Electrokinetic Properties of NaCl Solution via Molecular Dynamics Simulations with Scaled-Charge Electrolytes

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Scaling ionic charges has become an alternative to polarizable force fields for representing indirect charge transfer effects in molecular simulations. In our work, we apply molecular dynamics simulations to investigate properties of NaCl aqueous solutions in homogeneous and confined media. We compare classical integer- and scaled-charge force fields for the ions. In the bulk, we validate the force fields by computing equilibrium and transport properties and comparing them with experimental data. Integer-charge ions overestimate dielectric saturation and ionic association. Both force fields present an excess in ion-ion correlation, which leads to deviation in the ionic conductivity at higher ionic strength. Negatively charged quartz is used to simulate the confinement effect. Electrostatic interactions dominate counter-ion adsorption. Full-charge ions have stronger and more defined adsorption planes. We obtain the solution electroosmotic mobility by combining the shear plane location from non-equilibrium simulations with the ionic distribution from equilibrium simulations. From the Helmholtz-Smoluchowski equation, the zeta potential and the streaming potential coupling coefficient are computed. From an atomic-scale perspective, our MD simulations corroborate the hypothesis of maximum packing of the Stern layer, which results in a stable and non-zero zeta potential at high salinity. The scaled-charge model representation of both properties is in excellent qualitative and quantitative agreement with experimental data. With our work, we demonstrate how useful and precise simple scaled-charge models for electrolytes can be to represent complex systems, such as the electrical double layer.
I. INTRODUCTION

Electrolyte solutions are widely found in many natural systems and industrial and technological applications. The ubiquity and challenging behavior of ion-water mixtures motivates their investigation. Many molecular theories have been developed to investigate both ion-ion and ion-water interactions in these systems, ranging from the classical Debye-Hückel theory\(^1\) to the new equation of states, such as e-CPA\(^2,3\) and e-SAFT-VR Mie\(^4\). Due to the complexity of the highly directional water interactions and the free charge of ions, no universal model capable of representing the entire range of conditions and ions exists.

Molecular simulation may be applied to investigate the molecular structures and to estimate thermodynamic and transport properties of electrolyte solutions. By applying molecular dynamics and Monte Carlo techniques, prior studies have evaluated properties of inorganic salts and water mixtures, such as vapor pressure\(^5,6\), liquid density\(^5–10\), activity coefficients\(^11–14\), shear viscosity\(^5,7,10,15\), interfacial tension\(^5\), diffusion coefficients\(^9,10,14,15\), salt solubility\(^8,10–14\), thermal diffusion factor\(^16,17\) and coordination numbers\(^7–10\). The results from molecular simulation have demonstrated its ability to predict properties and molecular structures in a wide range of conditions. There is, however, still margin for improvement. For instance, classical force fields predict a decrease in water diffusivity for all types of salts, but it is known that chaotropic (structure-breakers) cations increase water diffusivity\(^15\).

Classical molecular simulations use pairwise additive and non-polarizable force fields. As a consequence, charge transfer caused by orbital overlap and electronic polarization caused by the many-body interactions are not directly represented\(^18\). Leontyev and Stuchebrukhov\(^19\) have proposed scaling down the charge of ions to represent indirectly the screening effect of the electronic continuum caused by the many-body forces, without using polarizable force fields. Scaled charge force fields for electrolytes have been developed using different scaling factors such as 0.75\(^19\), 0.804\(^20\), 0.85\(^7,21,22\), 0.885\(^23\) and 0.94\(^22\) and have demonstrated themselves to be able to reproduce various properties. Various properties, such as density, radial distribution function, water activity coefficient, osmotic pressure, ion diffusivity (including chaotropic ones), and potential of mean force between ions, may be accurately described by scaled-charge electrolytes\(^7,19–22\). On the other hand, for other properties at certain conditions, such as viscosity and surface tension at high salinity and enthalpy of solution, scaling charge can improve the predictions comparing with integer-charge force fields, but it still deviates from experimental data\(^7,24\).
Electrolyte solutions when confined by a surface develop a structure known as Electrical Double Layer (EDL). If the confining medium is a mineral, such as quartz, its surface may become electrically charged depending on pH and solution composition. The charged mineral surface attracts ions of opposite polarity (counter-ions) and partially excludes ions of the same polarity (co-ions) from the surface’s vicinity. Experimentally, a direct measurement of the electrostatic potential at the surface without disturbing the EDL is impossible. Therefore, the zeta potential ζ is the main experimental parameter to describe the EDL, which can be interpreted from the streaming potential established by the action of external mechanical force, or from the particle velocity or fluid flow by the action of an external electric field through electrophoresis, and electro-osmosis, respectively. The ζ potential is located at the shear plane (also known as the slip plane), which delimits the “immobile” layer from the “free” fluid. Through ζ, one can predict the stability and aggregation of inorganic nanoparticles, extracellular vesicles, polymers, biomolecules, colloids and suspensions. Its determination is crucial in applications such as biomedical, pharmaceutical, clays, water purification, detergents, paints, and electrodeposition.

Molecular dynamics (MD) simulations can be applied to gather molecular insights about the configuration of aqueous solutions and surface interfaces to investigate the EDL at the nanoscale. The simulations help in the understanding of experiments and may be used in situations where experiments are infeasible. MD simulations have been demonstrated to capture the EDL formation through the ions adsorption close to the mineral walls. Within the EDL, water molecule dipoles orient themselves in the vicinity of the charged surface due to the electric field; ion-specific adsorption may occur depending on the hydration energy.

By applying an external electric field parallel to the surface, the fluid is dragged by the ions within the EDL, establishing an electroosmotic flow. Through Non-Equilibrium Molecular Dynamics (NEMD) simulations, the electroosmotic flow experiments can be mimicked. The flow boundary condition (slip or stick) can be verified based on the velocity profile. To obtain reasonable statistics using NEMD for ζ potential determination, an amplified electric field is required. If the fluid velocity is linearly dependent on the applied electric field, the electroosmotic flow can be obtained by a balance between viscous and electric forces using equilibrium molecular dynamics (EMD) simulations. Hartkamp et al. have shown that the electroosmotic flow from NEMD and EMD are similar if one accounts for the enhancement of viscosity near the surface in the EMD approach. Otherwise, if a constant viscosity is applied, even the direction of the flow is predicted wrongly.
From the electroosmotic flow, the zeta potential may be determined through the Helmholtz-Smoluchowski (HS) equation:

\[
\zeta = -\frac{\eta \mu}{\varepsilon_0 \varepsilon_r}
\]

where \( \mu \), and \( \eta \) are, respectively, the water electroosmotic mobility, and viscosity in the bulk of the pore (away from surface) , \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon_r \) is the water dielectric constant.

Through MD, the zeta potential has been computed at the silica interface at pH levels ranging from 3 to 9 for different salts, such as NaCl, NaBr, KCl, KBr, RbCl, SrCl₂, CaCl₂, and CsCl. Rutile and montmorillonite surfaces and titania nanoparticles have also been investigated. With respect to both pH and salinity trends, qualitative agreement with experiments is obtained, but no direct comparison with experimental measurements at similar conditions is made. Furthermore, the zeta potential has not been evaluated with higher salinity brines (all available MD data are below 0.6 M). At high salinity, even the experimental data are limited. For ionic strength higher than 1 M, streaming potential method is the only alternative, since the electrophoretic mobility measurements cannot cope with such conditions.

In this work, we aim at studying properties of the NaCl aqueous solution using MD simulations. We have investigated properties of homogeneous solutions applying classical and scaled-charge force fields for electrolytes and validated them against experimental data. Then, we have investigated the electrical double layer of the NaCl solution confined by quartz substrates. We explore the limitations and advantages of EMD and NEMD simulations to obtain the electroosmotic mobility. The zeta potential is computed for various salt concentrations and compared with experimental values.

II. METHODS

A. Homogeneous Solution

We compute properties of bulk aqueous NaCl solutions via equilibrium molecular dynamics (EMD) simulations and compare the results with experimental data. To analyze the performance of electrolytes force fields, we compare classical integer-charge force fields from Smith and Dang (SD) with the Madrid-2019 scaled-charge for Na⁺ and Cl⁻ ions. The force field for water molecules is chosen based on its compatibility with the electrolytes model. The rigid three-point SPCE water is used with the integer-charge ions (SPCE-SD), and the rigid four-point
TIP4P-2005\textsuperscript{54} is used with the scaled-charge model (TIP4P-Madrid).

The mixture contains 2000 molecules of water and the number of salts depends on the desired salinity, which ranges from 0 to 3 mol·kg\textsuperscript{-1} (0 to 108 NaCl ion pairs). The bulk simulations are first equilibrated in the NPT ensemble fixing the temperature ($T$) at 300 K and the pressure ($P$) at 1 bar, and the density ($\rho$) is computed. Then, the production is performed at a fixed volume ($V$) in the NVT ensemble to avoid interference of the barostat in the properties determination. We then compute equilibrium and transport properties.

1. Equilibrium Properties

Concerning equilibrium properties, we compute the radial distribution functions ($g_{ij}(r)$), the number of contact ion pairs, ($n^{CIP}$) and the dielectric constant ($\varepsilon_r$). The radial distribution describes the structure of fluids at the molecular scale and is defined by the ratio between the local average number density at a certain position and the ideal gas density. The number of contact ion pairs relates to the ionic association and is defined based on the radial distribution function between cation (+) and anion (-):

$$n^{CIP} = 4\pi \rho_s \int_0^{r_{\text{min}}} g_{+-}(r)r^2 dr,$$

(2)

where $\rho_s$ is the number density of salt, and $r_{\text{min}}$ represents the end of the first interaction peak in $g_{+-}$.

Using explicit water molecules, the medium permittivity is an output from the molecular simulations. The dielectric constant is computed through the total dipole moment fluctuation by:

$$\varepsilon_r = 1 + \frac{\langle M^2 \rangle - \langle M \rangle^2}{3\epsilon_0 k_B TV},$$

(3)

where $\langle M \rangle$ is the average of the total dipole moment of water molecules, and $k_B$ is the Boltzmann constant. When using Electronic Continuum Correction (ECC) model, which is the case for scaled-charge force fields, the total dielectric response should account for both the nuclear and electronic contributions to represent the real water dipoles\textsuperscript{55}. Therefore, the dielectric constant for such models is given by $\varepsilon_r^{\text{ECC}} = \varepsilon_r^{\text{el}} + (\varepsilon_r^{\text{nuc}} - 1)/f_{sc}$, where $\varepsilon_r^{\text{el}}$ is the high-frequency component of the dielectric constant, given by the square of the refractive index of the solvent (1.33 for water), $\varepsilon_r^{\text{nuc}}$ is the nuclear part of the permittivity - Eq. (3) -, and $f_{sc}$ is the scaling factor of the force field (0.85 for Madrid-2019\textsuperscript{7}).
2. Transport Properties

We compute the viscosity, self-diffusivity, and ionic conductivity of the homogeneous electrolyte solutions. The viscosity (\( \eta \)) is obtained by the pressure tensor auto-correlation function using the Green-Kubo (GK) equation:

\[
\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t_0 + t)P_{\alpha\beta}(t_0) \rangle \, dt,
\]

where \( P_{\alpha\beta} \) represents the off-diagonal elements of the pressure tensor, and \( \langle \cdots \rangle \) denotes ensemble average. The convergence and precision of the GK viscosity depend on running and averaging multiple independent simulations\(^{56}\). Diagonal elements of the pressure tensor are applied to generate three more independent components to enhance the statistics, following the procedure proposed by Franco and Firoozabadi\(^{57}\).

Alternatively, we compute the viscosity using the macroscopic Stokes-Einstein equation, which correlates the diffusion of spherical particles with the solution viscosity:

\[
\eta = \frac{k_B T}{6\pi a D_w^s},
\]

in which \( a \) represents the hydraulic radius of the diffusing species and \( D_w^s \) is the self-diffusion coefficient of water. We consider the hydraulic radius as half the distance of the first peak of \( g_{OO}(r) \) (\( a = 0.14 \) nm for both force fields).

The self-diffusivity of species is obtained from Einstein’s equation, which correlates the diffusion with the slope of the mean squared displacement (MSD) evolution with time:

\[
D_i^s = \lim_{t \to \infty} \frac{1}{6 N_i t} \left\langle \sum_{j=1}^{N_i} \left[ \mathbf{r}_{j,i}(t_0 + t) - \mathbf{r}_{j,i}(t_0) \right]^2 \right\rangle = \lim_{t \to \infty} \frac{\text{MSD}_i}{6t}
\]

where \( N_i \) is the total number of molecules \( i \) and the sum is over the position \( r_{j,i} \) of all molecules of type \( i \). In contrast to the GK viscosity, which is a collective function of the system, the self-diffusivity is averaged by each molecule, making its convergence faster\(^{56}\). Multiple time origins \( t_0 \) are used to further increase the convergence. Finite size effects are significant in the self-diffusivity computation\(^\text{58}^\text{58}\). We correct the diffusion coefficients for system size effects using the analytical factor proposed by Yeh and Hummer\(^{59}\):

\[
D_w^s = D_i^s(L) + \frac{k_B T \psi}{6\pi \eta L},
\]
where $D^*_{\infty}$ is the infinite size self-diffusivity, $L$ represents the size of the cubic box and $\psi = 2.837298$ is a dimensionless correction factor. The GK viscosity is used because its finite-size effect is negligible. We suppress the $\infty$ symbol from now on, but all results shown are corrected with the finite-size factor.

As for the viscosity, we compute the ionic conductivity ($\kappa$) of the electrolyte solutions accounting for the collective transport. By using the Einstein-Helfand (EH) approach, the ionic conductivity can be expressed in terms of the Onsager coefficient of the ions as:

$$\kappa = \frac{e^2 Z^2 N_t}{k_B T V} (L_{++} + L_{--} + 2L_{+-}),$$

(8)

where $e$ is the elementary charge, $Z$ is the nominal valence of the ions (i.e. 1 for NaCl, even for scaled-charge ions because we use the nominal charge to represent the dipole moment surface), and $N_t$ the total number of particles (individual ions + water molecules). The Onsager coefficients represent the collective interaction between species and are given by:

$$L_{ij} = \lim_{t \to \infty} \frac{1}{6N_t} \left\langle \left[ \sum_{l=1}^{N_i} (\mathbf{r}_{l,i}(t_0 + t) - \mathbf{r}_{l,i}(t_0)) \right] \cdot \left[ \sum_{k=1}^{N_j} (\mathbf{r}_{k,j}(t_0 + t) - \mathbf{r}_{k,j}(t_0)) \right] \right\rangle$$

(9)

Again, the convergence of the ionic conductivity is slow due to the required collective motion. Alternatively, the ionic conductivity can be obtained from the Nernst-Einstein (NE) equation, which relates the medium electrical conductivity to the self-diffusion of the ions:

$$\kappa = \frac{e^2 Z^2}{k_B T V} \left( N_+ D^*_+ + N_- D^*_- \right)$$

(10)

Because it depends on self-diffusivity, the convergence is much faster compared to Green-Kubo or Einstein-Helfand. Nernst-Einstein equation is only valid at low ionic strengths. At higher concentrations, ionic association may happen and not all ions are free and contribute to the medium electrical conductivity.

B. Confined Solution

To simulate the confined solution via classical MD, (100) quartz mineral ($\alpha$-SiO$_2$) has been selected to represent the mineral phase. Usually, quartz has a Q$^2$ surface, with two silanol groups (Si(OH)) per superficial silicon (4.7 to 9.4 silanol groups per nm$^2$). Depending on the pH and the ionic strength, quartz may possess different surface charges. Quartz interface with an aqueous solution via MD simulations has been studied in the past. To represent the mineral in our
simulations, a constraint version of the CLAYFF force field is selected\textsuperscript{69}. This general force field is suitable for hydrated minerals in contact with aqueous solutions and is based on metal-oxygen ionic interactions (the only bonded interactions are in the terminal silanol groups)\textsuperscript{69}. The same force field combination for water and ions in the bulk simulations (SPCE-SD and TIP4P-Madrid) is used.

A (100) quartz mineral with $3.4 \times 3.4$ nm$^2$ of surface area and 1.8 nm thick is placed in contact with the electrolyte solution. The mineral has 9.4 hydroxyls per nm$^2$ in each surface and its structure has been provided by Emami et al.\textsuperscript{62}. The initial configuration is created with Packmol\textsuperscript{70}. The aqueous solution is placed 0.3 nm distant from the mineral, to avoid overlap between the fluid and the crystal at the beginning of the simulation. The aqueous solution is, then, confined within a slit pore-like structure, with mineral walls 5.1 nm apart from each other (Fig. 1), which is large enough to prevent EDL overlap. Periodic boundary conditions are applied in the three directions. There is no need to separate the images with a vacuum gap in the confinement direction, since the simulation box contains a single quartz slab in contact with the fluid (the second slab in Figure 1 is just a representation of the periodic image). The simulations are carried out in the NVT ensemble at 300 K. The number of water molecules and ions are determined based on the bulk density and salinity at the respective temperature (300 K) and pressure (1 bar) (Table I).

In classical MD simulations, the equilibrium reactions of protonation-deprotonation in the surface and the proton transfer in water molecules cannot be directly represented\textsuperscript{39}. Thus, the pH effect is accessed indirectly via the quartz surface charge. In our simulations, the surface charge, $\sigma$, follows the potentiometric titration experiments made by Riese\textsuperscript{71}, which correlates $\sigma$ with the NaCl molality $m_s$ and the pH value (Fig. 1). By setting the pH value to 7.2 in all simulations, the surface charge is determined for each condition (Table I).

To simulate the negative silica surface charge, protons are removed from the surface silanol groups and replaced by non-bonded Na$^+$. A sparse distribution of deprotonated silanols is chosen to minimize the interaction between them\textsuperscript{63}. For both SD and Madrid force fields the charge of Na$^+$ is greater than the hydrogen partial charge designed by the CLAYFF force field. Then, the excess charge is distributed between all superficial atoms, following quantum mechanics simulation made by the first deprotonation\textsuperscript{63}. The new partial charge of each atom $i$ from the quartz surface is given by:

$$q_i = q_i^0 + \Delta q_i - \left( \frac{(q_{Na^+} - q_{H}^0) N_{H_{out}} + \sum_i \Delta q_i^0 N_i}{\sum_i N_i} \right), \quad (11)$$
FIG. 1: Initial configuration for a quartz-aqueous solution system. The second quartz slab is a periodic image of the first one. The color scheme of each atom is displayed below the figure. The surface deprotonation model is shown with the correlation between the quartz surface charge with the pH and NaCl concentration. Closed symbols in the plot represent the experimental data, and the continuous lines represent the displayed fitted model.

where $q_i^0$ is the original CLAYFF charge, $\Delta q_i$ is the charge change due to one deprotonation, $N_i$ is the number of $i$ atoms at the surface, and $N_{H_{out}}$ is the number of removed protons. Originally, this method was designed for the CLAYFF-SPCE-SD force field combination. Nevertheless, we use the same approach for the CLAYFF-TIP4P-Madrid combination. A new parameterization of the clay force field should be performed in the future to determine how different would be the surface charge distribution with scaled-charge ions.

1. Electrostatic Potential

From the trajectory of the particles, the ion distribution within the pore is computed. Then, the electrostatic potential $\varphi$ is obtained by discretizing the Poisson’s equation in the $z$-direction (the direction perpendicular to the mineral surface):

$$\frac{d^2 \varphi}{dz^2} = -\frac{\rho_E}{\varepsilon_0 \varepsilon_r}$$

(12)

We assume that, at the center of the pore, both the electric field and electrostatic potential are zero. As for the valence in the ionic conductivity equation, the charge density is obtained using the nom-
TABLE I: Simulation setup for each investigated salinity $m_s$ under confinement for pH = 7.2. The number of removed protons ($N_{\text{Hout}}$) and the number of molecules ($N_w$ and $N_s$) are based on the computed surface charge ($\sigma$), and the computed bulk density ($\rho$) at 300 K and 1 bar for each force field.

<table>
<thead>
<tr>
<th>$m_s$ / mol·kg$^{-1}$</th>
<th>$\sigma$ / C·m$^{-2}$</th>
<th>$N_{\text{Hout}}$</th>
<th>$\rho$ / kg·m$^{-3}$</th>
<th>$N_w$</th>
<th>$N_s$</th>
<th>$\rho$ / kg·m$^{-3}$</th>
<th>$N_w$</th>
<th>$N_s$</th>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>998.2</td>
<td>1991</td>
<td>0</td>
<td>1989</td>
<td>0</td>
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<tr>
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<td>1002.9</td>
<td>1988</td>
<td>4</td>
<td>1985</td>
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<td>-0.064</td>
<td>5</td>
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<td>1983</td>
<td>9</td>
<td>1979</td>
<td>9</td>
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<td>6</td>
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<td>1952</td>
<td>35</td>
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<td>1871</td>
<td>101</td>
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<td>101</td>
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The zeta potential ($\zeta$) is computed through the Helmholtz-Smoluchowski equation (Eq. 1). Here, all properties from the HS equation are determined by MD simulations. The dielectric constant is computed by applying Eq. (3). We compute the electroosmotic mobility from both EMD and NEMD simulations to investigate advantages and limitations of each method. In NEMD simulations, a magnified electric field ($E_x$) is applied in one of the parallel directions to the surface, and the electroosmotic mobility is determined based on the fluid velocity $v_x$ in that direction ($\mu = \frac{v_x}{E_x}$). Because the same electric force should act on the ions regardless their effective charge, the NEMD scaled-charge electroosmotic mobility is divided by the scaling factor (0.85 for the
Madrid-2019\textsuperscript{7} to represent the effective electric field acting on these ions\textsuperscript{55,72}. In the limit when the applied electric field tends to zero, the electroosmotic mobility can be obtained via EMD simulations from a balance of viscous and electric forces\textsuperscript{47}:

\[
\mu(z) = \frac{z}{\eta(z')} \int_0^{L/2} \rho_E(z'') d\tau' dz'' d\tau',
\]

(13)

where \(L\) is the distance between the surface planes, whose zero position is given by the average location of the outer hydroxyls. At first, we consider the shear plane at the surface \((z = 0)\), but later we discuss the limitations of that assumption. The derivation of Eqs. (1) and (13) are detailed in the Supplementary Material.

The viscosity profile of the confined fluid required in Eq. 13 is obtained by assuming water as spherical particles and using the Stokes-Einstein equation (Eq. 5). The self-diffusivity of water is taken as the parallel to the surface component \(D_{\parallel}\) of the self-diffusion tensor. In the past, Einstein’s equation has been applied to obtain the confined diffusion profile\textsuperscript{47,73}. However, the fluid is no longer homogeneous when in confined spaces, and adequate modifications to the traditional Einstein’s method are required\textsuperscript{74,75}. Here, the parallel diffusion coefficients in the \(x\) and \(y\) directions are computed in various slabs in the \(z\) direction. To account for the inhomogeneity, \(D_{\parallel}\) is defined by the ratio of the parallel mean square displacement \((\text{MSD}_x(\tau)\) and \(\text{MSD}_y(\tau)\)) and the survival probability \((P(\tau))\) in the sub-interval of time \(\tau\textsuperscript{76}:

\[
D_{\parallel}(z) = \lim_{\tau \to \infty} \frac{\langle \text{MSD}_x(\tau) \rangle + \langle \text{MSD}_y(\tau) \rangle}{4\tau P(\tau)},
\]

(14)

where the sub-interval \(\tau\) is evaluated between 0 and 800 ps with trajectory extracted each 4 ps using multiple time origins, and the diffusion coefficient is the slope of the plot \(\tau\) vs. \(\text{MSD}(\tau)/(4P(\tau))\) defined in the linear region. Such an approach has already been applied to several different systems\textsuperscript{77–80}. Finite-size effects may also affect the confined self-diffusion coefficient depending on the confining distance and the parallel simulation box lengths\textsuperscript{81}.

C. Simulation Details

The non-bonded potential between atoms \(i\) and \(j\), \(U_{ij}\), is expressed through van der Waals and electrostatic interactions via the Lennard-Jones (LJ) and Coulombic potential, respectively:

\[
U_{ij}(r_{ij}) = 4\varepsilon_{ij} \left[ \frac{\sigma_{ij}^12}{r_{ij}} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}},
\]

(15)
where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \epsilon_{ij} \) is the energy depth of the Lennard-Jones interaction potential, \( \sigma_{ij} \) is the distance where the LJ interaction potential is zero, and \( q_i \) represents the atom partial charge. The Lorentz-Berthelot (LB) combining rules are applied for the LJ cross interactions parameters: \( \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \) and \( \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \)\(^8\), except for the optimized cross-interaction parameters from the Madrid-2019 force field\(^7\). The force field parameters are in Table S1 in the Supplementary Material.

All simulations are performed in GROMACS\(^8\). First, the steepest descent method of minimization is executed to eliminate bad contacts and overlaps between atoms. Then, Newton’s equations of motion are numerically integrated using the Leap-Frog algorithm. In the canonical (NVT) ensemble, the temperature is kept constant at 300 K by a velocity rescaling thermostat\(^8\) with a time constant of 1 ps. In the NPT bulk simulations, besides the thermostat, an isotropic Berendsen barostat\(^8\) keeps the pressure at 1 bar by using a time constant of 1 ps and compressibility of \( 4.5 \times 10^{-5} \text{ bar}^{-1} \). 20 short simulations of 2 ns NPT followed by 6 ns NVT are carried out to compute bulk properties for each salinity. In the case of GK viscosity, 20 more are executed to improve precision. In the EMD confined simulations, to allow the EDL formation, 6 longer simulations of 80 ns are performed for each salinity. The time step in both cases is set to 2 fs. Both van der Waals and electrostatic interactions are computed in the real space for distances below 1.2 nm. Above the cutoff distance, the LJ potential is truncated, and the long-range Coulombic interactions are computed in the reciprocal space applying the Particle-Mesh Ewald (PME)\(^8\). In bulk simulations, long-range dispersion corrections for energy and pressure are applied. All bonds in the quartz mineral are constrained by the LINEar Constraint Solver (LINCS)\(^8\), whereas water molecules are kept rigid by the SETTLE algorithm\(^8\). The Si–O–H angles are allowed to vibrate through a harmonic potential. The same simulation setup is applied to the NEMD simulations, in which, a constant electric field with magnitude ranging from 0.1 to 0.5 V·nm\(^{-1}\) is applied in the \( x \) direction. The direction of the applied electric field is under the influence of the thermostat, however, the electroosmotic mobility profile is unaffected by the thermostat action\(^49\).

III. RESULTS

The values of computed properties in the homogeneous (dielectric constant, shear viscosity, and ionic conductivity) and confined (electroosmotic mobility, zeta potential, and streaming potential coupling coefficient) solution are reported in Table S2 and S3, respectively, in the Supplementary Material.
A. Homogeneous Solution

The solution density of both force fields is very similar to each other and to the experimental correlation\(^89\) (Figure S1 in the Supplementary Material). From the average absolute deviation (AAD), we confirm that TIP4P-Madrid is the most accurate, with AAD = 0.01 \%, while SPCE-SD exhibits an AAD of 0.14 \%. The high accuracy for the liquid density of the Madrid-2019 force field is expected, because it is one of the target properties used to determine the optimized LJ parameters\(^7\). Figure S2 in the Supplementary Material shows the density of the SPCE-SD force field if no long-range dispersion correction for pressure is made. By not accounting for the LJ potential beyond the cutoff, the virial is not computed correctly and the barostat equilibrates the system at a lower pressure, underestimating the density (AAD = 0.45 \%).

Figure 2.A shows the dielectric constant (\(\varepsilon_r\)) variation with salinity. Without salt, the dielectric constant (\(\varepsilon_{r,W}\)) of the SPCE force field is closer to the experimental value than TIP4P. The SPCE force field represents a parameterization of the SPC model, in which polarization correction is applied to the water pair potential\(^53\). Indeed, this overpolarization improves the dielectric representation of water, but on the other hand, it impacts negatively the predictions of vapor pressure and the solubility of water in less polar environments, such as CO\(_2\)\(^90\). In the presence of dissociating salts, the orientation of water molecules within the hydration shells is rotationally bonded to screen the charge of ions\(^91\). By decreasing the solvent contribution to the dielectric relaxation, electrolytes decrease the medium capability to respond to an external electric field, thus decreasing the water permittivity (dielectric saturation)\(^91–93\). Both force fields capture the dielectric saturation. The relative variation of the dielectric constant (\(\delta\varepsilon_r = (\varepsilon_r - \varepsilon_{r,W})/\varepsilon_{r,W}\)) is better predicted with scaled-charge ions (inset of Figure 2), whereas integer-charge ones predict large deviations (larger salinity effect on the solution dielectric constant). If we use the ECC treatment to take into account the electronic contribution in the permittivity of the scaled charge force field, the dielectric constant increases and an excellent agreement is obtained between TIP4P-Madrid\(^{\text{ECC}}\) and the experimental data. In the case of SPCE-SD, the dielectric constant is expressed only through the nuclear contribution since nominal charges are used.

The radial distribution functions between ions and water molecules are computed (Figure S3 in the Supplementary Material). Overall, the molecular structures are quite similar for both force
Fig. 2: Structure and equilibrium properties of aqueous NaCl at 300 K for SPCE-SD and TIP4P-Madrid force fields. (A) Water dielectric constant compared with experimental values\textsuperscript{92}. The inset plot shows the relative variation of the dielectric constant with salinity. (B) Structure of ionic pairs: radial distribution function between Na\textsuperscript{+} and Cl\textsuperscript{−} and the number of contact ion pairs. $r_1$ and $r_2$ represent the ion’s direct-contact and solvent-separated distance, respectively. The solubility of the model is generally close to the concentration in which the number of contact pairs is 0.075 (purple dashed line)\textsuperscript{8}.

The presence of ions in solution decreases water self-association because some water molecules are immobilized in the ions solvation layer\textsuperscript{94}. Scaling down the charge of ions reduces the repulsion between cation-cation and anion-anion pairs. On the other hand, the interaction between cation-water is enhanced with integer-charge. At low salinity (0.11 mol·kg\textsuperscript{−1}), the hydration number ($n_{\text{HNc}}$) of Na\textsuperscript{+} is 5.7 and 5.4 for SPCE-SD and TIP4P-Madrid, respectively. By increasing salt concentration, the hydration number decreases with integer-charge sodium but remains constant with scaled-charge cation (Figure S4 in the Supplementary Material). The major difference between the models is in the ionic pair association (Figure 2. B). A significantly higher association is expected with the SD force field. The location of the second peak, which is related to the solvent-separated ion pair, is also different. From the number of contact ion pairs, the salt solubility can be estimated. Benavides, Aragones, and Vega\textsuperscript{8} have suggested that the salt concentration in which the number of contact ion pairs is 0.075 usually is close to the solubility for that model. Following this empirical rule, the NaCl solubility for SPCE-SD and TIP4P-Madrid models is expected to be around 1 and 3 mol·kg\textsuperscript{−1}, respectively, which are both quite lower than
the experimental\textsuperscript{95} (6.1 mol·kg\textsuperscript{-1}), although TIP4P-Madrid produces a better match to the experimental value of NaCl solubility in water. By rigorously computing the solubility via the chemical potential of the solid and aqueous phase, the NaCl solubility with the SPCE-SD\textsuperscript{8} is estimated at 0.7 mol·kg\textsuperscript{-1}, which is close by the one estimated using the empirical solubility value of number of contact ion pairs.

The self-diffusivities of water and ions are computed and compared with experimental data (Figure S5 in the Supplementary Material). The finite-size effect is significant and a correction of about 13%, 10%, and 7% for Na\textsuperscript{+}, Cl\textsuperscript{−}, and water, respectively, must be applied to the 2000-water system to represent the diffusion in the macroscopic mixture. The analytical correction proposed by Yeh and Hummer\textsuperscript{59} (Eq. 7) is in good agreement with the extrapolation of $1/L \to 0$ made with different system sizes (Figure S6 in the Supplementary Material). The presence of structure-making salts, such as NaCl, decreases the water diffusivity. Some water molecules are attached to ions through the hydration shell structures, and their diffusion is smaller than free water molecules\textsuperscript{15,96}.

The solution viscosity from the Stokes-Einstein and Green-Kubo equations is shown in Figure 3.A and B, respectively. The GK viscosity from both force fields is in reasonable agreement with the experimental data and predicts the increase of viscosity with salinity (viscosification) (Figure 3.B). At lower salinity, the TIP4P-Madrid model predicts the viscosity with excellent accuracy. Using the same force field, Zeron, Abascal, and Vega\textsuperscript{7} have shown that the viscosity is overestimated at higher ionic strength. The fluctuations in the GK viscosity decrease by increasing the number of independent simulations, but there is still some simulation noise related to the Green-Kubo convergence. Therefore, there is a trade-off between accuracy and computational time when applying Green-Kubo equations. The Stokes-Einstein equation may be applied as an alternative for faster convergence because it only depends on water self-diffusivity. By using the hydraulic radius from the water’s oxygen radial distribution function (Figure S3.A in the Supplementary Material) as $a = 0.14$ nm, the viscosity is underestimated (Figure 3.A). Alternatively, if the hydraulic radius is used as a fitting parameter ($a = 0.10$ and 0.11 nm for SPCE-SD and TIP4P-Madrid, respectively), a better agreement is obtained (Figure 3.A). However, from the slope of viscosity with salinity, the viscosification effect is overestimated for both force fields because they predict a higher impact of salinity on water self-diffusivity. Overall, when computing viscosity, Green-Kubo should be used for more accurate results, but Stokes-Einstein provides a faster path for a first estimation.
FIG. 3: Transport properties of aqueous NaCl at 300 K for SPCE-SD and TIP4P-Madrid force fields. Solution shear viscosity (A) from the Stokes-Einstein equation (Eq. 5) using the hydraulic radius from the water distribution function and as a fitting parameter, and (B) from the Green-Kubo equation (Eq. 4) compared with experimental values. Solution ionic conductivity (C) from the Nernst-Einstein equation (Eq. 10), and (D) from the Green-Kubo equation (Eq. 8) compared with experimental values.

The ionic conductivity of the solution is computed from both the Einstein-Helfand and Nernst-Einstein equations (Figure 3. C and D, respectively). At ionic strength below 1 mol·kg$^{-1}$, both methods converge to the experimental data. By increasing salt concentration, the ionic conductivity is overestimated by the NE equation, and underestimated by the EH method. NE conductivity accounts for the total diffusivity of charged species, without considering that opposite ions diffusing together as short-lived clusters do not contribute to the solution conductivity.

Jamali et al. has proposed that the Maxwell-Stefan diffusivity in binary mixtures, which depends on Onsager coefficients closely related as $\kappa^{EH}$, can be finite-size corrected applying the Yeh and Hummer correction divided by the thermodynamic factor. We investigate if the deviations from the EH conductivity are related to finite-size effects (Figure S7 in the Supplementary Material), but no clear trend is observed either for the conductivity or for the Onsager coefficients. A similar conclusion has also been reported by Shao et al. The EH conductivity accounts for the cross-correlations among all ions (including the same and different species).
Non-polarizable force fields for ions tend to overestimate the ion-ion correlation, thus decreasing the ionic conductivity\textsuperscript{101}. To investigate the contributions to different correlations, we decompose the $\kappa^{\text{EH}}$ into the $\kappa^{\text{NE}}$ contribution and the distinct (not accounting for the “self” term) ions correlation $\kappa_{++}$, $\kappa_{--}$, and $\kappa_{+-}^{100}$ (Figure S8 in the Supplementary Material), and find that the cross-correlation between distinct cation-anion ($\kappa_{+-}$) is negligible for all conditions. Therefore, the underestimation made by the Einstein-Helfand ionic conductivity at higher ionic strengths must be due to an over-repulsion between same-type ions (indicated by negative values of $\kappa_{++}$ and $\kappa_{--}$). Even by scaling down the ionic charge, the EH conductivity underestimation remains. A better description of the NaCl ionic conductivity using EH equation may be obtained by further scaling down the ionic charges (0.75)\textsuperscript{60}, which may decrease the repulsion between anion-anion and cation-cation pairs.

B. Confined Solution

The ionic concentration profiles for each NaCl molality are shown in Figure 4 averaged over independent simulations. The density is inhomogeneous close to the mineral surfaces due to the interactions between ions and quartz. The first sharp peak of Na\textsuperscript{+} represents the counter-ion adsorption. The negative net charge at the surface due to the deprotonation of the silanols group attracts the cations, resulting in a nearby region with an excess of positive charges. The anions are repelled by the negatively charged surface and the Cl\textsuperscript{–} concentration at the interface is lower than in the bulk region. There are still, however, some Cl\textsuperscript{–} ions within the Stern layer due to cation-anion interactions. Therefore, classical EDL models, which predict no, or very few, co-ions at the direct interfacial region of a charged surface, overestimate the exclusion of co-ions\textsuperscript{34}.

By scaling down the ion’s charge, the adsorption of Na\textsuperscript{+} is decreased by almost half of the one from the integer-charge model. This indicates that electrostatic interactions play a key role in the cation adsorption over negatively charged surfaces. In the SPCE-SD force field, the excluded volume and the excess of local positive charge prevent a higher cation concentration right after the first Na\textsuperscript{+} peak, but another peak appears due to the long-range electrostatic interactions with the negative wall. The adsorption plane is located further from the surface with scaled-charge electrolytes, close to the location of the second peak in the Na\textsuperscript{+} density from the SPCE-SD model.

From the ionic density profile, we compute the free charge density and the electrostatic potential profile within the pore (Figure 5). The surface electrostatic potential is negative as a result.
of net negative charge. Due to a more distant location of the adsorption plane and the lower dielectric constant (Figure 2.A), the surface potential predicted from the TIP4P-Madrid model is significantly higher in magnitude than SPCE-SD. The higher the salinity, the more compact the Stern layer, and the steeper the electrostatic potential gradient.

In more concentrated solutions \( (m_s > 1 \text{ mol} \cdot \text{kg}^{-1}) \), our simulations show that the counterions screening the surface overcompensate the surface negative charge, establishing an apparent positive charge in the interfacial region. This phenomenon is known as charge inversion (or overcompensation)\(^{102}\) and may be observed in the EDL regions where the electrostatic potential is positive (Figure 5). Charge inversion has already been reported in past MD simulations\(^ {34,35,102}\). Charge inversion has also been reported experimentally\(^ {103}\), and it has been used to explain non-obvious phenomena, such as the charged DNA condensation to packed structures\(^ {104}\), and protein adsorption to same polarity surfaces\(^ {25}\). The reason why there is an overcompensation of counterions at higher ionic strengths is still uncertain\(^ {105}\). For multivalent electrolytes, one would expect that the ion-ion electrostatic interactions would play a key role\(^ {103}\), whereas for monovalent salts the different sizes of ions may become crucial\(^ {102}\). Specific adsorption and high binding affinity

FIG. 4: Concentration of (A, B) Na\(^+\) cations and Cl\(^-\) anions within the quartz nanopore in the confined direction for (A, C) SPCE-SD, and (B, D) TIP4P-Madrid force fields.
between surface-counterion may also lead to ionic density charge above the surface charge\(^{106}\). Depending on the chemical composition, the surface, and the ionic strength, charge inversion may lead to polarity inversion of the measured streaming potential/current and zeta potential\(^{106}\); however, this does not necessarily always occur when there is charge inversion at the interface.

The Poisson-Boltzmann equation can be used to estimate the electrostatic potential in the Electrical Double Layer (Figure S9 in the Supplementary Material). Differently from the MD simulations, the PB potential at the surface decreases with salinity because it does not account for the dielectric saturation. The electrostatic potential from dilute solutions, in which ion-ion interactions are insignificant, is well described by the PB equation when compared with integer-charge ions. At higher ionic strength, electrostatic interactions become dominant, and the PB equation becomes inaccurate. For instance, PB does not capture charge inversion. MD simulations may be employed to improve the PB description of the EDL. Boltzmann distribution, for instance, may be modified to account for the ionic adsorption using the free energy profile from a potential of mean force (PMF)\(^{41}\). Alternatively, the potential and location of the outer-sphere surface complex in MD simulations may be used to delimit the Stern from the diffuse layer\(^{42}\).

From MD simulations, we estimate the water parallel self-diffusivity and the solution shear
viscosity (Figure 6). The solid-liquid interface represents a high-viscosity and low-diffusivity region because water molecules mobility is constrained by both the quartz surface and the counter-ion adsorption layer. The transition from the Stern to the diffuse layer is demonstrated through the diffusion and viscosity discontinuity at $z \approx 0.3$ nm, which is more defined for the SPCE-SD model because of its stronger cation adsorption. At the center of the pore, the salinity effect is the same as in the homogeneous solution, i.e. the higher the ionic strength, the lower the diffusivity (Figure 3.B and S5 in the Supplementary Material).

![FIG. 6: (A, B) Water parallel self diffusivity and (C, D) shear viscosity profile of confined aqueous NaCl solution at 300 K for (A, C) SPCE-SD and (B, D) TIP4P-Madrid force fields.](image)

The electroosmotic mobilities for $m_s = 0.11, 0.5, \text{and } 2 \text{ mol·kg}^{-1}$ are shown in Figure 7. We compare the results from NEMD (with different magnitudes of applied electric fields) and EMD (no electric field) simulations. There is an electroosmotic mobility dependency on the electric field, which is more evident for the integer-charge electrolytes at lower concentrations. Indeed, the magnified electric field disturbs the equilibrium interfacial structure (Figure S10 in the Supplementary Material). The external electric field reduces the effect of the internal electric field from the EDL on the fluid and as a consequence, the ionic distribution becomes flatter. Because the counter-ion adsorption is notably stronger with integer-charge ions, the effect of the external electric field on the EDL structure is more pronounced in the SPCE-SD force field. One could
advocate the use of reduced electric field, however, at higher ionic strength this could lead to excessive simulation noise and an inaccurate profile of electroosmotic mobility (see Figure 7.E and F).

FIG. 7: Effect of external electric field magnitude on the electroosmotic flow compared with equilibrium distribution at 300 K and (A, B) 0.11, (C, D) 0.50 and (E, F) 2.00 mol·kg$^{-1}$ for (A, C, D) SPCE-SD and (B, D, F) TIP4P-Madrid force fields. The vertical dashed line for each condition represents the closest point to the wall, where the electroosmotic mobility fitted by a polynomial interpolation is zero.

To avoid the use of magnified force fields, EMD may be applied. Nonetheless, by assuming the fluid velocity is zero only at the surface, the electroosmotic mobility is overestimated. At hydrophilic surfaces, the fluid sticks to the surface and there may be a layer of immobilized molecules$^{107}$. The position from the surface $z_{sp}$ in which $v_x = 0$ indicates the shear plane location. We have fitted the NEMD electroosmotic mobility with a polynomial interpolation to estimate the shear plane location (Figure 7). The dependency of the shear plane location on the electric field magnitude is not as strong as the dependency of the electroosmotic mobility on the applied electric field. Therefore, $z_{sp}$ may be obtained from NEMD simulations and used to shift the electroosmotic mobility profile in EMD simulations to $\mu(z_{sp}) = 0$ (EMD-NEMD). In the lower limit of the electric
field magnitude \((E = 0.1 \text{ V} \cdot \text{nm}^{-1})\), the results from NEMD and EMD-NEMD tend to be almost the same. Not always a smooth profile is obtained by the NEMD simulations at this condition, which makes the combination of EMD and NEMD a more reliable path to compute the electroosmotic flow. However, it is important to have in mind that the EMD and EMD-NEMD methods rely on the Stokes-Einstein viscosity, which is an approximation, particularly in a inhomogeneous system.

We focus our analysis on the EMD-NEMD combined simulations. The shear plane location is obtained with NEMD simulations by applying \(E = 0.2 \text{ V} \cdot \text{nm}^{-1}\) (Figure 8.A). For SPCE-SD at \(m_s \geq 1 \text{ mol} \cdot \text{kg}^{-1}\) we apply an enhanced electric field \((E = 0.5 \text{ V} \cdot \text{nm}^{-1})\); if the same \(E\) would be applied for this force field, the simulation noise at higher concentrations would difficult the determination of \(z_{sp}\). Alternatively, the shear plane location can be determined from EMD simulations using the electrostatic potential and the EMD zeta potential, in such a way that \(\phi(z_{sp}) = \zeta_{\text{EMD}}\). While the location of the shear plane emerges naturally from the electroosmotic velocity profile in NEMD simulations, in the EMD approach, it relies on the Helmholtz-Smoluchowski equation accuracy and on the Poisson equation with uniform permittivity under confinement validation. Nevertheless, there is reasonable agreement between approaches (Figure 8.A). The location of the shear plane from both methods decreases with salinity due to the compaction of the EDL. At higher ionic strength, \(z_{sp}\) becomes comparable with the Debye’s length (Figure 8.A), which is a parameter that describes the diffuse layer thickness in EDL classic models. This may be interpreted as a near-total collapse of the diffuse layer at such conditions due to the strong ionic adsorption onto the surface, which is consistent with a hypothesis of the maximum packing of the Stern layer with counter-ions. The hypothesis was suggested to explain the experimentally observed stabilization of the zeta potential at a constant value at high salinity\(^{108}\).

The EMD-NEMD electroosmotic mobility, represented from EMD simulations shifted by the NEMD shear plane, is shown in Figure 8.B. The original EMD and NEMD electroosmotic mobility profile is also shown in Figure S11 in the Supplementary Material. By increasing the ionic strength, the mass transport due to an external electric field is decreased because water molecules’ mobility is reduced. Furthermore, the charge compensation in the diffuse layer is more efficient at higher concentration of ions, because only layers containing uncompensated charges contribute to an increase in the streaming current. The bulk electroosmotic mobility in the TIP4P-Madrid model is enhanced because the electrostatic interactions between scaled charge electrolytes and water molecules are reduced. The charge inversion phenomenon is reflected through the non-monotonic behavior of \(\mu\). For the SPCE-SD force field, at \(m_s \geq 1 \text{ mol} \cdot \text{kg}^{-1}\), the electroosmotic
mobility is less dependent on salinity and is close to zero at the center of the pore. The negative values at higher concentrations may indicate a reversed electroosmotic flow\textsuperscript{106}.

The zeta potential is computed by applying the HS equation with the MD-computed values of shear viscosity, electroosmotic mobility, and dielectric constant (Figure 9). Overall, the higher the concentration, the lower (in absolute value) $\zeta$ potential. The concurrent increase in the surface charge, but decrease in zeta potential magnitude with the ionic strength is a consequence of the EDL structure: at higher salinity, the packing of counter-ions screening the surface leads to a lower apparent net charge and a higher capacitance of the Stern layer\textsuperscript{109}. At higher ionic strengths, however, zeta potential tends to become independent of the salinity, which is consistent with many experimental studies\textsuperscript{108,110–113}. At that condition, the diffuse layer no longer behaves as a Boltzmann distribution, being controlled by ion-ion interactions\textsuperscript{113}. Using integer-charge force field for electrolytes, the ionic association is overestimated (Figure 2.B), which may cause the inversion in the zeta potential polarity at $m_s \geq 1$ mol·kg\textsuperscript{-1}. With SPCE-SD, most of the counter-ions accumu-
late in the Stern layer (see the first adsorption layer in Figure 4), which decreases the net charge density of the diffuse layer, leading to its collapse and a positive and close to zero zeta potential at high salinity.

FIG. 9: Zeta potential of aqueous NaCl solution confined by quartz at pH = 7.2 and 300 K compared with experimental values from Fontainebleau (FB) and Lochaline (LC) sandstones$^{108,112,113}$. The error bar shown is an average of the experimental uncertainty for results obtained at high salinity ($m_s > 1 \text{ mol-kg}^{-1}$)$^{108}$. The errors were not reported for Lochaline samples.

The zeta potential computed via MD simulations is compared with experimental data for the NaCl-quartz system at 300 K, and pH ranging from 6.4 to 7.5$^{108,112,113}$. To validate our results, only experimental data from “clean” sandstones (>99 %wt quartz), such as Lochaline and Fontainebleau samples, are used$^{108,112,113}$. Many zeta potentials reported at ionic strength higher than 1 M are interpreted from the streaming potential measurements on natural sandstones, most of which have a substantial clay content, and therefore we do not use them for comparison. Still, the experimental data are somehow scattered due to the use of real minerals, which may contain defects, different geometries, mineralogy, shapes, grain roughness, and crystallographic planes$^{114}$; furthermore, if not controlled, pH variation may significantly affect the zeta potential interpretation$^{112,113}$. At higher salinities, there may be large uncertainties associated with the experimental data due to the lower streaming potential established, which deteriorates the reproducibility of experiments$^{108}$. In our MD simulations, we use an idealized mineral with no defects. Zhang, Lu, and Chen$^{45}$ have shown that the surface roughness, for instance, may affect the zeta
potential from molecular simulations.

There is a good agreement in zeta potential value and trend between the TIP4P-Madrid model and experiments in the entire range of simulated salinity, especially with Fontainebleau sandstones. On the other hand, for SPCE-SD, a reasonable representation of the zeta potential is only achieved at lower salinity. From experiments, a linear relationship between \( \log m_s \) vs \( \zeta \) is expected at lower ionic strength, and a stabilization of the zeta potential at a non-zero value \( (\zeta_0) \) at salinity higher than an EDL saturation salinity \( (m_{s}^{\text{sat}}) \)\(^{108,110-113} \):

\[
\zeta = \begin{cases} 
  a + b \log m_s, & \text{if } m_s \leq m_{s}^{\text{sat}} \\
  \zeta_0, & \text{if } m_s > m_{s}^{\text{sat}}
\end{cases}
\]  

\( (16) \)

Experimentally, the EDL saturation concentration is estimated at around 0.45 M\(^{110,113} \). Due to the scatter in the high salinity data, there is considerable uncertainty associated with the experimental zeta potential offset, with reported values ranging from -20\(^{110} \), -17\(^{108,112} \), -15\(^{111} \), -13\(^{112} \), and -10\(^{113} \) mV. From our simulations, \( m_{s}^{\text{sat}} \) is expected to be around 1 mol.kg\(^{-1} \) for both force fields. In Figure S12 of the Supplementary Material, we show the fitting of our MD simulation and experimental data to Eq. 16. The offset zeta potential expected to the SPCE-SD, TIP4P-Madrid models and experimental dataset from FB and LC sandstones are -0.7 \( \pm \) 1.2, -9.7 \( \pm \) 0.9, -13.6 \( \pm \) 0.3 and -19.9 \( \pm \) 0.7 mV, respectively. Therefore, the offset zeta potential from the TIP4P-Madrid model is close to the one predicted by the experimental dataset of Fontainebleau samples and is exactly the same as the one reported by Vinogradov, Jackson, and Chamerois\(^{113} \). By extrapolating the MD results to infinite dilution, the predicted zeta potentials of both force fields are close to the cloud of experimental data. A better representation of such conditions may be obtained by simulating lower salinity points since only four points are suitable for the linear regression \( (m_s \leq m_{s}^{\text{sat}}) \).

The slope \( (b) \) could be adjusted to match the experimental one for both models, nevertheless, the stabilized zeta potential is unequivocally better predicted by TIP4P-Madrid.

Alternatively from electroosmotic flow measurements, the zeta potential may be obtained by streaming potential measurements\(^{110,112,113} \). From the coupling phenomena between momentum (pressure-driven) and electric charge (potential-driven) transfer, the streaming potential coupling coefficient \( (C_{sp}) \) emerges. This coefficient quantifies the electrostatic potential (streaming potential) generated by a pressure gradient and is given by\(^{115} \):

\[
C_{sp} = \frac{\Delta \phi}{\Delta P} = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta \kappa}.
\]  

\( (17) \)
We test the transferability between electroosmosis and streaming potential, by computing $C_{sp}$ applying the Green-Kubo shear viscosity and Einstein-Helfand ionic conductivity (Figure 10). The results are not much influenced by using the Stokes-Einstein solution viscosity and Nernst-Einstein ionic conductivity as shown in Figure S13 in the Supplementary Material. The overall trend of the salinity dependence of the streaming potential coupling coefficient is in good agreement with the experiments. By the analysis of the log scale, we note larger deviations at higher ionic strength for the SPCE-SD model due to the almost zero zeta potential obtained by this force field, which, therefore, produces a high numerical noise (uncertainty) in computing the streaming potential coupling coefficient (inset of Figure 10). Once again, the agreement between TIP4P-Madrid and experiments is excellent.

![Streaming coupling coefficient of aqueous NaCl solution confined by quartz at pH = 7.2 and 300 K compared with experimental values from Fontainebleau (FB) and Lochaline (LC) sandstones](image)

FIG. 10: Streaming coupling coefficient of aqueous NaCl solution confined by quartz at pH = 7.2 and 300 K compared with experimental values from Fontainebleau (FB) and Lochaline (LC) sandstones. The inset represents the data in log scale

A comparison of the electroosmotic mobility in the bulk, the zeta potential, and the streaming potential coupling coefficient for the different methods (EMD, NEMD, EMD-NEMD) is shown in Figure S14 in the Supplementary Material. Scaled charge electrolytes are less sensitive to magnified electric fields. As a consequence, all three properties are almost identical in the entire range of salinity between NEMD and EMD-NEMD methods. On the other hand, the effect of an external electric field is significant in the system with integer-charge electrolytes. Even at $m_s = 0.11$ mol·kg$^{-1}$, the electric field with magnitude of $E = 0.2$ V·nm$^{-1}$, overestimates the electroosmotic mobility (Figure 7.A). Although the zeta potential and $C_{sp}$ at higher salinity for NEMD are closer to the experiments, a more magnified electric field ($E = 0.5$ V·nm$^{-1}$) is applied to obtain the shear plane location. Therefore, the NEMD zeta potential magnitude at such conditions is overestimated,
and the EMD-NEMD represents more realistic force field results.

IV. CONCLUSIONS

The interfacial electrochemical and fluid properties of quartz-NaCl solution systems are investigated with MD simulations. We employ both integer-charge and scaled-charge force fields for electrolytes to compare their performance. In a first stage, we compute properties of the solution in the bulk. Integer-charge force field overestimates the ionic association and the dielectric saturation, whereas the dielectric constant of the scaled-charge force field is described with high accuracy if electronic continuum correction is applied. From the ionic conductivity accounting for the cross-correlation, we show that there is an over-repulsion between same type ions, which leads to an underestimation in the conductivity of both force fields. The solution viscosification caused by the presence of electrolytes is captured. If the hydraulic radius of the water molecule is adjusted accordingly, the Stokes-Einstein equation provides a fast framework to estimate the viscosity.

Under confinement, we investigate the electrical double layer established by the salt solution. We propose a new method to accurately predict the zeta potential over a broad range of salinities up to 3 mol·kg⁻¹. We advocate for using equilibrium and non-equilibrium molecular dynamics simulations together. From NEMD, the shear plane location is obtained, and it does not depend on the magnitude of the applied electric field. Then, from EMD, using the macroscopic Stokes-Einstein approximation for viscosity, the electroosmotic mobility profile with ionic distribution at the equilibrium is determined. Combining EMD and NEMD, we can shift the EMD electroosmotic profile to represent the shear plane at the right distance from the mineral surface.

By using scaled-charge force field, our method accurately matches available zeta potential and streaming potential coupling coefficient experimental data for the quartz-NaCl system. At higher ionic strength a stabilization of the zeta potential at -9.7 mV is predicted, which is close to the experimental value reported by Fontainebleau sandstones (-13.6 mV). From the molecular-scale perspective, our MD simulations explain the observed stabilization of ZP at high salinity attributed to maximum packing of the Stern layer, thus promoting the understanding of the EDL structure and behavior at high ionic strength.

Overall, we show that scaled-charge force fields for electrolytes provide a good representation of saline solutions. In the future, we encourage to put more effort in this direction for the representation of electrolytes in molecular simulations, with the development, for instance, of force
fields for the confining media consistent with scaled-charge ions. The molecular insights obtained by the work between quartz mineral and aqueous NaCl pave the way for simulating more complex systems in the future, containing, for instance, salts mixtures, multivalent electrolytes, different mineral surfaces, and multicomponent brine mixtures.

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SUPPLEMENTARY MATERIAL

The Supplementary Material contains Poisson-Boltzmann and Helmholtz-Smoluchowski equations; force field parameters; analysis of properties, and structure of bulk NaCl solution (density, radial distribution function, cation hydration number, diffusivity, viscosity, and ionic conductivity); comparison of equilibrium and non-equilibrium MD in properties of confined NaCl solution (electroosmotic mobility, zeta potential, and streaming potential coupling coefficient); values of computed properties of the homogeneous and confined solution (PDF).

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