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► To cite this version:

Christophe Tournassat, Ian C. Bourg, Carl I. Steefel. Breakdown of the modified Gouy-Chapman model for clay surfaces in equilibrium with a CaCl_2 electrolyte: a molecular dynamic study. Clays in Natural and Engineered Barriers for Radioactive Waste Confinement, Mar 2015, Brussels, Belgium. hal-01118802

HAL Id: hal-01118802

<https://brgm.hal.science/hal-01118802v1>

Submitted on 20 Feb 2015

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Breakdown of the modified Gouy-Chapman model for clay surfaces in equilibrium with a CaCl_2 electrolyte: a molecular dynamic study.

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Clay minerals have a high specific surface area that enhances their ability to influence water in their vicinity. Their surface charge, which varies as a function of physical-chemical conditions of the surrounding water, results in a complex organization of solute ions as a function of distance from the surface. This organization is known as the electrical double layer where counter-ions are electrostatically attracted to the surface whereas co-ions are repelled from it. Abundant and convincing spectroscopic evidence has emerged of a complex layering of water molecules and ionic species adsorbed at specific distances from the charged surfaces, a feature that can be captured by surface complexation models derived from Stern theory. The modified Gouy-Chapman model (MGC), or its modified version based on the resolution of the full Poisson-Boltzmann equation, is often used to calculate the electrostatic potential value in the diffuse region between the Stern layer and the bulk solution. Based on a comparison of the MGC model with Monte-Carlo simulations of discrete hard-sphere ions immersed in an implicit solvent, it was demonstrated long ago that the resolution of the full Poisson-Boltzmann equations can give accurate results for cations and anions distribution in the vicinity of a charged surface if both anions and cations are monovalent, if their total concentration does not exceed 0.1 mol/dm^3 and if the surface charge is not too high. When divalent (or multivalent) ionic species are present, the MGC model fails at reproducing Monte-Carlo simulations results in most conditions, because the MGC model neglects ion-ion interactions. For example, for 2:1 electrolytes the MGC model is thought to be inaccurate at salt concentrations greater than 0.005 mol/dm^3 (Torrie and Valleau, 1982; Carnie and Torrie, 1984; Boda et al., 2004).

Deviations from Poisson-Boltzmann model predictions probed by spectroscopic tools are now also available. Bu et al. (2006) demonstrated, using anomalous X-ray reflectivity data, that the MGC model is strikingly accurate at a highly charged interface in contact with a homovalent monovalent salt background up to a concentration of $10^{-2} \text{ mol dm}^{-3}$. Another study performed in similar conditions found that while accurate at 0.01 mol dm^{-3} , the Poisson-Boltzmann model failed to reproduce X-ray reflectivity data at higher concentrations (Luo et al., 2006). Molecular dynamics (MD) calculation studies have provided broadly similar results to those obtained by X-ray reflectivity (Wang and Chen, 2007; Lima et al., 2008; Lee et al., 2012). However, these studies were performed using homovalent monovalent electrolytes that are not generally representative of environments that are rich in clay minerals, whose surface sites tend to be occupied by divalent cations in natural clay formations.

In the present study, we evaluated the accuracy of MGC model predictions in a clay/water system in the presence of divalent cations and monovalent anions using MD calculations. Clay surfaces present several advantages with regards to molecular simulations owing to the 2D pseudo-periodicity of the clay particles. This system is particularly well suited to enabling accurate comparison between the MGC model prediction and the actual distribution of ions at the solid-water interface. Amongst clay minerals, montmorillonite has been the matter of multiple of MD simulation studies, but the vast majority of them involved only monovalent cations in interlayer spaces without the presence of anions. Few studies have been focused on divalent cations and/or charged surfaces in contact with large pores where the diffuse layer can fully extend without overlapping (Tournassat et al., 2009; Bourg and Sposito, 2011). We will

show that the MGC model prediction of the electrostatic potential value at the surface as well as the charge compensation over the distance from the surface are considerably more accurate than previously inferred from its comparison with Monte-Carlo simulations of discrete hard-sphere ions immersed in an implicit solvent.

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