the changes in relative permittivity and screening length is presented in Figure 6. Thermodynamically we are able to divide the chemical potential and activity coefficient into either relative permittivity or constant screening length, where the ICCP also has an influence. However, this is only a mathematical tool that respects the laws of thermodynamics.

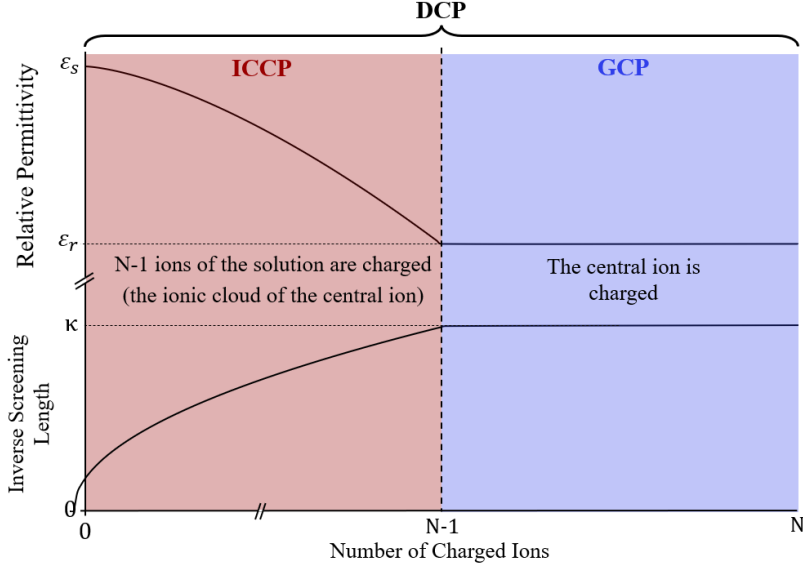


Figure 6: Schematic diagram of the behavior of relative permittivity and screening length during the ICCP and GCP parts of the DCP, relating to the physical picture of both processes in a pedagogical approach. The ICCP encloses both the decrease of relative permittivity and the increase of the inverse screening length. Even for the constant relative permittivity case, there is an influence of the ICCP due to the change in the screening length.

We have already discussed in a previous work<sup>66</sup> why the GCP and DCP are equal at the MIAC level, and we have analytically shown in this work this result proving that the  $\Delta\sigma_0$  contribution is zero at the MIAC level, but not at the IIAC level as this term is the only difference between GCP and DCP when the relative permittivity is constant. The same derivation is true for  $\Delta\sigma_1$ , as this term is mostly affected when the relative permittivity concentration dependency is considered before the charging process, as shown by the non-zero  $\Delta\sigma_2$  term even at the MIAC level. The previous explanation relied on the size-asymmetric effects that gave rise to the  $\Delta\sigma_0$  are averaged out at the MIAC level, and this term becomes zero. Now we also have an extra influence on this term due to the charging variable being integrated simultaneously with the relative permittivity, which makes it non-zero even at the MIAC level, as shown by our results. At all levels of relative permittivity concentration dependency (with different models for  $\epsilon_r$  and for the potential being charged), we reach the same conclusion that the ICCP is a complement to GCP, and its addition amounts to the DCP contribution to the electrostatic chemical potential and activity coefficient.

A possible concern might arise from a physical aspect stating that as we go through the ICCP, we break the system charge-neutrality, and therefore the process should not be considered at all. This is the same case for the GCP, but in this process, we are completing a 'missing' charge in the system. However, we note that only the DCP would respect the charge neutrality through all the steps of the process, further enhancing that both the ICCP and GCP would complete each other to provide a more meaningful physical picture. These processes are, therefore, imaginary, and the splitting we are providing here is presented and proven from a thermodynamical standpoint. Further, this is unavoidably important to understand which contributions can arise from which of the processes and also show how both of the processes are important to be considered. This splitting of the DCP to ICCP and GCP is based on the classical thermodynamics framework, and we do not consider, given these arguments, this concern to be a significant problem.

## **4.2 The impact of relative permittivity derivatives, and the ICCP**

Our results point out that the derivatives of relative permittivity are by no means naturally canceled at any level or should be disregarded as being of low magnitude, both for DH and Born equations, contrary to some previous comments<sup>87,88</sup>. We highlight that some recent studies also note that the derivatives of relative permittivity have a great impact on the activity coefficients of electrolyte solutions<sup>31,33</sup>.

In order to better understand the magnitude of the terms which contain the relative permittivity derivatives with respect to composition, we present the relative contributions in Figure 7.



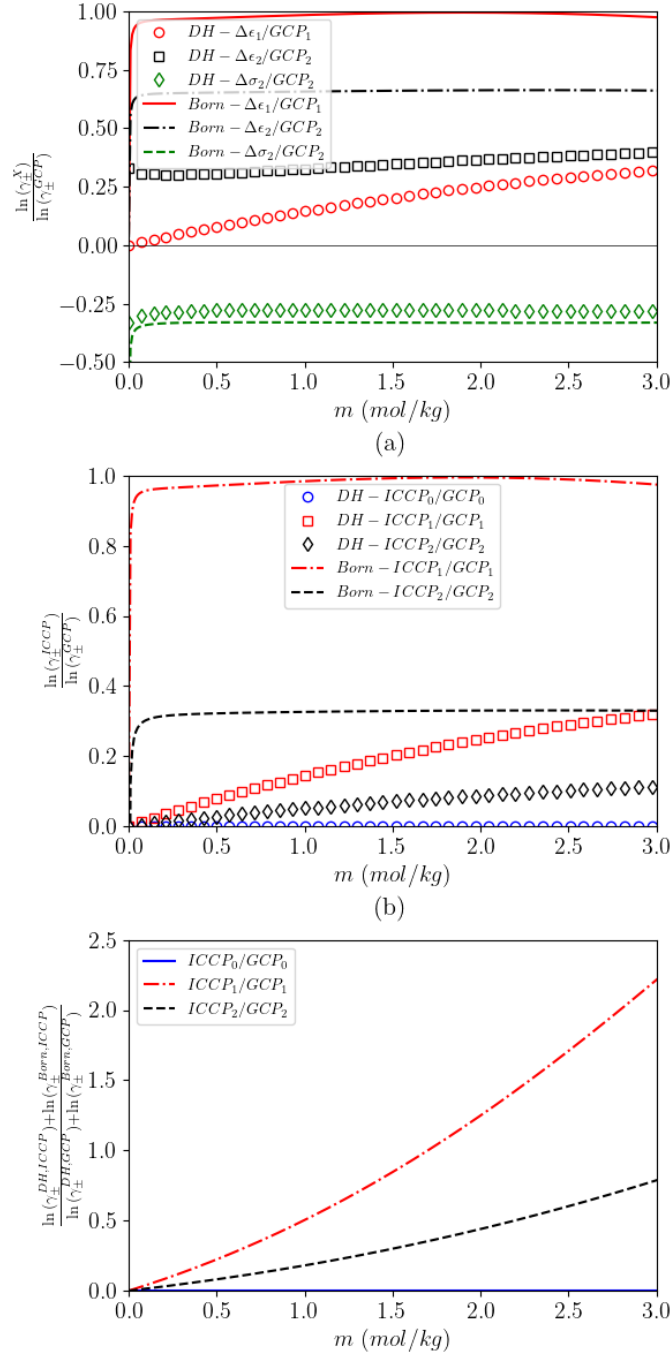


Figure 7: Ratios of different activity coefficient contributions for *NaCl* – *water* at 298.15K using the Experimental Correlation relative permittivity model. (a) Ratios between  $\Delta\sigma$  and  $\Delta\epsilon$  terms by *GCP*. (b) Ratios between *ICCP* by *GCP* separated by DH and Born contributions. (c) Ratios between *ICCP* by *GCP* considering the sum of DH and Born contributions. "X" refers to a given contribution detailed in the legend.

In Figure 7(a), the  $\Delta\sigma$  contribution (which, for the MIAC, is zero at all other levels except for the  $\epsilon_r(\lambda)$  case), is roughly at constant 1/4 of an order of magnitude when compared to the GCP. The  $\Delta\epsilon$  contribution, on the other hand, for the case where the relative permittivity is considered after the charging process, is of equal order of magnitude when compared to the GCP for the Born term and increasingly important for the DH term. When considering  $\epsilon_r(\lambda)$ , its magnitude reduces to roughly 60% of the GCP for the Born term while increasing to a roughly constant 30% of the GCP for the DH term.

A special case is seen we consider these two terms summed into the ICCP term and compare it with the GCP term, as presented in Figure 7(b). Specifically, when changing from the  $\epsilon_r$  case, where the relative permittivity concentration dependency is considered only after the charging process, to the  $\epsilon_r(\lambda)$  case. It becomes more clear that the ICCP reduces its magnitude, when compared to the GCP, for both the DH and Born contributions but still remains with a considerable order of magnitude. Finally, from Figure 7(c), we see that the full ICCP term, considering the sum of DH and Born terms, is increasingly important in magnitude when compared to the GCP as the molality of the solution increases. It also surpasses the magnitude of the GCP term, as seen by the ratio above 1. The same conclusions were seen with the MMB model, although with different orders of magnitude. This result is presented in the Supplementary Material.

Although we show that these terms are expected naturally for activity coefficients, there is a problem in evaluating the magnitude of the derivatives from different models. The experimental data of relative permittivity data is measured against the concentration of the salt, while the thermodynamic models are derived with respect to the mole compositions of the ions. This disconnection between the measured property to be derived, and the derivative calculated in the model, prevents us from analyzing the "correctness" of the derivatives from different models. Therefore, although different models, such as the ones used in this work, represent almost equally well the relative permittivity concentration dependency, they might not represent equally well the derivative of relative permittivity with respect to the

composition of the ions. Further discussion is necessary to clarify this subject.

Another important note is the difference between using charge-dependent or charge-independent relative permittivity models. Charge-dependent models should naturally be considered as Case 2. The reason is that they already contain charges in their models, which must scale during the charging process because the charges of the ions change through it. Reserving the analysis to this type of model, we see that either for the DH and Born equations, all the terms derived here are preserved at all levels of thermodynamic properties considered in this work.

The picture for charge-independent models is rather different. There is no natural way to consider it as a function of the partial charging variable. We need, therefore, to consider an arbitrary method to introduce it in the model as Case 2. In our previous work<sup>67</sup>, we have derived a method that is able to also conserve the influence of all the terms of ICCP into the final equation. Thus preserving the influence of the derivatives of relative permittivity with respect to the ion mole numbers, which naturally appear during the derivation. We have also highlighted that the SL model, as demonstrated by diverse authors<sup>69–72</sup>, did not preserve such derivatives. Their model, therefore, equals a model derived using only the GCP.

A diagram highlighting which terms are (or are not) conserved in each of these models is presented in Figure 8. There is no consensus yet in literature as to the importance of these terms, but as discussed in this work, they are naturally expected at the chemical potential and activity coefficient level when using models without the arbitrary introduction of the partial charging variable. We have also highlighted how important and magnitude they are to the final model. Therefore, we deem it important that their influence remains preserved in the final equations.

Finally, we have demonstrated that only in the constant relative permittivity case we have an equality between the electrostatic pressure and entropy, which results in an equality between internal energy and Gibbs free energy. When moving to the other cases, these

contributions are no longer equal.

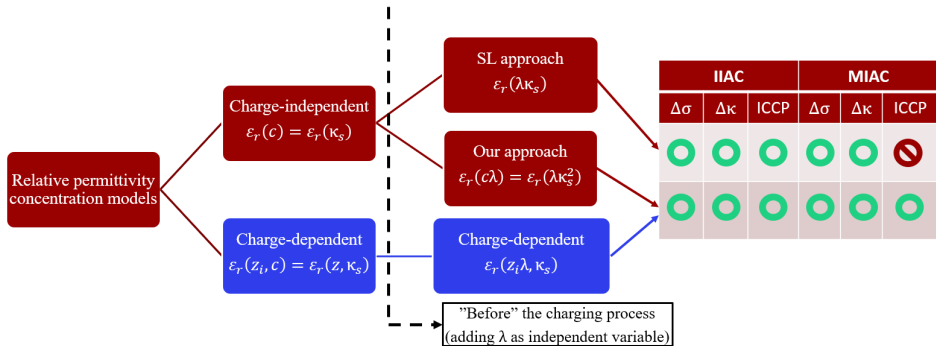


Figure 8: Schematic diagram highlighting the division of relative permittivity models into charge-dependent, and charge-independent models, with the methods used to introduce the dependency of the partial charging variable. The influence of the ICCP in the MIAC of the SL model is zero because for this model and level,  $\Delta\sigma = -\Delta\epsilon$ . The schematic is valid for both the Born and DH contributions.

### 4.3 On the divergence between our method and the Shilov-Lyashchenko model for concentration-dependent relative permittivity

Shilov and Lyashchenko, in a series of works<sup>68,80–84</sup>, have developed a model to calculate the activity coefficient of ions and solvent in solution by using the Debye Charging Process. They have considered that the relative permittivity also depends on the partial charging variable as  $\epsilon_r(\kappa_w, \lambda)$ . Their model achieves very good results for activity coefficients for a series of electrolytes in solution. Other authors, including also Shilov and Lyashchenko<sup>70,72,89,90</sup> have demonstrated that their model equals the DHFULL-0 and Born-0 models (for reference of the models' derivation and equations, we reference our previous work<sup>67</sup>). These DHFULL-0 and Born-0 models are Debye-Hückel and Born equations where the relative permittivity depends on the concentration. However, their activity coefficients and chemical potentials equations do not have the derivatives of relative permittivity with respect to the ions' concentration.

In our previous work<sup>67</sup>, we have demonstrated how a different way of considering the relative permittivity dependency on the partial charging variable is capable of preserving the derivatives in the chemical potential and activity coefficient. We deem it necessary to

use a correlation for relative permittivity, which naturally contains the charges of the ions (such as the MMB model) and also conserves the derivatives at the chemical potential and activity coefficient level.

We have shown in our results that the SL model does contain the  $\Delta\epsilon$  and  $\Delta\sigma$  contributions. However, they cancel out for both the DH-SL and Born-SL equations. The basic difference from our previous DHFULL-2 model to the SL model is considering  $\epsilon_r(\kappa_0^2\lambda)$  (which is equivalent to  $\epsilon_r(c\lambda)$ ), instead of  $\epsilon_r(\kappa_0\lambda)$ . To explain how a little difference of the  $\epsilon_r(\lambda)$  model can make these contributions cancel out, we have derived the activity coefficient equation for a general  $\epsilon_r(\kappa_0^n\lambda)$  model. For the Born equation, considering a common ion-size approach, we have

$$\left(\frac{\partial A^{Born}}{\partial n_i}\right)_{T,V,n_j} = N_A \frac{z_i^2 e_0^2}{4\pi\epsilon_0} \frac{1}{2b_i} \left( \frac{1}{\epsilon_r(\kappa_0^n\lambda)} - \frac{(n-1)\lambda^2}{\epsilon_r(\kappa_0^n\lambda)^2} \left( \frac{\partial \epsilon_r(\kappa_0^n\lambda)}{\partial \kappa_0^n\lambda} \right) d\kappa_0^n\lambda \right) \quad (74)$$

As shown in the above equation, the term that contains the derivative of relative permittivity with composition (in this derivation, this term considers  $\Delta\epsilon + \Delta\sigma$ , which is the ICCP term) is multiplied by  $n - 1$ , where  $n$  is the power of  $\kappa_0^n$ . As the SL model considers this power to be one, it is, therefore, a special case of the above equation where this term is going to be zero. Therefore, the influence of the ICCP is zero in the final equation, and thus the final model is equal to the GCP model. A schematic diagram relating how the ICCP and GCP models are considered in the SL model is presented in Figure 9.

The full derivation for the Born and DH equations of the above case are presented in the Supplementary Material of this work, together with the MIACs of the unrestricted case for DH and Born, which have the same conclusion. It is not the aim of this work to discuss which is the best method of  $\epsilon_r(\kappa_0^n\lambda)$ . A comparison between the two models is already presented in our previous work<sup>67</sup>. However, we highlight again that the derivatives are preserved when we consider a concentration-dependent correlation model for relative permittivity, which already contains the charges in it.

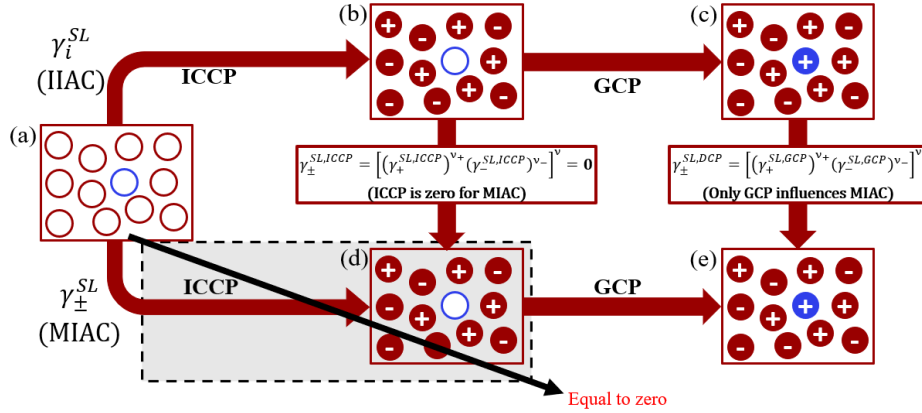


Figure 9: Schematic diagram of the DCP steps when deriving the SL model. The ICCP part of the Debye Charging Process is zero for the MIAC. Therefore, the MIAC calculated using the DCP is equal to the GCP. The IIAC conserves the ICCP influence in the final equation. The solution states in each Figure are: (a) all ions uncharged. (b,d) all ions are charged, with the exception of the central observed ion. (c,e) all ions fully charged. (b) and (c) consider the calculation of the IIAC, while (d) and (e) consider the calculation of the MIAC.

## 5 Conclusions

We have derived a new theory, the ICCP, to explain the differences between the DCP and GCP. We have demonstrated how the ICCP connects the GCP and DCP at any given level of relative permittivity. Moreover, we have tested the hypothesis not only using the DH potential, but also the self-potential used to calculate the Born term. We have also used different relative permittivity concentration correlations (charge-dependent and charge-independent), and the result was the same. We demonstrated how the SL model also contains the terms from the ICCP, but they cancel out during the calculation of the MIAC (but not of the IIAC). The derivatives of relative permittivity have great impact on the results of MIAC and IIAC, representing an important part of the model, and also distancing the electrostatic contribution to the Gibbs free energy and internal energy. The ICCP parts that come from DH and Born, although having contrary signs, do not cancel out. Although important in magnitude, the ICCP shows in the observed cases, for MIAC and IIAC, the same qualitative behavior of the GCP, as expected when comparing the qualitative behaviors

of GCP and DCP, which are the same, and therefore, the ICCP is also expected to have the same behavior.

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## Supplementary Material

We provide a Supplementary Material containing more details on the derivations of the models, and further results for other relative permittivity concentration dependent models, and salts.

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# TOC Graphic

