Sodium Chloride, NaCl/ε: New Force Field

Raúl Fuentes-Azcatl* and Marcia C. Barbosa*

Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970, Porto Alegre, RS, Brazil

E-mail: razcatl@hotmail.com; marcia.barbosa@ufrgs.br

*To whom correspondence should be addressed
Abstract

A new computational model for Sodium Chloride, the NaCl/\(\varepsilon\), is proposed. The Force Fields employed here for the description of the NaCl is based on a set of radial particle-particle pair potentials involving Lennard-Jones (LJ) and Coulombic forces. The parameterization is obtained fitting the density of the crystal and the density and the dielectric constant of the mixture of salt with water at diluted solution. Our model shows good agreement with the experimental values for the density and surface tension for the pure system and for the density, the viscosity, the diffusion, and the dielectric constant for the mixture with water at various molal concentrations. The NaCl/\(\varepsilon\) together with the water TIP4P/\(\varepsilon\) model provide a good approximation for studying electrolyte solutions.

Introduction

Sodium Chloride is present in our lives from the chemical balance of our body to the geophysical and biological equilibrium of the planet. In addition to these natural applications, NaCl it is also largely used in industry, particularly to preserve food. Therefore, the understanding of physical-chemical properties of sodium chloride as a pure substance or in mixtures is important. Due to the abundance of NaCl dissolved in water, one of the key questions regarding salt is how the it behaves in solution under different pressures and temperatures and also under confinement.\(^{1-4}\)

A number of experimental studies have addressed the behavior of Sodium Chloride in water. However, even though they provide the thermodynamic and dynamic quantities as a function of temperature and pressure, due to the high number of variables that influence this behavior, it becomes difficult to identify which is the main mechanisms that governs the properties of the mixture only from experimental observations. The theoretical methods are, therefore, a complementary tool for understanding the salt solutions. Due to the long range nature of the Coulombic interactions, analytical approaches for describing the behavior of
the ions, $Na^+$ and $Cl^-$, in water require approximations that either limit the analysis to very low dilution\textsuperscript{5} or systems far from phase separations.\textsuperscript{6} Consequently simulations became an important strategy to study electrolyte solutions.

The crucial step in the simulations is to have an appropriated Force Field for the interaction potential between the ions and the water. The usual strategy is to fit the theoretical potential with the experimental results for the density and structure of the pure system for a determined pressure and temperature. The Coulombic forces are then taken into account by a combination of numerical methods.\textsuperscript{7,8} Thanks to these methods a number of models for Sodium Chloride\textsuperscript{9} capable to reproduce the density of the pure system have been developed.

Recently Smith, W.R. et al\textsuperscript{9} studied thirteen of the most common NaCl Force Fields. These models, even thought reproduce some of the properties of the crystal are unable to capture others. For instance, just one of them reproduced the correct density and other one reproduce the chemical potential of the solid phase at room temperature. In parallel a similar strategy has been employed to build computational models for water.\textsuperscript{10–13} These models reproduce the density of water around $300 \, K$ and atmospheric pressures\textsuperscript{14} but fail to provide good values for the dielectric constant.\textsuperscript{15}

In the case of studying electrolyte solutions, the common strategy is to combine one model for water and one model for salt that have been obtained by fitting the properties of the pure systems or in the mixture. Then, the mixture of these two models is tested. The solubility is one of the main properties used validate the model of salt. When dissolved in water, the molecule of sodium chloride dissociates in one cation, $Na^+$, and one anion,$Cl^-$. Due to the polarizability of the water molecule both ions become surrounded by water molecules.\textsuperscript{16} For certain salt concentrations the system phases separates in a salt rich and salt poor phases. The solubility is proportional to the density of salt at this coexistence.

Therefore, in addition to selecting a model for water and a model for salt as explained above, the computation of the solubility from the simulations. This is not a simple task because it requires to estimate the equilibrium state of crystals in saturated solution. One
strategy is by estimating the chemical potentials of both saturated solution and crystal. To do this, the chemical potential of the crystal and solutions at various concentrations is calculated and the concentration at which the two chemical potentials are equal indicates saturation concentration.\(^{17,18}\) For the solid phase the absolute free energy of crystals can be computed using the method proposed by Frenkel and Ladd.\(^{19}\) Employing this method, Sanz and Vega\(^{18}\) determined the solubility of KF and NaCl in water solution. In other works the solubility of several salts in water was obtained using this approach with the generalized reaction field (GRF) method for the treatment of the long-ranged Coulombic interactions\(^{20–22}\) instead of the Ewald Sums.\(^7\) Using a combinations of strategies a number of thermodynamic and trasport properties of the salt solution were explored.\(^{23,24}\)

The best comparison, however, between the experimental values for the solubility and the simulations was computed by Smith and coworkers.\(^9\)

Another method is to use a sufficiently large crystal in contact with an almost saturated ion solution.\(^{25}\) The main assumption is that this crystal and the solution reach an equilibrium state after long simulations to fully equilibrate the heterogeneous mixture.

The drawback of these models for the NaCl reliability of the ion Force Fields is significantly affected by the specific choice of water model. In this work we present a new model for NaCl that reproduces properties of the pure salt. Then the behavior of the model is also tested in water-salt solution for two water models, SPC/\(\varepsilon\)\(^{26}\) and TIP4P/\(\varepsilon\)\(^{15}\) The properties calculated, density and surface tension of the pure system and density, dielectric constant, viscosity and solubility of the solution agree with experiments.

The remaining of the paper goes as follows. In the section 2 the new model for NaCl is introduced and two water models were reviewed. Section 3 summarizes the simulation details and the results are analysed in Section 4. Conclusions are presented in the section 5.
The Models

The NaCl/$\epsilon$ Model

The Force Field employed here for the description of the NaCl in aqueous solutions is based on a set of radial particle-particle pair potentials involving Lennard-Jones (LJ) and Coulombic contributions, namely

$$u(r_{ij}) = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \lambda_i \lambda_j \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \quad (1)$$

where $r_{ij}$ is the distance between sites $i$ and $j$, $q_i$ is the electric charge of site $i$, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_{ij}$ is the LJ energy scale and $\sigma_{ij}$ the distance scale given by the distance between the $ij$ pair.

We assume that pure water and ion potentials are compatible, this mean have the same functional form, the cross interactions between water molecules and ions can be calculated by the Lorentz-Berteloht LB combing rules for the conformal LJ potential,

$$\sigma_{\alpha\beta} = \left( \frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2} \right) ; \quad \varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta}} . \quad (2)$$

For the NaCl/$\epsilon$ model the Lennard-Jones (LJ) energy, $\varepsilon_{ij} = \varepsilon_{LJ}$, and the distance scale, $\sigma_{ij} = \sigma_{LJ}$, are the same for any $i$ and $j$ namely Na-Na, Cl-Cl or Na-Cl. NaCl is considered as a rigid non-polarizable molecule. The spherical anions and cations involve a single interactive site at their centers, carrying charges $q_i = \pm e$ where $e$ is the charge of an electron. In order to correct for the nonpolarizability of the model the Coulombic term is corrected by a screening factor $\lambda_i = \lambda_C$ for both sodium and chloride ions. Therefore, there are three parameters, namely $\lambda_C$, $\sigma_{LJ}$ and $\varepsilon_{LJ}$ to be adjusted with experimental data for each ion.

The parameters are selected so the NaCl/$\epsilon$ force field reproduces the experimental value for the density of the crystal in the face centred cubic phase at the room temperature. There are a number of possible parameterizations that gives the proper density value. Then
these possible values are checked with the radial distribution function, \( g(r) \), and select a subset of parameters that are appropriate for describing the structure of the salt crystal at room temperature. This step provides the first approximation for the parameters of the model.

The next step of the parameterization is to select the parameters that give the proper density and the dielectric constant in the mixture of the salt with water at room temperature and pressure at diluted molal concentration. The parameterization was done using 4 molal concentration, where the ions are hydrated and there is not clusters starting a nucleation. The result from these two steps process for the force field of the NaCl/\( \varepsilon \) model is shown in the Table 1.

| Model | \( q/e \) | \( \lambda_c \) | \( \sigma/\AA \) | \( (\varepsilon/k_B)/K \) |
|-------|-------|-------|-------|-----------------|
| Na    | +1    | 0.885 | 2.52  | 17.44           |
| Cl    | -1    | 0.885 | 3.85  | 192.45          |

Table 1: Force field parameter of NaCl/\( \varepsilon \).

TIP4P/\( \varepsilon \) Water Model

The TIP4P/\( \varepsilon \) model defines the water molecule as rigid, non-polarizable with the same geometry of TIP4P as illustrated in the Figure 1. The intermolecular force field between two water molecules is given by the LJ and the Coulomb interactions as given by the Eq. ??.

The TIP4P models have a positive charge at each hydrogen and a negative charge along the bisector of the HOH angle located at distance \( l_{OM} \) of the oxygen as shown in the Figure 2. The geometry and parameters of the Force Fields for the TIP4P/\( \varepsilon \) are given in the Table 2. In the case of the TIP4P/\( \varepsilon \) model the \( \lambda_O = \lambda_H = 1 \) in the Eq. ??
Figure 1: Schematic representation of the Tip4p water model. The distance between the oxygen and the hydrogen is $r_{OH}$ and the angle between the oxygen and the two hydrogens is $\theta$. The hydrogens have positive charge while the negative charge is located at a point $M$ $r_{OM}$ distant from the oxygen that contains no charge.

Table 2: Force field parameters of TIP4P/$\epsilon$ water model. The charge in site $M$ is $q_{M} = -(2q_{H})$.

| Model     | $r_{OH}$/Å | $\Theta$/° | $q_{H}$/e | $q_{M}$/e | $r_{OM}$/Å | $\sigma$/Å | $(\epsilon/k_B)$/K |
|-----------|------------|------------|-----------|-----------|------------|------------|------------------|
| TIP4P/$\epsilon$ | 0.9572     | 104.52     | 0.527     | 1.054     | 0.105      | 3.165      | 93               |

SPC/$\epsilon$ Model

The SPC/$\epsilon$ is another model for water. It is based on the SPC model geometry\(^2\) but with a different set of parameters. The SPC/$\epsilon$ model\(^26\) defines water as a rigid, non-polarizable as illustrated in the Figure\(^2\). The intermolecular force field between two water molecules is given by the LJ and the Coulomb interactions as given by Eq. ?? with $\lambda_O = \lambda_H = 1$. The parameterization was made using the dipole moment of the minimum density method $\mu_{md}$\(^15\).

The SPC/$\epsilon$ model gives similar thermodynamic and dynamic properties as the SPC\(^10\) and the SPC/E\(^11\) models, but a better agreement with the experiments for the dielectric constant\(^30\).

The geometry and parameters of the Force Fields analyzed in this work are given in the\(^3\)
Figure 2: Schematic representation of the SPC water model. The distance between the oxygen and the hydrogen is $r_{OH}$ and the angle between the oxygen and the two hydrogens is $\theta$. The hydrogens have positive charge while the oxygen carries the negative charge.

Table 3: Force field parameters of water model, SPC/$\epsilon$. The charge of Oxygen is $q_O = -(2q_H)$.

| Model   | $r_{OH}$/Å | $\Theta$/° | $q_H$/e | $\sigma$/Å | $(\epsilon/k_B)$/K |
|---------|------------|------------|---------|------------|--------------------|
| SPC/$\epsilon$ | 1          | 109.45     | 0.445   | 3.1785     | 84.9               |

**NaCl mixture with water Model**

Due to the high dielectric constant of water, when salt is dissolved in water, the ions dissociated forming a positive and a negative ion that is solvated by water.

Then the combination of the water dipole moment with the electrostatics of the ions makes the structure of the ion distribution in the mixture with water quite different when compared to the pure salt system. In principle, one could expect that the structure of the ion distributions could be obtained from infrared (IR)$^{31,32}$ or from the dielectric$^{33-35}$ experimental data. However, the dielectric and IR experiments sample the total response spectrum contain all individual and collective dynamic contribution of the solvent and solute. This makes it difficult to distinguish the dynamics of water in the vicinity of an ion, in most or dynamic ion pairs. As a result, the interpretation of complex microscopic system is very difficult to study.

Then the use of computational models becomes an important tool to identify the indi-
vidual structure of the water and the ions in the mixture. The goal of this work is show that the mixture of water and salt can be described by the combination of the TIP4P/\(\varepsilon\) water model that reproduces the properties of bulk water and the NaCl/\(\varepsilon\) salt model designed to reproduce the density of the crystal and the properties of the mixture.

Then the parameterization of the NaCl/\(\varepsilon\) model initially done by fitting only with the experimental density of the crystal is complemented by fitting the additional parameters with the density and the dielectric constant of the mixture with the TIP4P/\(\varepsilon\) water at diluted molal concentration. The parameterization was done using 4 molal concentration, that is a thermodynamic state where the ions are hydrated and there is not a crystal in the mixture. After adjust the density and the dielectric constant is computed for different molalities and temperatures.

The Simulation Details

Molecular dynamic (MD) simulations were performed using GROMACS\textsuperscript{36} (version 4.5.5.). The equations of motion were solved using the leap-frog algorithm\textsuperscript{8,36} and the time step was 2 \(fs\). The calculus of the shear viscosity, however, employed 1 \(fs\). Ewald summations were used to deal with electrostatic contributions. The real part of the Coulombic potential is truncated at 10. The Fourier component of the Ewald sums was evaluated by using the smooth particle mesh Ewald (SPME) method\textsuperscript{37} using a grid spacing of 1.2 and a fourth degree polynomial for the interpolation. The simulation box is cubic throughout the whole simulation and the geometry of the water molecules kept constant using the LINCS procedure.\textsuperscript{38} Temperature has been set to the desired value with a Nosé Hoover thermostat.\textsuperscript{39} The pressure is obtained using the Parinell-Rahman barostat with a \(\tau_P\) parameter of 1.0 ps.\textsuperscript{36}

The MD simulations of pure NaCl made in the NPT ensemble were carried out under 1 \emph{bar} pressure condition, on a system of 1024 NaCl pairs, with a time step \(\Delta t = 2 \, fs\). The coexisting liquid and vapor phases of NaCl were analyzed in the NVT ensemble. The densities
of the two phases were extracted from the statistical averages of the liquid and vapor limits of the density profiles. The corresponding surface tension $\gamma$ of one planar interface was calculated from the mechanical definition of $\gamma$

$$\gamma = 0.5L_z[P_{zz}0.5P_{xx} + P_{yy}]$$

where $P_{aa}$ are the diagonal elements of the microscopic pressure tensor. The factor 0.5 outside the squared brackets takes into account the two symmetrical interfaces in the system.

For Sodium chloride, NaCl/$\varepsilon$ in water, the simulations have been done using 864 molecules in the isothermic-Isobaric ensemble NPT, in liquid phase at different molalities and at room conditions. The molality concentration is obtained from the total number of ions in solution $N_{ions}$, the number of water molecules $N_{H_2O}$ and the molar mass of water $M_{H_2O}$ as:

$$[NaCl] = \frac{N_{ions} \times 10^3}{2N_{H_2O}M_{H_2O}}.$$  \hspace{1cm} (4)

The division by 2 in this equation accounts for a pair of ions and $M_{H_2O} = 18$ g mol$^{-1}$. The $N$ gives the value of the molality for each point of calculus.

The static dielectric constant is computed from the fluctuations$^{42}$ of the total dipole moment $M$,

$$\varepsilon = 1 + \frac{4\pi}{3k_BT隽}(< M^2 > - < M >^2)$$

where $k_B$ is the Boltzmann constant and $T$ the absolute temperature. The dielectric constant is obtained for long simulations at constant density and temperature or at constant temperature and pressure. The shear viscosity is obtained using the autocorrelation function of the off-diagonal components of the pressure tensor $P_{\alpha\beta}$ according to the Green-Kubo
Table 4: Composition of NaCl solutions used in the simulations at 298.15 K and 1 bar.

| Molality (m) | $N_{H_2O}$ | $N_{ions}$ |
|--------------|-------------|------------|
| 0.06         | 862         | 2          |
| 0.99         | 832         | 32         |
| 1.99         | 806         | 58         |
| 3.07         | 778         | 86         |
| 4.05         | 754         | 110        |
| 5.0          | 732         | 132        |
| 5.93         | 712         | 144        |
| 6.02         | 710         | 154        |
| 6.31         | 704         | 160        |

The self-diffusion coefficient, $D$ is obtained from the Einstein equation

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{R}_i(t) - \mathbf{R}_i(0)|^2 \rangle,$$

where $\mathbf{R}_i(t)$ is the center of mass position of molecule $i$ at time $t$ and $\langle \ldots \rangle$ denotes time average.

### Results

**The Pure Sodium chloride NaCl/ε**

The pure NaCl is analysed. First, we fit the parameters so the density of the crystal of NaCl at the room temperature and pressure would be 2.163 g cm$^{-3}$, the experimental data. The radial distribution for Na-Na, Cl-Cl and Na-Cl is illustrated in the and it shows a peak in the curve for the Na-Cl at 2.76 in agreement with the experiments. The structure of the
g(r) function is in agreement with a FCC crystal like the NaCl crystal.

The Lattice Energy (LE) of NaCl/\( \varepsilon \) is 669 kJ/mol while the experimental data is 790 kJ/mol.\(^\text{16}\) The Lattice Constant (LC) is 5.58 and the experimental value is 5.64.\(^\text{16}\)

![Radial distribution function g(r) versus the distance r at room temperature for: Na-Na (red line), Cl-Cl (green line) and Na-Cl (black line).](image)

Figure 3: Radial distribution function g(r) versus the distance r at room temperature for: Na-Na (red line), Cl-Cl (green line) and Na-Cl (black line).

In order to validate our model the\(^\text{15}\) shows the values of density, the Lattice Energy and the Lattice Constant for our model in comparison with other Force Fields all at a room pressure and temperature. While the Alejandre et al.\(^\text{41}\) gives good results for the density the SD\(^\text{28}\) model and the two parameterizations of the JC\(^\text{29}\) (here called by JC1 and JC2) approach show good results for the Lattice Crystal and Lattice Energy when compared with the experiments. Our model gives good agreement with the experiments\(^\text{16}\) in the density of the crystal and the Lattice Constant, but is a quite far from the reproduction of the Lattice Energy.

Another important check for our model is to check if the density of the liquid phase, for temperatures higher than the region from which the fitting was done, agrees with the experimental results. \(^\text{4}\) illustrates the density versus temperature for the NaCl/\( \varepsilon \) (solid circles) and for the experimental data (solid and dashed lines).\(^\text{16}\) The graph shows that our model is able to show good agreement with experiments for both solid and liquid NaCl.
Table 5: Density of NaCl at room pressure and temperature, Lattice Energy, Lattice Crystal of various Force Fields and for experiments.16

| Model Ions          | \( \rho/(g/cm^3) \) | LC/Å | LE/(kcal/mol) |
|---------------------|----------------------|------|---------------|
| SD                  | 1.90                 | 5.7  | 792.88        |
| JC1                 | 2.86                 | 5.7  | 800.4         |
| JC2                 | 2.01                 | 5.78 | 792.88        |
| Alejandre et al. 41 | 2.16                 | 5.47 | 816.37        |
| this work          | 2.163                | 5.58 | 669.21        |
| experimental16      | 2.163                | 5.64 | 789.95        |

In addition to the density, the surface tension was also computed.5 shows the temperature versus surface tension for our model, compared to the experiments indicating the same trend and reasonable numerical agreement.

**Sodium chloride NaCl/\( \varepsilon \) in the TIP4P/\( \varepsilon \) water**

The NaCl/\( \varepsilon \) was parametrized to fit the dielectric constant and density at room temperature, mixture with water at diluted molal concentration. In order to validate our model a number of quantities, not used to parameterize the model, were computed and checked with experimental results.

First, the dielectric constant for different molal concentrations was also computed.6 shows that the values for \( \varepsilon \) at room temperature and pressure obtained from our model show an excellent agreement with experimental data.16 With this result we are in the possibility to indicate that the electrostatic interaction in dilute concentration is induced by the Cl\(^-\) ion, in this step is where the MD can help us to understand this behavior. We know that the Cl\(^-\) ion is very electronegative and we know that these contribute to dissociate diversity of molecules in its presents.

We have experimental result from many years ago, but in this moment we can not study for example the self diffusion coefficient of each ion in diluted solutions. With the results in this job we can study more about this process in diluted concentration. In next jobs, there
Next, the densities of the mixture of NaCl and water as a function of the molal concentration at standard condition of 1 bar and 298 K were calculated and are shown in the figure. Our results for the density of the solution at different concentrations of the salt are in excellent agreement with the experimental data. Then the density indicated that the distribution of the water molecules around of ions is in excellent behavior with the electrostatic described by the dielectric constant, this mean that the space that is occupied by the molecules are in order to an acceptable nature representation.

In addition to the thermodynamic functions already tested, it is important to validate our model with dynamic properties. Then, the shear viscosity $\eta$ of NaCl into water at different molal concentrations and room conditions was evaluated. It illustrates viscosity versus molal concentration of the salt showing an increase of $\eta$ as the salt concentration increases what implies that the system becomes more viscous. This result is consistent with
Figure 5: Surface Tension versus temperature for the pure NaCl system at room pressure. The black line is the experimental data\textsuperscript{16} and the blue circles are our results.
Figure 6: Dielectric constant versus molal concentration of the salt. The black line is the experimental data and the blue filled diamond is the results of our model. All data are at room conditions. Violet circle is the diluted concentration where was made the parameterization.
The black line is the experimental data and the blue filled diamond are the results of our model. Violet circle is the diluted concentration where was made the parameterization. the experimental values also shown in the figure.

Another important aspect of the mobility of the particles is the diffusion. In this particular case it is interesting to observe how the water and the two ions change their mobilities with the increase of the salt concentration. This analysis can provide a good picture of the hydration process. In the the self diffusion coefficient of water was measured for various salt concentrations. As the molal concentration of the salt increases the mobility of water molecules decreases. This behaviour is consistent with the idea that as the concentration of salt increases, hydration increases, forming larger hydrated ions what slow down the dynamics of water. It is also in agreement with the increase of viscosity illustrated in the 8.

The diffusion coefficient of Chloride ions is shown in the 10. In this case the experimental data at infinite dilution of diffusion coefficient is \( D_{Cl} = 2.032 \times 10^{-5} \text{cm}^2\text{s}^{-1} \). The system shows a decrease in mobility with the increase of the concentration what is the natural
Figure 8: Viscosity versus molal concentration of the salt at temperature and pressure at room conditions. The black line is the experimental data¹⁶ and the blue filled diamond are the results for our model.
behavior of any molecular system. The increase of the number of particles, decreases the mobility. Our results in extremely low molal concentrations show a very large error bars. However, extrapolating our result for finite concentrations to the infinite dilution case, the value becomes very similar to the experimental value.

The diffusion coefficient of the Sodium versus the molal concentration of the salt is shown in the figure. The diffusion coefficient is almost constant when the salt concentration is increased. With this in mind, we can say that the process is defined by the Cl\(^-\) ion by their electronegativity and the Na\(^+\) ion contribute least in the mixture. This is because the chloride ion has a higher electronegativity which affects the dipole moment of the water molecule, which makes that decreases the dielectric constant and increase the density of the mixture.

In this case the experimental data for the diffusion coefficient at infinite dilution is D\(_{Na}\) = 1.334 \(10^{-5}\) cm\(^2\) s\(^{-1}\). Our results in extremely low molal concentrations show a very large...
Figure 10: Diffusion coefficient of Chloride versus molal concentration of the salt at room temperature and pressure. The filled black diamond is the experimental data and the blue filled diamonds are the results for our model.

error bars. However, the extrapolation of our results for finite concentrations to the infinite dilution case, the value becomes very similar to the experimental value.
Figure 11: Diffusion coefficient of Na versus the molal concentration of the salt at room pressure and temperature. The filled black diamond is the experimental data and the blue filled diamonds are the results for our model.

The experimental aqueous solubility\textsuperscript{16} of NaCl at 298.15 K of temperature and 1 bar of pressure is 6.153 mol kg\textsuperscript{-1}. The value obtained in our model is 6.12 mol kg\textsuperscript{-1} with and error the ± 0.7 mol kg\textsuperscript{-1} what is quite reasonable. The error bar is due to approximations in the method employed to calculate the solubility.\textsuperscript{43} This is an excellent result, because the parameterization was made to adjust the density and dielectric constant of the mixture and not for the solubility. The correct calculus of this thermodinamic properties at a diluted concentration was enough to have a good description of the solubility.
NaCl/ε in the SPC/ε water

In order to further validate our model, we analyze the behavior of the NaCl/ε in solution with a different water model from the one it was parametrized. For this purpose the SPC/ε was selected. This Force Fields reproduce very well the dielectric constant and the density of pure water at various thermodynamic states. It fails, however, to reproduce the transport properties. 26

First, the dielectric constant of the solution was computed at room temperature and pressure for different molal concentrations of salt. 12 illustrates that ε decreases as the concentration of salt increases as due to the hydration effects as it would be expected. Our results show a good agreement with the experimental results. 16

Next, the density was computed for different molal concentrations of the salt. 13 illustrates that in the accordance with the experimental results is better at lower salt concentrations. 16 This might be due to the fact that the SPC/ε water model has a higher dipole moment when compared with the TIP4P/ε model.
Figure 12: Dielectric constant versus molal concentration of salt for room temperature and pressure. The black line is the experimental data and the filled red circles are the results for our model.
Figure 13: Density versus molal concentration of the salt at room temperature and pressure. The black line is the experimental data and the red circles are the results for our model.
Here we also test the dynamics of the system. Figure 14 shows the viscosity, $\eta$ versus the molal salt concentration at room temperature and pressure. The viscosity increases with the increasing of the salt concentration what due to the solvation it would be expected. However, the results show a shift when compared with the experimental results. The origin of this shift is probably related to the fact that the SPC/$\epsilon$ does not perform well for dynamic properties. The constant shift therefore might be due to the constant concentration of water present in the solution. This is important to understand the transferability of the Force Fields, there are many contradictions in a diversity of calculus, this is because the force fields have not been sufficiently tested alone and in mixtures, so we must be very careful with the experimental data that are able to reproduce.

![Graph showing shear viscosity versus molal concentration of salt at room temperature and pressure. The black line is the experimental data and the filled red circles are the results for our model.](image)

Figure 14: Shear viscosity versus molal concentration of salt at room temperature and pressure. The black line is the experimental data and the filled red circles are the results for our model.

In order to test if the incorrect dynamical behavior of the NaCl/$\epsilon$ and SPC/$\epsilon$ mixture
is due to the problems in the water model, the diffusion coefficient is also computed. Illustrates the diffusion coefficient of water versus the molal concentration of the salt at room pressure and temperature. $D$ decreases with the increasing concentration of salt due to the solvation effects but the values are much lower than the values observed for the TIP4P/ε water model and far below the experimental results.

![Graph](image)

**Figure 15:** Diffusion coefficient of water versus molal concentration of the salt at room temperature and pressure. The filled black diamond is the experimental data and the filled red circles are the results for our model.

The diffusion coefficient of the Chloride is shown in the It shows an smooth decrease with the concentration of salt, but a value far below the experimental data. Again the reason for this discrepancy might be that the water model is not suitable for quantitative values of the dynamics. Figure shows the diffusion coefficient versus the salt concentration at room temperature and pressure for the Sodium. Similarly to anion, the water model seems not to capture the proper mobility of the system.

The value obtained for the solubility is $5.6 \text{ mol kg}^{-1}$ with and error the $\pm 0.7 \text{ mol kg}^{-1}$. The error bar is due to approximations in the method employed to calculate the solubility. The error in the calculation of the solubility is due to the water model SPC/ε, because
Figure 16: Diffusion coefficient of Cl versus molal concentration of the salt at room temperature and pressure. The filled black diamond is the experimental data and the filled red circles are the results for our model.

Figure 17: Diffusion coefficient of Na versus molal concentration of the salt at room temperature and pressure. The filled black diamond is the experimental data and the filled red circles are the results for our model.
the force field has deficiencies in the reproduction of various experimental data, these are reflected in the calculation of the mixture with water. In this case the calculation of the solubility is underestimated by 9.2 percent of the experimental value.

Conclusions

In this paper, we have proposed the NaCl/ε nonpolarizable model for NaCl. Within our approach the interaction potential of the ions combines a Lennard-Jones term and a Coulombic potential. The combination of the two terms is balanced by a parameter $\lambda_i$ for each particle. The parameterization of our model uses experimental results for both the pure salt system and the mixture between the salt and water. In the parameterization process the water model employed in the salt-water mixture should be able to show the appropriated dielectric constant. Therefore the TIP4P/ε water model was selected.

Then our model was validated by computing the density, the dielectric constant, the surface tension, the diffusion and the viscosity for various concentrations of the salt. Our results show a good agreement with the experiments, particularly when compared with other models for salt in the literature.

Finally, our salt model is tested with another water for water that also gives good bulk dielectric constants, the SPC/ε. In this case, the thermodynamic quantities perform well, while the diffusion show discrepancies that in fact are consistent with the discrepancies of the bulk diffusion coefficient for this model.

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