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Research paper

## Density functional theory of electrolyte solutions in slit-like nanopores II. Applications to forces and ion exchange

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## ABSTRACT

An extended reference fluid density approach/weighted correlation approximation (RFD/WCA) of density functional theory (DFT) for size-asymmetric electrolytes presented in part I is applied to calculate the forces and the ion exchange for Ca- and Na-montmorillonite systems in equilibrium with salt solutions. Our modeling shows that the DFT calculations are in excellent agreement with Monte Carlo simulations and experimental results. The results indicate that the ion size plays an important role in force-distance relation. Due to the excluded volume effect, the osmotic pressure curve predicted by DFT is shifted towards larger separation distances with increasing the diameter of counterions. Additionally, the interaction can be switched from attraction to repulsion with increasing diameter of counterions from standard to hydrated ionic size. Furthermore, the quantitative characterization of the exchange of calcium for sodium at room temperature on Wyoming bentonite is investigated with the DFT modeling in aqueous solutions at pH 7.0. It is found that a significant variation of the selectivity coefficient could be observed with the surface charge density, ionic diameter and interlayer separations. This implies that ion selectivity in compacted bentonite differs from that in dilute smectite dispersions.

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## 1. Introduction

An electrical double layer (EDL) is created when a charged surface is in contact with an electrolyte (Attard, 1996; Fawcett, 2004; Henderson and Boda, 2009). Phenomena involving the EDL are common in aqueous electrolyte systems of clays (Spitzer, 1989; Norrish and Quirke, 1954), colloids (Evans and Wennerström, 1999) and membranes. In all these systems, the effective electrical forces between dispersed colloids (Guldbrand et al., 1984; Valleau et al., 1991; Kjellander and Marcčlja, 1984), and adsorptions of ions at charged interfaces (Lamperski and Outhwaite, 2008; Valiskó et al., 2007) arise from the ionic distributions in the interfacial region. Theoretical description of ionic structure therefore plays a significant role in explaining problems such as the flocculation or coagulation of natural bentonites (Neretnieks et al., 2009), the stability of colloidal dispersions (Guldbrand et al., 1984; Valleau et al., 1991; Kjellander and Marcčlja, 1984) and ion exchange in clays (Karnland et al., 2011; and Nachod, 2012).

In the traditional theory of describing the EDL, the Guoy-Chapman (GC) model using the Poisson-Boltzmann (PB) equation has been the main approach for studying the ionic structure of electrolyte solutions. However, the PB theory assumes ions to be point charges, as a result, entirely neglects the ion size causing ion-ion correlations (Kjellander et al.,

1988). In later development, integral equation theory (Kjellander and Marcčlja, 1984, 1985; Plischke and Henderson, 1988; Lozada-Cassou et al., 1982), modified PB theory (Borukhov et al., 1997), computer simulations (Torrie and Valleau, 1980) and density functional theory (DFT) (Rosenfeld, 1993; Hansen and Löwen, 2000; Hansen and McDonald, 2006; Henderson, 1992; Tang et al., 1990; Mier-y-Teran et al., 1991; Patra and Ghosh, 1994; Wu, 2006; Wu and Li, 2007) have successfully addressed the correlations and all specific interactions between ions for the description of EDL systems with the primitive model (PM), which is the simplest and “standard” model of electrolyte in these theories. As one of the most accurate tools, the DFT has been applied to more complicated real systems, for instance, predicting the zeta potentials of latex particles (Yu et al., 2004), swelling pressures of different types of bentonite (Liu, 2013), overcharging (Wang et al., 2004), preferential interactions between DNA and small mixed counterion (Wang et al., 2007), osmotic coefficients (Wang et al., 2008) of DNA in aqueous electrolyte solutions, and ion selectivity in a calcium channel (Peng and Yu, 2009).

Recently, the DFT of inhomogeneous fluid with the PM such as weighted density approximation (Curtin and Ashcroft, 1985, 1986), reference fluid density approach (Gillespie et al., 2002, 2003, 2005; Knepley et al., 2010) and weighted correlation approach (Wang and Liu, 2012a,b; Wang et al., 2011) have been widely applied to study the structures and thermodynamic properties of EDL systems, especially, the reference fluid density approach (RFD) and the weighted

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correlation approach (WCA) (Pizio et al., 2012; Pizio and Sokolowski, 2013; Borówko et al., 2012; Jiang et al., 2014). In order to quantitatively evaluate the advantage and disadvantage of different DFT approaches, a systematic comparison of different DFT approaches was made by Yang and Liu (2015). The RFD/WCA approach was found to be the most accurate one in the strong coupling regime, and has a similar accuracy as the other DFT approximations in the weak regime for the restricted primitive model (RPM). Subsequently, the RFD/WCA approach was then extended to the non-restricted primitive model (non-RPM) for modelling ions with different size (Yang et al., 2016).

Like MD, MC simulations explicitly take into account all atom interactions in the system. These computer simulations therefore have the advantage of giving accurate representations of the ionic density profiles in the vicinity of the charged surfaces (Skipper et al., 1995, 2006). MC or MD, though more time consuming than DFT, nevertheless, still is one of the most popular methods for the descriptions of the EDL because they can give the exact answer to the PM. That is why all the theoretical approximations have to be validated by comparing with the MC or MD simulations.

For the purpose of studying the stabilities of charged interfaces, the electrical double layer forces between two charged layers for planar EDL systems have been extensively investigated with the help of MC simulations. For instance, Guldbrand et al. (1984) and Valteau et al. (1991) reported the existence of attractions in the presence of multivalent counterions (Kjellander et al., 1988). These attractive electrostatic forces between charged surfaces cannot be predicted either by PB or the DLVO theory. More recent work to probe the ionic size effect conducted by Ibarra-Armenta et al. (2011) and Martín-Molina et al. (2011) also used MC simulations with the PM of electrolyte to analyze the influence of ion size on the colloidal forces between two charged layers by increasing the ionic diameter from standard bare ion size of 0.4 nm to hydrated ion size of 0.7 nm for monovalent and 0.85 nm for divalent ions. In addition, Valiskó et al. (2007) recently carried out the MC simulations together with DFT calculations of the selective adsorption, which is determined with the surface excess for the study of the stability of charged interface for EDL systems.

The goal of the present study is motivated by these MC simulations as well as by the success of the RFD/WCA approach presented in the companion paper (Yang et al., 2016) on accurately predicting the ionic density for the planar EDL systems containing size asymmetric ions. In this sense, this work is designed to test the capability of the newly developed RFD/WCA approach in studying the stability of Na- and Ca-bentonite. Bentonite consists mainly of montmorillonite, which has been considered as candidate, in the KBS-3 disposal concept as an engineered barrier between the copper canister and the bedrock for nuclear waste repositories in Sweden (SKB, 2006). Montmorillonite in aqueous solutions has been extensively modeled as EDL due to the layer structure of montmorillonite with around only one nm thickness but with several hundred nanometers in the other two directions of an individual layer (Segad et al., 2010). Considering the EDL structure of montmorillonite, the RFD/WCA approach of DFT within the framework of the PM is introduced here to predict the forces and the excess adsorption for Na- and Ca-bentonite systems. In addition, for the first time, the DFT modeling is applied to calculate the selectivity coefficient of ion exchange equilibrium with Gaines-Thomas convention (Gaines and Thomas, 1953) by comparing with experimental results. Therefore, another goal is to test the use of the Gaines-Thomas thermodynamic formulation within the framework of DFT for describing the exchange of  $\text{Ca}^{2+}$  for  $\text{Na}^+$  on montmorillonite complex in aqueous solutions.

The paper is organized as follows. In Section 2, the thermodynamic relations of forces and ion exchange are formulated with the Gaines-Thomas convention for montmorillonite systems within the framework of DFT. In Section 3, we validate the novel DFT modeling of the RFD/WCA approach with the RPM and non-RPM of EDL in comparison with MC simulations and experimental results under a wide range of conditions. We discuss the DFT calculations of osmotic pressure

between charged layers at equilibrium in aqueous solutions in Section 3.1 and the selectivity coefficient at interfaces in Section 3.2, respectively. Finally, some concluding remarks are given.

## 2. Calculations of osmotic pressure and selectivity coefficients

In this work, the applications of the RFD/WCA approach are illustrated for the study of swelling properties and ion exchange for clay mineral systems within the framework of the primitive model. The systematic descriptions of the DFT modeling with the RFD/WCA approach can be found in the companion paper (Yang et al., 2016). We wish to test if also osmotic pressure between smectite layers can be predicted. This is done by comparison with MC simulations for the EDLs in the presence of two charged layers, which are assumed to be infinitely large, impenetrable and planar charged walls located at  $x = 0$  and  $x = h$  respectively, where  $h$  is defined as the separation between the two surfaces. Hence, the hard-sphere part of the external potential for the interaction between the walls and the anion at  $x$  can be given by

$$u_i^{hs}(x) = \begin{cases} 0, & d_i/2 < x < h - d_i/2 \\ \infty, & \text{otherwise} \end{cases} \quad (1)$$

and the mean electrostatic potential is written as (Yang and Liu, 2015; Tang et al., 1992)

$$\psi(x) = \frac{e}{\epsilon_0 \epsilon_r} \sum_j \int_x^{h/2} dx' (x-x') \rho_j(x') z_j + \psi(h/2) \quad (2)$$

with the overall electro-neutrality condition,

$$\sum_j \int_0^{h/2} dx \rho_j(x) z_j e + \sigma = 0 \quad (3)$$

where  $\sigma$  is the surface charge density of the wall and  $x$  is the distance of the ion from the wall. For two similarly charged walls the net osmotic pressure between the confined region of two charged platelet-like particles and the bulk solution are given by contact value theorem (Henderson et al., 1979):

$$P_{osm}^{net} = k_B T \sum_j \rho_j(d_j/2) - \frac{\sigma^2}{2\epsilon_0 \epsilon_r} - P_{osm}^{bulk} \quad (4)$$

where  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature ( $T = 298$  K),  $\epsilon_0$  is the vacuum permittivity and  $\epsilon_r$  is the relative permittivity or a dielectric constant of the solvent i.e., water ( $\epsilon_r = 78$ ).  $\rho_j(d_j/2)$  are the contact densities, i.e. density of ion "j" at a distance of half an ion diameter from the wall, of ion species at the internal side of charged layers,  $P_{osm}^{bulk}$  is the osmotic pressure in the bulk phase.

The surface excess  $\Gamma$  is the integral of the difference of the local density profiles  $\rho_i(x)$ , and the bulk concentration  $\rho_i^b$ . For an EDL containing two charged walls, we can write (Valiskó et al., 2007)

$$\Gamma_i = \int_0^h (\rho_i(x) - \rho_i^b) dx \quad (5)$$

The sum of the adsorption values for all ion species weighted by valences gives

$$e \sum_j z_j \Gamma_j = -2\sigma \quad (6)$$

For the EDL system such as a Na-bentonite system in equilibrium with bulk solution containing a mixture of  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , the ion

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