



Molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl–CaCl₂) solutions

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ABSTRACT

We report new molecular dynamics results elucidating the structure of the electrical double layer (EDL) on smectite surfaces contacting mixed NaCl–CaCl₂ electrolyte solutions in the range of concentrations relevant to pore waters in geologic repositories for CO₂ or high-level radioactive waste (0.34–1.83 mol_c dm⁻³). Our results confirm the existence of three distinct ion adsorption planes (0-, β-, and d-planes), often assumed in EDL models, but with two important qualifications: (1) the location of the β- and d-planes are independent of ionic strength or ion type and (2) “indifferent electrolyte” ions can occupy all three planes. Charge inversion occurred in the diffuse ion swarm because of the affinity of the clay surface for CaCl⁺ ion pairs. Therefore, at concentrations ≥0.34 mol_c dm⁻³, properties arising from long-range electrostatics at interfaces (electrophoresis, electro-osmosis, co-ion exclusion, colloidal aggregation) will not be correctly predicted by most EDL models. Co-ion exclusion, typically neglected by surface speciation models, balanced a large part of the clay mineral structural charge in the more concentrated solutions. Water molecules and ions diffused relatively rapidly even in the first statistical water monolayer, contradicting reports of rigid “ice-like” structures for water on clay mineral surfaces.

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1. Introduction

The electrical double layer (EDL) on charged solid surfaces in contact with an aqueous electrolyte solution containing small inorganic ions is known to consist of three kinds of adsorbate species: inner-sphere surface complexes (ISSC), outer-sphere surface complexes (OSSC), and diffuse swarm (DS) species [1,2]. This view is adopted, for example, as the molecular basis for the widely-applied triple layer model (TLM [3–5]), on which the distribution of ions near a charged planar solid surface is calculated under a set of simplifying assumptions that include assigning all ISSCs to a plane at the solid surface (0-plane), all OSSCs to a second plane lying farther into the aqueous phase (β-plane), and all DS species to a region lying beyond a third plane farther out than the β-plane (d-plane) (Fig. 1). Computational and physical closure in the TLM is achieved as in other surface speciation models, by invoking charge-potential relationships in which the electrostatic potential drops between the 0- and β- and the β- and d-planes are modeled with the help of two capacitance factors, while that across the diffuse swarm is modeled with the well-known Poisson–Boltzmann equation.

Inferences about EDL surface speciation and molecular structure from experimental data on proton and ion adsorption [6–8],

salt filtration efficiency [9], second harmonic generation [10], electrophoretic mobility [11], or interparticle forces [12] are necessarily sensitive to simplifying EDL model assumptions such as those just described for the TLM [13–16]. Models of the EDL that approximate liquid water as a uniform dielectric continuum (such as the Poisson–Boltzmann equation [17,18], hypernetted chain theory [19,20], or the primitive model [18,21]) inherently cannot describe surface complexes [17,18]. Spectroscopic methods that probe the local molecular environment of “reporter atoms” (for example, nuclear magnetic resonance (NMR) [22,23] or X-ray absorption spectroscopy (XAS) [24,25]) have shown that adsorbed inorganic ions can adopt several different configurations that include both fully- and partly-solvated species. Resonant anomalous X-ray reflectivity (RAXR) studies, which probe solute concentration as a function of distance from a planar surface, have confirmed that EDL ions can adsorb simultaneously in both ISSCs and OSSCs [26–30]. However, spectroscopic techniques have not yet succeeded in simultaneously detecting all three adsorbate species to show that they can coexist in the same nanoscale interfacial region, nor have they been able to resolve their fine structure.

The present state of affairs in theory and experiment thus leaves open some key fundamental questions about EDL structure: Are there three—and only three—well-defined adsorption planes [27,29,31]? Are the typical “indifferent electrolyte” ions [1], such as Na⁺ and Cl⁻, excluded from the 0-plane [5] or from both the 0- and β-planes [13]? Can the capacitance factors applied to model

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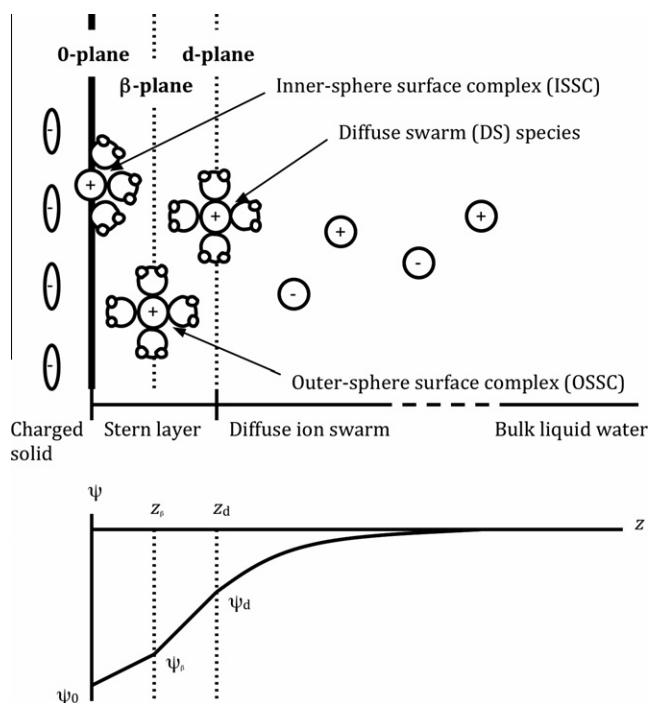


Fig. 1. Conceptual model of EDL structure (top) and electrostatic potential $\psi(z)$ (bottom, relative to a reference state in the bulk liquid) as a function of distance from a negatively charged surface according to the TLM [1,4]. On the TLM, the electrostatic potential drop in the Stern layer is modeled by analogy with two capacitors: $\psi_\beta - \psi_0 = -\sigma_0/C_1$ and $\psi_d - \psi_\beta = \sigma_d/C_2$, where σ_0 is the surface charge density (solid structural charge plus the charge of all species adsorbed in the 0-plane), σ_d is the excess charge in the diffuse layer, ψ_0 , ψ_β , and ψ_d are the electrostatic potentials at the 0-, β -, and d-planes, and C_1 and C_2 are the capacitances of the space between the 0- and β -planes and between the β - and d-planes, respectively. The electrostatic potential in the diffuse ion swarm is modeled using the Poisson–Boltzmann equation for a flat surface: $d^2\psi/dz^2 = -(\epsilon_0\epsilon_w)^{-1} \sum_i [Z_i F c_{i0} \exp(-Z_i F \psi / RT)]$, where ϵ_0 is the permittivity of vacuum, ϵ_w is the dielectric constant of water, Z_i and c_{i0} are the valence and bulk aqueous concentration of species i , F is the Faraday constant, R is the molar gas constant, and T is absolute temperature.

the region between the 0- and d-planes [8,21] and the model binding constants describing the adsorption of background electrolyte ions in the β -plane [32] be predicted instead of inferred from experimental data as fitting parameters, often poorly constrained [13,16,33]? And finally, the abiding question, how accurately does the Poisson–Boltzmann equation used in all EDL models predict ion distributions and electrostatic potentials in the diffuse swarm [21,34]?

For more than a decade, molecular dynamics (MD) and Monte Carlo (MC) simulations have provided insight into the behavior of water and ions near flat charged surfaces [2,18,35–54]. In particular, these simulations have confirmed that ions confined between planar charged surfaces do form ISSC, OSSC, and diffuse swarm species [35] in agreement with most EDL models. However, few simulations have investigated the molecular structure of the EDL in water films sufficiently thick (>4 nm [50]) to probe the transition from adsorbed water to bulk liquid water [39,51,52]. Of the few studies that have done this, most used simulation times too short (<2 ns) to allow counterions to exchange extensively between ISSC, OSSC, DS, and bulk electrolyte species. To our knowledge, only Tournassat et al. [52] have carried out a long (10 ns) MD simulation of a full EDL on a planar charged surface. These authors simulated the structure of a 0.1 mol dm⁻³ NaCl solution near a negatively-charged Na-smectite basal-plane surface. Although the Na⁺ and Cl⁻ distributions they found were qualitatively consistent with the TLM, there were significant quantitative

differences from model predictions. For example, the TLM overestimated anion exclusion from the clay surface by about 50%.

Here we present the results of MD simulations that extend the work of Tournassat et al. [52] to a mixed electrolyte of environmental importance (NaCl/CaCl₂), a broad range of electrolyte charge concentration (0.34–1.83 mol_c dm⁻³), and much longer simulation timescales (50 ns). Following Tournassat et al. [52], we focus on smectites because these ubiquitous clay mineral nanoparticles play important roles in soil chemistry [55,56], soil mechanics [57], fault friction [58,59], materials chemistry [60], landfill and contaminated site isolation [61,62], high-level radioactive waste storage [63,64], CO₂ sequestration [65,66], and gas hydrate stability in marine sediments [67,68]. Their adsorption properties for small inorganic ions have been extensively studied using macroscopic [55,56,69], spectroscopic [24,25], and MD simulation techniques [18,35,37,45,49,52]. Furthermore, smectites are isostructural with the well-crystallized micas used in surface force [12,70], X-ray reflectivity [26,27], and MD and MC simulation studies of EDL properties [38,44,51]. Our choice of mixed electrolyte solution (hereafter termed “brine”) allows comparison of the adsorption behavior of two major environmental cations, and our range of charge concentration (0.34–1.83 mol_c dm⁻³) covers that in high-level radioactive waste repositories (0.07–0.6 mol_c dm⁻³ [71–73]), seawater (0.6 mol_c dm⁻³ [74]), methane hydrates in ocean sediments (0.6–4.1 mol_c dm⁻³ [75,76]), and saline aquifers being considered for CO₂ sequestration (0.7–2.2 mol_c dm⁻³ [65,77–79]). Finally, our long simulation times (50 ns) allow a more stringent evaluation of current EDL models such as the TLM.

2. Molecular dynamics simulation methodology

Molecular dynamics simulations (50 ns, preceded by 1.2 ns of equilibration at 298 K) of NaCl/CaCl₂ brine confined in a 58 Å-wide nanopore between smectite basal surfaces were carried out in the microcanonical (*NVE*) ensemble with the program MOLLY 3.6 [80]. Our periodically replicated simulation cell contained one lamellum of Otay-type montmorillonite composed of 18 unit cells (dimension 30.8928 × 26.9932 Å in the *xy* plane) and a brine-filled nanopore containing 1620 water molecules (Fig. 2). The width of our simulated nanopore was chosen such that roughly one-third of all the water molecules in the system would behave as they do in bulk liquid water [50]. Our clay mineral structure was the same as that used by Bourg and Sposito [54]: montmorillonite atomic coordinates were fixed on the basis of the pyrophyllite structure of Bickmore et al. [81], and the negative structural charge of our clay lamella (1.2 mol_c kg⁻¹) resulted from 16 isomorphous substitutions of Al³⁺ by Mg²⁺ [average unit cell formula Si₈(Al_{3.111}Mg_{0.889})O₂₀(OH)₄] randomly scattered in the octahedral sheet [82] under the constraint that substitutions could not occur in adjacent OH-sharing octahedral sites [83]. Simulations were carried out for Na/Ca/Cl compositions of 12/6/8, 16/8/16, 24/12/32, and 32/16/48 atoms per simulation cell, resulting in bulk chloride concentrations of 0.34, 0.67, 1.25 and 1.83 mol dm⁻³. Prior to our simulations, cell *z* dimensions were determined by equilibrating each system for 200 ps at 298 K and constant volume, then for 400 ps at 298 K and constant gauge pressure $P_z = 0$ (*NVE* and *NP_zE* ensemble simulations, respectively, with molecular velocities scaled to 298 K every 10 ps). Average *z* cell dimensions during the last 300 ps of this equilibration were 66.65, 67.09, 67.59 and 68.17 Å for simulations with electrolyte concentrations of 0.34, 0.67, 1.25 and 1.83 mol_c dm⁻³, respectively. Total energy conservation during our 50 ns simulations was better than 99.99%. Long-range Coulomb interactions were treated by Ewald summation with parameters chosen to yield an Ewald sum accuracy of 99.99%.

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