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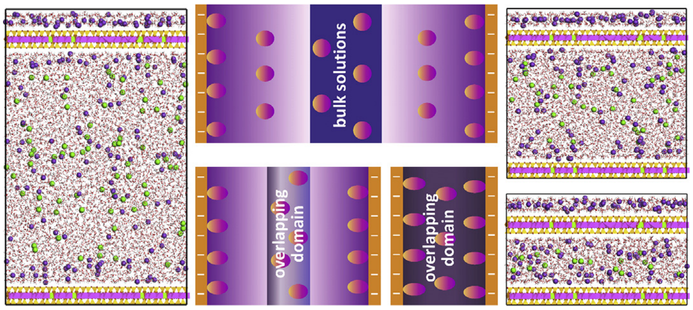
Confinement effects and mechanistic aspects for montmorillonite nanopores

Xiong Li, Chang Zhu, Zengqiang Jia, Gang Yang *

College of Resources and Environment & Chongqing Key Laboratory of Soil Multi-scale Interfacial Process, Southwest University, Chongqing 400715, China

GRAPHICAL ABSTRACT



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ABSTRACT

Owing to the ubiquity, critical importance and special properties, confined microenvironments have recently triggered overwhelming interest. In this work, all-atom molecular dynamics simulations have been conducted to address the confinement effects and ion-specific effects for electrolyte solutions within montmorillonite nanopores, where the pore widths vary with a wide range. The adsorption number, structure, dynamics and stability of inner- and outer-sphere metal ions are affected by the change of pore widths (confinement effects), while the extents are significantly dependent on the type of adsorbed species. The type of adsorbed species is, however, not altered by the magnitude of confinement effects, and confinement effects are similar for different electrolyte concentrations. Ion-specific effects are pronounced for all magnitudes of confinement effects (from non- to strong confined conditions), and Hofmeister sequences of outer-sphere species are closely associated with the magnitude of confinement effects while those of inner-sphere species remain consistent. In addition, mechanistic aspects of confinement have been posed using the electrical double layer theories, and the results can be generalized to other confined systems that are ubiquitous in biology, chemistry, geology and nanotechnology.

1. Introduction

Understanding the properties of confined microenvironments is critical for a wide spectrum of fields such as nanofludics [1,2], desalination devices [3,4], flow sensing [5], catalysis [6] and biological functions [7]. It is known that ions and molecules are significantly affected by the spatially confined microenvironments and exhibit particular diffusion, adsorption and catalytic behaviors that are distinct from bulk systems [2,6,8,9]. To attain the detailed atomic-level information regarding to these confinement behaviors is of great importance, not only for improving the knowledge of chemical and biological processes, but also for the development of advancing technologies.

Davis and collaborators [10–13] conducted an extensive study on the molecular theory, structure and dynamics of fluids confined

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* Corresponding author.
E-mail address: theobiochem@gmail.com (G. Yang).

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in micropores. In 2001, Hummer et al. [14] used molecular dynamics (MD) simulations and observed that water molecules are spontaneously and continuously transmitted through the hydrophobic carbon nanotubes (CNT). Since then, MD simulations have been used extensively providing valuable information otherwise inaccessible with respect to confinement effects [15–23]. Li et al. [17] tried a number of CNTs with different diameters and found that (8,8)CNT is the most appropriate for the selective transportation for K^+ vs. Na^+. Dai et al. [20] investigated the ion rejection within layer-to-layer assembled graphene oxides and confinement effects therein were attributed to the size exclusion of ion hydration and the surface interaction from functional groups. Argyris et al. [22] reported the structure and dynamics of NaCl and CsCl solutions confined within the charged silica nanopores, where the pore width equals 10.67 Å and charges are associated with surface hydroxyl groups. Neither Na^+ nor Cs^+ was detected to contact directly with silica surfaces, and as compared to Na^+ ions, Cs^+ ions show an enhanced in-plane mobility, which was attributed to the exclusion from the well-defined water layers. However, with a different pore width (42.0 Å), Hartkamp et al. [23] demonstrated that Na^+ and Cs^+ have consistent distances from the surfaces of charged silica nanopores. Till date, how confinement effects are correlated with the pore widths and further affect the adsorption structure and dynamics of ions as well as ion-specific effects corresponding to different confinement effects remain largely enigmatic.

Montmorillonite (MMT), widely used in chemical and pharmaceutical manufacturing, oil drilling industry, engineered barriers as well as catalysts and promoters [24–27], has recently gained enough attention [28–44]. Similar to other systems such as the charged silica nanopores, previous reports of MMT are mainly restricted to the interfacial adsorption corresponding to specific pore widths. The pore widths of MMT are of variable sizes and thus serve as a good prototype to investigate confinement effects. In this work, MD simulations were conducted for KCl solutions confined within MMT nanopores and the confinement effects were demonstrated at a molecular level through the gradual regulation of pore widths (L = 90–20 Å).

Holmboe et al. [44] detected that the diffusion coefficients of metal ions in the narrow interlayers of MMT, which are generally ascribed to strongly confined systems (*vide post*), are sensitive to the water content, and herein we showed that the diffusion coefficients for metal ions within MMT nanopores also show strong dependence to the pore widths (L). Accordingly, diffusion coefficients were presently used and the mechanistic aspects of confinement effects were deciphered where the physical principles are underpinned; Meanwhile, this work represents a step forward for the electrical double layer (EDL) theories, especially during the interpretation of colloid aggregation. As claimed by Kunz et al. [45], ion-specific effects are as important in the scheme of things as was Mendel's work to genetics. Does regulation of confinement effects affects ion-specific effects, and if yes, how are ion-specific effects altered by the different confinement conditions? To address these issues, MD simulations were performed for other electrolyte solutions (NaCl, CsCl, $CaCl_2$ and $PbCl_2$) confined within MMT nanopores spanning a wide range of pore widths (L = 90–20 Å), as in the case of KCl solutions. It showed that the sequence of ion-specific effects may vary significantly due to the change of confinement effects and the sensitivity to confinement effects relies strongly on the identity of metal ions.

2. Computational details

Montmorillonite (MMT) generally has a chemical formulas of $(Mg_{0.75}Al_{3.35})_4Si_8O_{20}(OH)_4$, corresponding to an octahedral layer charge of $-0.75\ e\cdot uc^{-1}$ that was balanced by metal ions such as K^+ and Ca^{2+} (*e* and uc stand for the elementary charge and unit cell, respectively.) [46]. The simulation cells were composed by 128 unit cells ($8 \times 8 \times 2$ along *x*, *y* and *z* directions, where *z* is the direction normal to the MMT surfaces). Fig. 1 illustrated the initial configurations of 0.48 mol/L KCl solutions confined within MMT nanopores. A two-layer hydrated state was constructed in the interlayer region [28]. The confinement effects of MMT nanopores, which are the focus of this study, were simulated through the gradual reduction of pore widths (L). As indicated in Fig. 1, the widths of MMT nanopores were designated to be 90, 80, 70, 60, 50, 40, 30, 20 Å that were subsequently filled with 8919, 7928, 6937, 5946, 4955, 3964, 2973, 1982 water molecules to maintain a density of $1.0\ g\cdot cm^{-3}$. For each pore width (L), 0.48 mol/L KCl solutions confined within MMT nanopores were attained by replacing certain numbers of water molecules with K^+-Cl^- ion pairs. Other systems accounting for a wide range of pore widths (L = 90–20 Å) were prepared similarly as those of 0.48 mol/L KCl solutions, including 0.16 and 0.96 mol/L KCl solutions as well as 0.48 mol/L NaCl, CsCl, $CaCl_2$ and $PbCl_2$ solutions.

All-atom MD simulations employing the periodic boundary conditions (PBC) were conducted using the Gromacs-4.6.5 software [47]. MMT and ions were described by the CLAYFF potential parameters [48], which, in combination with the SPC water model [49], have been sufficiently verified to account for the interfacial interactions of MMT and electrolyte solutions [28–41,43,44]. The long-range interactions were treated by means of the Particle-Mesh-Ewald (PME) method while the short-range interactions were summarized over the van der Waals (vdW) and electrostatic terms represented by the 12-6 Lennard-Jones and Coulomb potentials, respectively. The leapfrog algorithm was employed to integrate the equations of motion with the time step of 2.0 fs [50], and the atomic coordinates were updated every 1.0 ps. The simulation temperature (T = 300.0 K) and pressure (p = 1.0 bar) were controlled respectively by the V-rescale thermostat [51] and Parrinello-Rahman barostats [52]. 10.0 ns MD simulations were performed for each system, and all analyses were based on the latter 5.0 ns trajectories that have reached the equilibrium states. The potentials of mean force (PMF) for adsorbed metal ions were estimated using the umbrella sampling technique [53,54]. The final configurations of MD simulations were utilized to initiate the steered molecular dynamics (SMD) simulations with the pulling velocity $v = 0.1\ nm\cdot ns^{-1}$ and spring constant $k = 10000\ kJ\cdot mol^{-1}\cdot nm^{-2}$. Every SMD simulation was run for 1.0 ns, and the weighted histogram analysis method (WHAM) was then performed to derive the PMF profiles [55]. The diffusion coefficients (*D*) of ions parallel to the MMT surfaces (*x*-*y* plane) were calculated using the Einstein relation [34,56],

$$\langle \Delta x(\tau)^2 + \Delta y(\tau)^2 \rangle = 4D\tau$$

where $\langle \Delta x(\tau)^2 + \Delta y(\tau)^2 \rangle$ refers to the mean-square displacement over a time interval (τ).

3. Results and discussion

3.1. 3.1. Confinement effects for K^+ ions

For all pore widths (L = 90–20 Å), 0.48 mol/L KCl solutions within MMT nanopores show the resembling adsorption trends: As MD simulations proceed, a large portion of K^+ ions approach the MMT surfaces successively and are adsorbed as inner-sphere (**IS**) and outer-sphere (**OS**) species while Cl^- ions are prone to stay in solutions (Figs. 2 and S1), in agreement with previous results obtained using specific pore widths (L) [32,57]. Throughout the entire range of pore widths (L = 90–20 Å), there always exist three distinguishable peaks in the atomic density profiles that