Transp Porous Med (2010) 85:23–44
DOI 10.1007/s11242-010-9545-4

A Three-Scale Model of pH-Dependent Flows and Ion Transport with Equilibrium Adsorption in Kaolinite Clays: I. Homogenization Analysis

Sidarta Araújo de Lima · Márcio A. Murad ·
Christian Moyne · Didier Stemmelen

Received: 24 April 2009 / Accepted: 11 February 2010 / Published online: 10 March 2010

Abstract A new three-scale model to describe the coupling between pH-dependent flows and transient ion transport including sorption phenomena in kaolinite clays is proposed. The kaolinite is characterized by three separate nano-micro and macroscopic length scales. The (micro)-scale consists of micro-pores saturated by an aqueous solution containing four monovalent ionic species (Na^+, H^+, Cl^-, OH^-) and charged solid particles surrounded by thin electrical double layers. The movement of the ions is governed by the Nernst-Planck equations and the influence of the double layers upon the flow is dictated by the Helmholtz–Smoluchowski slip boundary condition in the tangential velocity. In addition, sorption interface conditions for ion transport are postulated in the sense of Auriault and Lewandowska (Eur. J. Mech. A 15:681–704, 1996) to capture the immobilization of the ions in the electrical double layer and on particle surface due to protonation/deprotonation reactions. The intensity of sorption relative to diffusion effects is quantified by the Damköhler number, whose order of magnitude is estimated by invoking the nanoscopic modeling of the thin EDL based on Poisson–Boltzmann problem for the local electric potential coupled with a non-linear surface charge density with constitutive law dictated by the protonation/deprotonation reactions. The two-scale nano/micro model including sorption and slip boundary condition is homogenized to the core scale leading to a derivation of macroscopic governing equations.

S. A. de Lima · M. A. Murad (✉)
Laboratório Nacional de Computação Científica LNCC/MCT, Av Getúlio Vargas 333,
25651–070 Petrópolis, RJ, Brazil
e-mail: murad@lncc.br

S. A. de Lima · C. Moyne · D. Stemmelen
LEMTA, Nancy-University, CNRS, 2, avenue de la Forêt de Haye, 54504 Vandoeuvre les Nancy Cedex,
France
e-mail: sidarta@lncc.br

C. Moyne
e-mail: Christian.Moyne@ensem.inpl-nancy.fr

D. Stemmelen
e-mail: Didier.Stemmelen@ensem.inpl-nancy.fr

Keywords Kaolinite clays · Homogenization · Ion-sorption · Protonation/deprotonation reactions · Electro-osmosis · Electro-migration · Poisson–Boltzmann · pH effects · Electrokinetic remediation

1 Introduction

Soils often get contaminated with heavy metals due to improper disposal of sludges and waste water and therefore the removal of pollutants plays a crucial role in environmental remediation. The demand for innovative in situ or on-site clean-up methods has motivated the development of a substantial body of attempts to utilize alternative enhanced technologies. Since the discovery of the electrokinetic phenomenon (EK) and the initial practical application in the field (Casagrande 1949), EK remediation technology became one of the developing technologies successfully reported and cost-effective for the cleanup of soils contaminated with heavy metals and has been intensively investigated as a remediation method for polluted soils (Acar et al. 1995; Acar and Alshawabkeh 1993). The remediation process involves passing a low-level DC electric current/electric field between electrode pairs embedded in the polluted soil to induce the movement of electrolyte solution and the transport of soluble contaminants toward the electrodes (Acar and Alshawabkeh 1993).

The fundamental thermodynamic processes underlying electrokinetic phenomena involve several couplings such as transport of mobile ions near charged surfaces (electro-migration), flow and motion of charged particles driven by an electric field (electro-osmosis and electrophoresis), dissolution/precipitation reactions, electrolysis of water, sorption, desorption, protonation/deprotonation chemical reactions and movement of H^+ ions generated by water electrolysis at the anode towards the cathode. Among the different couplings involved the movement of ionic species appears mainly dictated by electromigration and electroosmosis (Acar et al. 1995).

Unlike the approaches purely conducted at the macroscale, within the framework of multiscale methods the effective medium behavior is rigorously derived by upscaling the constitutive behavior of several complex couplings of different physicochemical and electrochemical nature occurring at disparate space and time scales.

Under the absence of surface chemical reactions the local EDL potential, governed by the Poisson–Boltzmann problem, fulfills a Neumann boundary condition at particle surface with a constant surface charge density solely due to the isomorphous substitutions (Moyne and Murad 2006a,b). Whence the effects of the pH upon the magnitude of the partition and retardation coefficients were overlooked. The generalization of the model to incorporate partially dissociated H^+ and OH^- ions in the aqueous solution along with the pH-dependent protonation/deprotonation chemical reactions giving rise to a pH-dependent retardation coefficient remains an open issue. The aim of this article is to fill this gap. First attempts at incorporating pH effects within the framework of homogenization were pursued in Lemaire et al. (2007) and Lima et al. (2008) for steady flow and ion transport with transient sorption effects neglected.

As a canonical application of the multiscale model proposed herein we consider a kaolinite clay with three disparate length scales (nano, micro and macro) (Fig. 1). Kaolinite's mineralogy is characterized by hydrous aluminum silicates composed of stacked silicate sheets (Si_2O_5) linked through oxygen atoms to aluminum oxide/hydroxide layers ($Al(OH)_3$) common referred to as gibbsite layers. The silicate and gibbsite layers are tightly bonded together forming a 1:1 arrangement composed of layered-sheet structure elongated hexagonal plates.

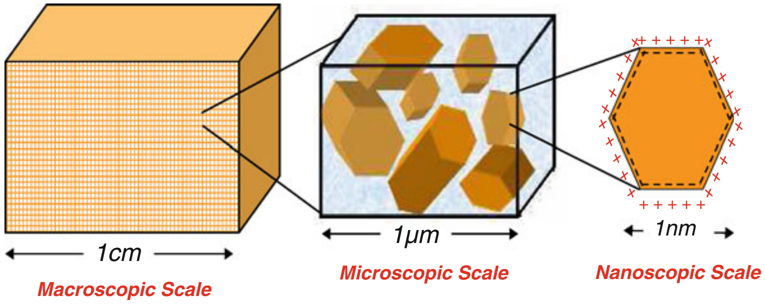

Fig. 1 Portrait of natural length scales in kaolinite

The primary structural unit is formed by dioctahedral minerals composed of one octahedral sheet, occupied by aluminum, condensed with one tetrahedral sheet.

Kaolinites have a very low permanent charge associated with isomorphous substitutions and their surface charge is primarily ruled by the net proton surface excess located at the pH-dependent charged sites at particle edges (Avena et al. 2003; Mitchell 1993). This wall surface charge attracts counter-ions giving rise to a thin EDL with thickness smaller than the characteristic size of the pores.

The finest scale of kaolinite is the nanoscale $\mathcal{O}(10^{-9}m)$ considered herein of the same order of the thickness of the thin EDLs surrounding each particle, or of the order of the Debye's length L_D. At this scale equilibrium protonation/deprotonation reactions take place at particle surface and are coupled with electrokinetics in the electrolyte solution lying in the thin sharp EDL next to the solid. The equilibrium nature of the reactions along with the fast characteristic time scale of the electro-chemical phenomena in the EDL lead to local thermodynamic equilibrium (Lima et al. 2008). Consequently, the electric potential in the electrolyte solution is ruled by the Poisson–Boltzmann problem with a pH-dependent surface charge at the Neumann interface condition (Basu and Shrarma 1997).

Microscopic phenomena in kaolinite occur at a typical length scale associated with the square root of the permeability $\ell = \sqrt{\kappa}$ of $O(\sqrt{0.1mD}) = O(10^{-8}\text{m}) = O(10L_D)$ usually smaller than the averaged size of the micro pores $\mathcal{O}(10^{-6}m)$. Since $\ell > L_D$ the effects of the thin EDLs remain adjacent to the particle interface and consequently the equations governing the bulk solution (Stokes problem and Nernst-Planck equations (Samson et al. 1999)) are free of EDL effects.

At the macroscale $(O(10^{-4}\text{m}))$ the clay particles and bulk fluid are envisioned as overlaying continua with averaged properties defined at every macroscopic location (Fig. 1). Assuming local periodicity of the microscopic particle/micro pore arrangement the effective medium behavior is rigorously derived within the framework of homogenization based on formal matched asymptotic expansion techniques (Sanchez-Palencia 1980).

An outline of the article is as follows: In Sect. 2, we present the computational nanoscopic model for the electro-chemistry of the kaolinite/electrolyte solution interface and reconstruct numerically the constitutive laws at this finest scale. In Sect. 3, we review the microscopic hydrodynamics and ion transport and propose new boundary conditions at particle fluid interface. In Sect. 4, we upscale the microscopic model to the macroscale using the homogenization procedure. In particular, we provide computational estimates of the Damköhler numbers and derive the set of macroscopic governing equations along with the closure microscopic problems for the effective parameters.

2 Nanoscale Modeling for Sorption

We begin by presenting the nanoscopic modeling of the electro-chemistry of the particles/electrolyte solution interface. Consider a two-phase system composed of kaolinite particles (assumed rigid) which bear an interface charge excess. The solid matrix is filled by a continuum dielectric aqueous dilute solution (where ion activities are replaced by concentrations) containing four monovalent electrolytes (Na^+, H^+, Cl^-, OH^-). In a similar fashion to Murad and Moyne (2008) we adopt the thin electrical double layer assumption wherein the Debye's length L_D, whose magnitude is of the same order of the thickness of the diffuse layer, is assumed small compared to the characteristic length scale of the micro-pores. Under this assumption, adjacent double layers do not overlap and variations in the electric potential in the direction normal to the particle are much more pronounced than in the tangential one. Consequently, the electric problem is governed by the one-dimensional version of the Gauss–Poisson equation (Hunter 1994; Van Olphen 1977). In addition to the ionic concentrations in the electrical double layer (EDL), sorption phenomena owing to protonation/deprotonation reactions involving the H^+ ions also take place at particle surface. Such chemical reactions have a paramount influence on the magnitude of the surface charge density and the zeta potential and must be incorporated in the nanoscopic description (Avena and De Pauli 1996; Huertas et al. 1997; Schroth and Sposito 1997). The equilibrium nature of chemical reactions along with the fast characteristic time-scale of the electro-chemical processes taking place in the EDL compared to the one associated with the hydrodynamics in the bulk fluid in the micropores suggest adopting the local equilibrium hypothesis at the nanoscale. Such assumption implies in the local EDL potential governed by the Poisson–Boltzmann problem (Murad and Moyne 2008).

2.1 Ionization Reactions in the Bulk Fluid

Let C_{i_b} ($i = \mathrm{Na}^+, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{OH}^-$) be the molar concentration of each ionic solute and C_b the total concentration of cations (or anions) in the bulk fluid, respectively. The electroneutrality condition enforces the constraint

$$C_b := C_{\mathrm{Na}_\mathrm{b}^+} + C_{\mathrm{H}_\mathrm{b}^+} = C_{\mathrm{Cl}_\mathrm{b}^-} + C_{\mathrm{OH}_\mathrm{b}^-}. \tag{1}$$

The appearance of ions completely or partially dissociated in the aqueous solution is explained by the ionization theory which describes the thermodynamic equilibrium between ions and non-ionized solvent molecules. For example, water molecules are often partially dissociated due to a weak phenomenon commonly refereed to as auto-ionization. Such partial dissociation is commonly described the ionic product of water K_W

$$K_W := C_{\mathrm{H}_\mathrm{b}^+} C_{\mathrm{OH}_\mathrm{b}^-} = 10^{-14}\,(\mathrm{mol/l})^2\,. \tag{2}$$

In contrast, sodium chloride NaCl in water is completely dissociated and commonly referred to as a strong electrolyte.

2.2 Electrical Double Layer

Let $\{F, R, T\}$ be the set composed of Faraday constant, universal ideal gas constant and absolute temperature. Further, let φ be the electric potential of the EDL and C_i ($i = \mathrm{Na}^+$, H^+, Cl^-, OH^-) the molar concentration of the ionic species in the EDL. Denoting $\overline{\varphi} = F\varphi/RT$ the corresponding dimensionless EDL electric potential, the ionic concentrations in the EDL and in the bulk fluid are related by the Boltzmann distribution (Dormieux et al. 1995; Van Olphen 1977)

$$C_{i^\pm} = C_{i^\pm_b} \exp\left(\mp\overline{\varphi}\right) \quad i = \mathrm{Na}^+, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{OH}^-. \tag{3}$$

Let $\Omega^l_* = (0, L_D)$ be the one-dimensional nanoscopic domain in the direction normal to the clay surface occupied by the electrolyte solution with $L_D := \left(\widetilde{\epsilon}_0\widetilde{\epsilon}_r RT/2F^2C_b\right)^{1/2}$ the Debye's length, $\widetilde{\epsilon}_0$ the permittivity of the free space and $\widetilde{\epsilon}_r$ the dielectric constant of the solvent. Further, let $E = -\mathrm{d}\varphi/\mathrm{d}z$ be the component of the electric field orthogonal to the surface, where z is the normal coordinate with origin located at the solid surface. Considering $z = \ell_*$ a point further away from the interface between the electrolyte solution and bulk fluid ($\ell_* > L_D$), the one-dimensional Gauss-Poisson problem reads as

$$-\frac{\mathrm{d}E}{\mathrm{d}z} = \frac{\mathrm{d}^2\varphi}{\mathrm{d}z^2} = -\frac{q}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r} \quad \text{in } \Omega^l := (0, \ell_*) \tag{4}$$

where $q := F\left(C_{\mathrm{Na}^+} + C_{\mathrm{H}^+} - C_{\mathrm{Cl}^-} - C_{\mathrm{OH}^-}\right)$ is the net charge density. Using the Boltzmann distribution (3) we have $q = FC_b\left[\exp\left(-\overline{\varphi}\right) - \exp\overline{\varphi}\right] = -2FC_b \sinh\,\overline{\varphi}$. Together with (4) this yields the Poisson–Boltzmann equation

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}z^2} = \frac{2FC_b}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r}\sinh\,\overline{\varphi} \quad \text{in } \Omega^l := (0, \ell_*). \tag{5}$$

The above equation is supplemented by boundary conditions at particle wall $z = 0$ and at the distance $z = \ell_*$ away from the interface between the EDL and the bulk solution. For non-overlapping adjacent EDLs the electric field at $z = \ell_*$ vanishes, whereas at the particle surface the electric field balances the surface charge density σ, yielding the Neumann conditions

$$\frac{\mathrm{d}\varphi}{\mathrm{d}z} = 0 \quad \text{at } z = \ell_* \quad \text{and} \quad \frac{\mathrm{d}\varphi}{\mathrm{d}z} = -\frac{\sigma}{\widetilde{\epsilon}_0\widetilde{\epsilon}_r} \quad \text{at } z = 0. \tag{6}$$

In contrast to the bulk solution, where the electroneutrality condition (1) is fulfilled pointwisely, in the electrolyte solution next to the kaolinite particles such constraint gives rise to a compatibility condition between surface and net charge density. Using (4) and (6a) in (6b), we have

$$\sigma = -\widetilde{\epsilon}_0\widetilde{\epsilon}_r \left.\frac{\mathrm{d}\varphi}{\mathrm{d}z}\right|_{z=0} = \widetilde{\epsilon}_0\widetilde{\epsilon}_r \int_0^{\ell_*} \frac{\mathrm{d}^2\varphi}{\mathrm{d}z^2}\mathrm{d}z = -\int_0^{\ell_*} q\,\mathrm{d}z.$$

The unidimensional Poisson–Boltzmann problem (5) together with boundary conditions (6) govern the local behavior of electric potential at the nanoscale around the kaolinite particle. Under the thin double layer assumptions an analytical relation between φ and the zeta potential $\zeta := \varphi(z = 0)$ can be obtained (Lima et al. 2008)

$$\varphi = \frac{4RT}{F}\,\mathrm{arctanh}\left[\tanh\left(\frac{F\zeta}{4RT}\right)\exp\left(-\frac{z}{L_D}\right)\right]. \tag{7}$$

Furthermore, combining (6) and (7) and using the definition of L_D we deduce the following relation between σ and ζ

$$\sigma = \frac{2\widetilde{\epsilon}_0\widetilde{\epsilon}_r RT}{FL_D}\sinh\left(\frac{F\zeta}{2RT}\right) = \sqrt{8\widetilde{\epsilon}_0\widetilde{\epsilon}_r RTC_b}\,\sinh\left(\frac{F\zeta}{2RT}\right). \tag{8}$$

2.3 Ion Sorption in the Electrical Double Layer

The charge density of the kaolinite adsorbs counter-ions to the vicinity of the surface giving rise to the sorbed concentration of the EDL Γ_i (i $=\mathrm{Na}^+$, H^+, Cl^-, OH^-). We begin by computing this quantity at the nanoscale and later on upscale this information to micro and macroscale. For each solute Γ_i is a surface concentration property defined by the integration over the EDL thickness of the excess in each ion concentration relative to its bulk counterpart

$$\Gamma_i := \int_{z=0}^{z=\ell_*} \left(C_i - C_{i_b}\right) \mathrm{d}z \tag{9}$$

Denoting $\bar{z} = z/L_D$ the dimensionless normal coordinate, to derive an analytical expression for Γ_i we multiply the Poisson–Boltzmann equation (5) by $2\mathrm{d}\bar{\varphi}/\mathrm{d}\bar{z}$ and use the chain rule. Then, integrating from an arbitrary $\bar{z}$ inside the EDL to the point $\bar{\ell}_* = \ell_*/L_D$ in the bulk solution and using boundary condition (6a) along with the thin double layer assumption ($\bar{\varphi} = 0$ at $z = \bar{\ell}_*$), the Eq. 5 can be rewritten as

$$\left(\frac{\mathrm{d}\bar{\varphi}}{\mathrm{d}\bar{z}}\right)^2 = 2\left(\cosh\bar{\varphi} - 1\right) \tag{10}$$

Using the relation $\sinh\left(\bar{\varphi}/2\right) = \left[\left(\cosh\bar{\varphi} - 1\right)/2\right]^{1/2}$ the above result can be rephrased in the form

$$-\,\mathrm{d}\bar{z} = \frac{\mathrm{d}\bar{\varphi}}{2\sinh\left(\bar{\varphi}/2\right)} = \frac{\mathrm{d}\bar{\varphi}}{\exp\left(\bar{\varphi}/2\right) - \exp\left(-\bar{\varphi}/2\right)}$$

Denoting Γ_i^+ and Γ_i^- the restrictions of Γ_i to cations and anions, respectively, using the Boltzmann distribution (3) along with the above change of variable in (9) gives

$$\Gamma_i^{\pm} = -C_{i_b} L_D \int_{\bar{\zeta}}^{\bar{\varphi}=0} \frac{\exp\left(\mp\bar{\varphi}\right) - 1}{\exp\left(\bar{\varphi}/2\right) - \exp\left(-\bar{\varphi}/2\right)} d\bar{\varphi} = 2\,C_{i_b} L_D \left[\exp\left(\mp\frac{\bar{\zeta}}{2}\right) - 1\right]. \tag{11}$$

with $\bar{\zeta} := F\zeta/RT$ the dimensionless ζ-potential. The system of algebraic Eqs. 7, 8 and 11 define our nanoscopic model in terms of the unknowns $\{\varphi, \zeta, \Gamma_i\}$ provided σ is known. However, as the surface charge and the ζ-potential vary strongly with the pH of the electrolyte solution, the closure of the system is tied-up to the construction of the such dependence which can be accomplished by incorporating protonation/deprotonation reactions in σ (see also (Avena and De Pauli 1996; Chorover and Sposito 1995; Ganor et al. 2003; Huertas et al. 1997).

2.4 H^+ Sorption at Particle Surface due to Protonation/Deprotonation Reactions

In addition to ion immobilization in the EDL, protonation/deprotonation chemical reactions take place at particle edges leading to sorption of H^+ ions at the surface and to the consequent dependence of the surface charge σ and sorbed concentration in the EDL Γ_i on the pH of the aqueous solution. Considering hexagonal geometry of the kaolinite particles (Chi and Eggleton 1999; Mitchell 1993) we assume that the charge excess on the basal hydroxyl and siloxane planes at the upper and lower sites of the hexagonal solid particle are negligible compared to the one produced at the lateral edges containing aluminol and silanol groups (Fig. 2) (Brady et al. 1996; Chi and Eggleton 1999). Therefore, the charge density induced by

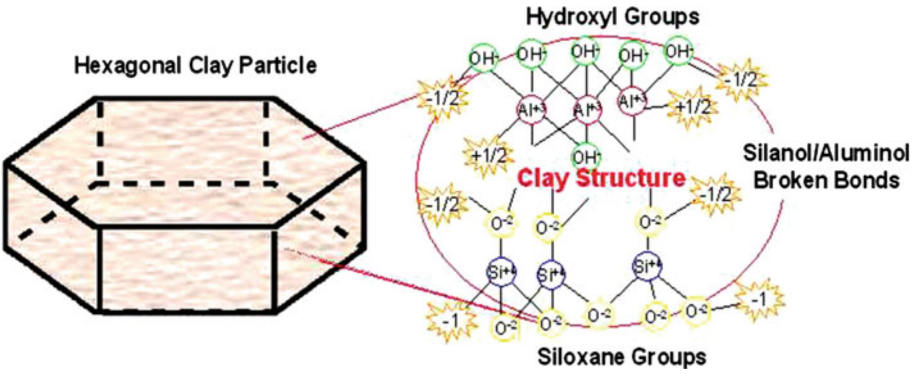

Fig. 2 Kaolinite particle geometry with structure composed of siloxane/hydroxyl planes and broken bond edges

isomorphous substitutions is negligible compared to the pH-dependent charge due to broken bonds on particle edges (Bolland et al. 1979). Following Lima et al. (2008), we adopt a model based on a single protonation/deprotonation chemical reaction which takes place at a typical site $(>M - \mathrm{OH})^{-1/2}$ representative of the reactive groups at the lateral edges of the solid surface. Under the local equilibrium assumption such protonation/deprotonation reaction can be represented in the form

$$(> M - \mathrm{OH})^{-1/2} + H^{+} \rightleftharpoons (> M - \mathrm{OH}_2)^{+1/2} \tag{12}$$

where M represents a metallic ion lying in the tetrahedral (Si^{4+}) or octahedral (Al^{3+}) layers. Under equilibrium we adopt the law of Mass Action and define the equilibrium constant K associated with (12) as the ratio between the molarity product of the reagents and product constituents. Denoting γ_j the surface density of the reagent/product $j = (M - \mathrm{OH})^{-1/2}$, $(M - \mathrm{OH}_2)^{+1/2}$ and $\Gamma_{\mathrm{MAX}} := \gamma_{\{(>M-\mathrm{OH}_2)^{+\frac{1}{2}}\}} + \gamma_{\{(>M-\mathrm{OH})^{-\frac{1}{2}}\}}$ the maximum surface density (mol/m^2) and $\{j\} = \gamma_j / \Gamma_{\mathrm{MAX}}$ the dimensionless surface concentration of the **j** species, we have by definition

$$K := \frac{\{(> M - \mathrm{OH}_2)^{+1/2}\}}{\{(> M - \mathrm{OH})^{-1/2}\} C_{\mathrm{H}_0^+}} \tag{13}$$

where $C_{\mathrm{H}_0^+}$ denotes the H^+ concentration (mol/l) at the kaolinite surface. From the above definition the excess in surface charge due to the protonic adsorption γ_{H^+} is defined as

$$\sigma := F\, z_{\mathrm{val}}\, \gamma_{\mathrm{H}^+} := F\, z_{\mathrm{val}} \left(\gamma_{\{(>M-\mathrm{OH}_2)^{+\frac{1}{2}}\}} - \gamma_{\{(>M-\mathrm{OH})^{-\frac{1}{2}}\}} \right) \tag{14}$$

where $z_{\mathrm{val}} = 1/2$ is the valence. To complete the characterization of σ one needs to postulate a constitutive law for γ_{H^+} which can be derived by using (13) together with the definition of the maximum surface density Γ_{MAX}, we have

$$\gamma_{\{(>M-\mathrm{OH})^{-\frac{1}{2}}\}} = \frac{\Gamma_{\mathrm{MAX}}}{1 + K C_{\mathrm{H}_0^+}} \quad \text{and} \quad \gamma_{\{(>M-\mathrm{OH}_2)^{+\frac{1}{2}}\}} = \frac{\Gamma_{\mathrm{MAX}} K C_{\mathrm{H}_0^+}}{1 + K C_{\mathrm{H}_0^+}} \tag{15}$$

Using (15) and the Boltzmann distribution (3) in (14) we deduce

$$\sigma := \frac{F\Gamma_{\mathrm{MAX}}}{2}\left(\frac{KC_{\mathrm{H}_0^+}-1}{KC_{\mathrm{H}_0^+}+1}\right) \quad \text{and} \quad \gamma_{\mathrm{H}^+}=\frac{2\sigma}{F} \tag{16}$$

with $C_{\mathrm{H}_0^+} = C_{\mathrm{H}_b^+}\exp(-\overline{\zeta})$. The above results provide the constitutive laws for the pair $(\sigma, \gamma_{\mathrm{H}^+})$. Experimental data for the constants K and Γ_{MAX} can be obtained by invoking Huertas et al. (1997) who provided the dependency of γ_{H^+} on the pair $\{C_{\mathrm{H}_b^+}, C_{\mathrm{Na}_b^+}\}$ by performing titration experiments. By comparing the curves obtained from (16) with the experimental results reported in Huertas et al. (1997) this yields $K = 10^{5.5}$ mol/l and $\Gamma_{\mathrm{MAX}} = 3.0\,\mathrm{sites/nm}^2$ (Lima et al. 2008). We are now ready to formulate our nanoscopic problem for the electro-chemistry of the particle-fluid interface. As independent input variables we select the cation concentrations in the bulk fluid $\{C_{\mathrm{Na}_b^+}, C_{\mathrm{H}_b^+}\}$. Given this pair, the anion concentration $\{C_{\mathrm{Cl}_b^-}, C_{\mathrm{OH}_b^-}\}$ can be computed using the electroneutrality and ionization conditions (1) and (2). Thus, for each pair $\{C_{\mathrm{Na}_b^+}, C_{\mathrm{H}_b^+}\}$ our nanoscopic model consists of solving the set of nonlinear algebraic equation (3), (7), (8), (11) and (16) for the unknowns $(C_{\mathrm{H}_0^+}, \sigma, \zeta, \varphi, \Gamma_{i^\pm}, \gamma_{\mathrm{H}^+})$.

2.5 Numerical Reconstruction of the Nanoscopic Constitutive Laws

The above nonlinear system is solved numerically using Newton's method and the discrete constitutive laws are reconstructed for the unknowns $(\zeta, \gamma_{\mathrm{H}^+}, \Gamma_i)$ which will be subsequently used in the interface conditions for the fluid velocity and ion fluxes at the microscale. In the subsequent figures we display the numerical constitutive response of $\{\zeta, \gamma_{\mathrm{H}^+}, \Gamma_{\mathrm{Na}^+}\}$ as a function of $\{\mathrm{pH}, C_{\mathrm{Na}_b^+}\}$ adopting the dilute solution approximation in the range $3 \leq \mathrm{pH} \leq 9$ and $10^{-4}\mathrm{mol/l} \leq C_{\mathrm{Na}_b^+} \leq 10^{-2}\mathrm{mol/l}$ assuming unitary value for the activity coefficient of the salt. The accuracy of such approximation relies on experimental data provided by the National Bureau of Standards (see, e.g. Zemaitis et al. 1986) which show the activity coefficient lying in the interval $[1, 0.8]$ for the range of salinity considered above.

The numerical constitutive response $\zeta = \zeta(C_{\mathrm{Na}_b^+}, C_{\mathrm{H}_b^+})$ is depicted in Fig. 3. One may clearly observe the appearance of acid and alkaline regimes characterized by positive and negative values of the ζ-potential in the ranges of $\mathrm{pH} < 5.5$ and $\mathrm{pH} > 5.5$ where protonation and deprotonation reactions take place, respectively. We may note strong dependence of the ζ-potential on the pH in a nearly skew-symmetric fashion around the point of zero charge (isoelectric point) $\mathrm{pH} = 5.5$. The increase in basification gives rise to the deprotonation reaction leading to a decrease in ζ towards negative values and vice-versa in the acid regime.

In Fig. 4, we depict the protonic adsorption at particle surface γ_{H^+} as a function of the pH for three Na^+ concentrations. At the isoelectric point $\mathrm{pH} = 5.5$ both σ and γ_{H^+} vanish. In the basic regime ($\mathrm{pH} > 5.5$) the system is ruled by the deprotonation reaction which increases the electro-negativity of the surface charge and proton desorption. Conversely in the acid regime ($\mathrm{pH} < 5.5$) both σ and γ_{H^+} increase toward positive values. In Fig. 5, we display the constitutive response of the sorbed concentration Γ_{Na^+}. When the pH increases the deprotonation reaction implies in desorption of H^+ ions which increase negatively the surface charge leading to increase of Γ_{Na^+}. Below the isoelectric point the increase in salinity leads to protonation and positivity of the surface charge implying in desorption of the Na^+ in the EDL and the consequent decrease of Γ_{Na^+}.

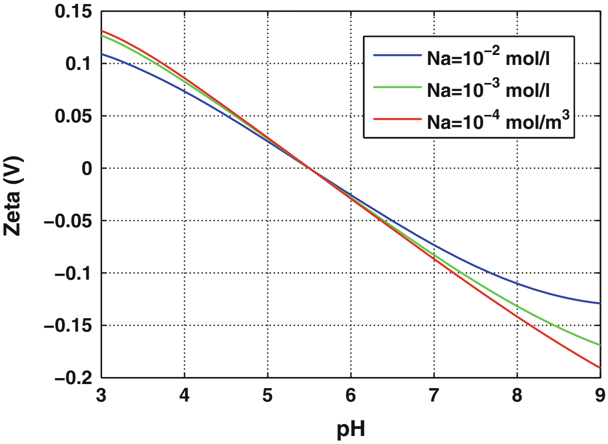

Fig. 3 Constitutive response of the ζ-potential as a function of pH for three Na^{+} concentrations

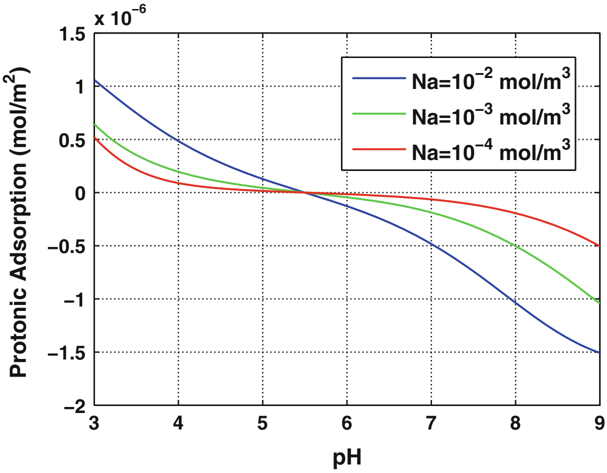

Fig. 4 Constitutive response of the H^{+} chemical adsorption $\gamma_{\text{H}^{+}}$ as a function of pH and $C_{\text{Na}_b^{+}}$

3 Microscopic Modeling

At the microscale the clay is envisioned a two phase system composed of kaolinite particles and micropores filled by the aqueous solution. The characteristic length of the micropores $l(O(10^{-6}\,\text{m}))$ is much larger than the thickness of the EDL. Whence we incorporate the nanoscopic description of the EDL and protonation reactions through effective boundary conditions (Lima et al. 2008; Murad and Moyne 2008).

3.1 Microscopic Governing Equations

Following the usual framework of multiscale models we begin by establishing the microscopic governing equations. Let $\Omega = \Omega_s \cup \Omega_f \subset \Re^3$ be the microscopic domain occupied by the biphasic media composed of solid particles and micro-pores filled by a bulk fluid. The

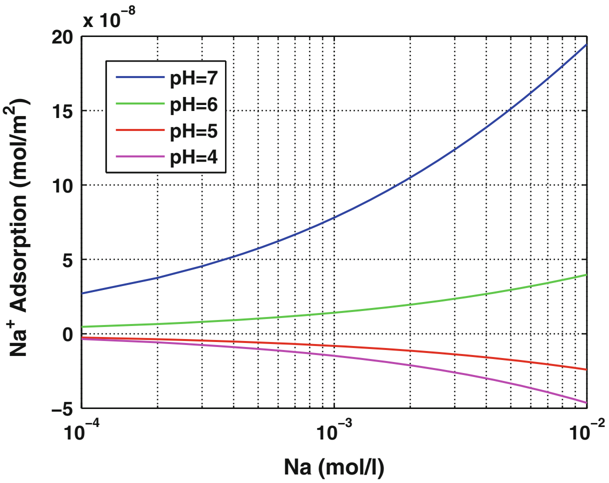

Fig. 5 Constitutive response of the Na^+ adsorption in the EDL Γ_{Na^+} as a function of pH and $C_{\mathrm{Na}_b^+}$

solid phase occupies the domain Ω_s and is formed by kaolinite particles carrying the non-linear surface charge density σ whereas the subdomain Ω_f is occupied by the bulk solution containing the four ionic monovalent solutes Na^+, H^+, Cl^-, OH^-. In our subsequent analysis, we consider the aqueous solution movement and ion transport governed by the classical theory of viscous fluids and transient Nernst-Planck equations, respectively (Samson et al. 1999).

3.1.1 Hydrodynamics

Assuming the bulk fluid an aqueous Newtonian incompressible solution, neglecting gravity and convection/inertial effects, the hydrodynamics is governed by the classical Stokes problem

$$\begin{aligned} \nabla \cdot \mathbf{v} &= 0 \\ \mu_f \Delta \mathbf{v} - \nabla p &= 0 \quad \text{in } \Omega_f \end{aligned} \tag{17}$$

where $\mathbf{v}$ is the fluid velocity, p the pressure and μ_f the water viscosity.

3.1.2 Ion Transport

In addition to the advection induced by the velocity $\mathbf{v}$, ionic diffusion is due to the sum of Fickian and electromigration components which govern the spreading of the solutes under concentrations and electric potential gradients, respectively (Sasidhar and Ruckenstein 1981; Sherwood 1994). Denoting t the characteristic time scale of the transport, recalling the notation $C_{i_b} (i = \mathrm{Na}^+, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{OH}^-)$ for molar concentration in the bulk solution, the ion movement is governed by the Nernst-Planck equations (Samson et al. 1999)

$$\frac{\partial C_{i_b}}{\partial t} + \nabla \cdot \left(C_{i_b} \mathbf{v}\right) - \nabla \cdot \left[D_i \left(\nabla C_{i_b} + z_i C_{i_b} \nabla \overline{\phi}\right)\right] + \dot{m} = 0 \quad \text{in } \Omega_f \tag{18}$$

where $D_i (i = \mathrm{Na}^+, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{OH}^-)$ denote the binary water-ion diffusion coefficients, z_i the ion valence, $\overline{\phi} := F\phi/RT$ the dimensionless microscopic electrical potential and $\dot{m}$ a source term which quantifies the mass production of H^+ and OH^- due to water hydrolysis (2) ($\dot{m} = 0$ for $i = Na^+$ and Cl^-).

3.1.3 Formulation in Primary Unknowns

We now formulate the microscopic governing equations in primary unknowns, selected as velocity, pressure, electric potential, and cation concentrations. We then proceed by eliminating the anion concentrations and the source term $\dot{m}$. Using the ionic product of the water (2) and subtracting the OH^- from H^+ equations in (18), the system in terms of $\{\mathbf{v}, p, \phi, C_{H_b^+}, C_{Na_b^+}\}$ is rephrased as

$$\frac{\partial\left(\Theta C_{H_b^+}\right)}{\partial t} + \nabla \cdot \left(\Theta C_{H_b^+}\mathbf{v}\right) - \nabla \cdot \left[\widehat{D}\left(\nabla C_{H_b^+} + C_{H_b^+}\nabla\overline{\phi}\right)\right] = 0 \tag{19}$$

$$\text{with } \widehat{D} := D_{H^+} + D_{OH^-}K_W/C^2_{H_b^+} \quad \text{and} \quad \Theta := 1 - K_W/C^2_{H_b^+}$$

The above nonlinear form of the Nernst-Planck equation will be henceforth refereed to as the transient pH-equation though we shall bear in mind that it actually states net mass conservation for H^+–OH^-. Further, to derive an equation for the electric potential ϕ we invoke conservation of charge. Defining the electric current $\mathbf{I}_f$

$$\mathbf{I}_f := F\left(\tilde{\mathbf{J}}_{Na^+} + \tilde{\mathbf{J}}_{H^+} - \tilde{\mathbf{J}}_{Cl^-} - \tilde{\mathbf{J}}_{OH^-}\right) \text{ where } \tilde{\mathbf{J}}_i := C_{i_b}\mathbf{v} - D_i\left(\nabla C_{i_b} \pm C_{i_b}\nabla\overline{\phi}\right)$$

denotes the total convective/diffusive ionic flux of each solute ($i = Na^+, H^+, Cl^-, OH^-$). By subtracting the Nernst-Planck relations (18) for the anions from the cations and using the above definition together with the electroneutrality condition (1) we obtain conservation of charge

$$\nabla \cdot \mathbf{I}_f = 0 \qquad \text{with } \mathbf{I}_f = A\nabla C_{Na_b^+} + B\nabla C_{H_b^+} + C\nabla\overline{\phi}$$

and

$$A := F\left(D_{Na^+} - D_{Cl^-}\right) \quad B := F\left[D_{H^+} - D_{Cl^-} + \frac{\left(D_{OH^-} - D_{Cl^-}\right)K_W}{C^2_{H_b^+}}\right]$$

$$C := F\left[\left(D_{Na^+} + D_{Cl^-}\right)C_{Na_b^+} + \left(D_{H^+} + D_{Cl^-}\right)C_{H_b^+} + \frac{\left(D_{OH^-} - D_{Cl^-}\right)K_W}{C_{H_b^+}}\right]$$

In particular the coefficient C designates the microscopic electric conductivity of the aqueous solution in the micropores which commonly appears in Ohm's law.

3.1.4 Boundary Conditions

To close our microscopic model it remains to postulate boundary conditions on the particle/micropore interface Γ_{fs} and initial conditions. We then begin by establishing the proper velocity interface condition for the Stokes problem (17). Owing to the presence of the thin electrical double layer surrounding the particles we postulate the so-called Smoluchowsky slip wherein the tangential velocity exhibits a discontinuity at the interface (Murad and Moyne 2008). Denoting $\mathbf{n}$ and $\boldsymbol{\tau}$ the unitary normal and tangential vectors at Γ_{fs} we have

$$\mathbf{v} \cdot \boldsymbol{\tau} = V_{slip} \quad \text{and} \quad \mathbf{v} \cdot \mathbf{n} = 0 \quad \text{on} \quad \Gamma_{fs} \tag{20}$$

where V_{slip} is a scalar field defined at the interface which governs the jump in the tangential velocity component. The slip velocity is nothing but the transversal averaging across the thin diffuse layer of the nanoscopic electroosmotic tangential velocity governed by the modified Stokes problem including the additional body force term of Coulomb type (Moyne and Murad 2006b). For thin double layers the up-scaling procedure gives rise to the well known Smoluchowski slip wherein V_{slip} is governed by the electroosmotic component in Darcy's law with the electroosmotic permeability K_E dictated by the magnitude of the ζ-potential (Edwards 1995; Hlushkou et al. 2005; Murad and Moyne 2008)

$$V_{\text{slip}} = \mathbf{v}\cdot\boldsymbol{\tau} = -K_E\nabla\phi\cdot\boldsymbol{\tau} \quad \text{with } K_E = -\frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta}{\mu_f} \quad \text{on } \Gamma_{fs}. \tag{21}$$

The complete characterization of the slip velocity is accomplished by invoking the constitutive law $\zeta = \zeta(C_{\text{Na}_\text{b}^+}, C_{\text{H}_\text{b}^+})$ already reconstructed in the nanoscopic modeling in Fig. 3. It remains to establish the interface conditions for the Nernst-Planck equations. Since from (20), the normal advective flux vanishes on Γ_{fs}, by invoking conservation of mass at the interface, the time derivative of the nanoscopic sorption EDL quantities Γ_i and protonic adsorption γ_{H^+} balance the diffusive flux normal to the particle surface for each solute (Auriault and Lewandowska 1996). This yields

$$-D_i\left(\nabla C_{i_b} + z_i C_{i_b}\nabla\overline{\phi}\right)\cdot\mathbf{n} = \frac{\partial\Gamma_i}{\partial t} + \frac{\partial\gamma_i}{\partial t} \quad \text{on } \Gamma_{fs} \tag{22}$$

with $\gamma_i = 0$ for $i = \text{Na}^+, \text{CL}^-, \text{OH}^-$. Again, by eliminating the anion concentration through (1) and (2) we can rephrase (22) in terms of primary unknowns

$$\begin{aligned}
-D_{\text{Na}^+}\left(\nabla C_{\text{Na}_\text{b}^+} + C_{\text{Na}_\text{b}^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} &= \frac{\partial\Gamma_{\text{Na}^+}}{\partial t} \qquad \mathbf{I}_f\cdot\mathbf{n} = 0\\
-\widehat{D}\left(\nabla C_{\text{H}_\text{b}^+} + C_{\text{H}_\text{b}^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} &= \frac{\partial}{\partial t}\left(\gamma_{\text{H}^+} + \Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}\right) \quad \text{on } \Gamma_{fs}
\end{aligned}$$

3.2 Summary of the Two-Scale Model

The two-scale nanoscopic/microscopic model consists in: Given the constants $\{\mu_f, K_W, D_{\text{Na}^+}, D_{\text{H}^+} D_{\text{Cl}^-}, D_{\text{OH}^-}, F, R, T\}$ the functions $\{\Theta, \widehat{D}, B\}$ depending on $C_{\text{H}_\text{b}^+}$, and $\{\Gamma_i, \gamma_{\text{H}^+}, C\}$ depending on $\{C_{\text{Na}_\text{b}^+}, C_{\text{H}_\text{b}^+}\}$, find the microscopic fields $\{\mathbf{v}, p, C_{\text{Na}_\text{b}^+}, C_{\text{H}_\text{b}^+}, \phi\}$ satisfying

$$\begin{cases}
\nabla\cdot\mathbf{v} = 0\\
\mu_f\Delta\mathbf{v} - \nabla p = 0\\
\dfrac{\partial C_{\text{Na}_\text{b}^+}}{\partial t} + \nabla\cdot\left(C_{\text{Na}_\text{b}^+}\mathbf{v}\right) = \nabla\cdot\left[D_{\text{Na}^+}\left(\nabla C_{\text{Na}_\text{b}^+} + C_{\text{Na}_\text{b}^+}\nabla\overline{\phi}\right)\right] \quad \text{in } \Omega_f\\
\dfrac{\partial\left(\Theta C_{\text{H}_\text{b}^+}\right)}{\partial t} + \nabla\cdot\left(\Theta C_{\text{H}_\text{b}^+}\mathbf{v}\right) = \nabla\cdot\left[\widehat{D}_H\left(\nabla C_{\text{H}_\text{b}^+} + C_{\text{H}_\text{b}^+}\nabla\overline{\phi}\right)\right]\\
\nabla\cdot\left(A\nabla C_{\text{Na}_\text{b}^+} + B\nabla C_{\text{H}_\text{b}^+} + C\nabla\overline{\phi}\right) = 0
\end{cases} \tag{23}$$

supplemented by boundary conditions on Γ_{fs}

$$\begin{aligned}
&\mathbf{v}\cdot\boldsymbol{\tau} = \frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta}{\mu_f}\nabla\phi\cdot\boldsymbol{\tau}; \quad \mathbf{v}\cdot\mathbf{n} = 0; \quad D_{\text{Na}^+}\left(\nabla C_{\text{Na}_\text{b}^+} + C_{\text{Na}_\text{b}^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} = \frac{\partial\Gamma_{\text{Na}^+}}{\partial t};\\
&\mathbf{I}_f\cdot\mathbf{n} = 0; \quad \widehat{D}_H\left(\nabla C_{\text{H}_\text{b}^+} + C_{\text{H}_\text{b}^+}\nabla\overline{\phi}\right)\cdot\mathbf{n} = \frac{\partial}{\partial t}\left(\gamma_{\text{H}^+} + \Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}\right).
\end{aligned} \tag{24}$$

4 Homogenization

In this section we apply the asymptotic homogenization theory (Sanchez-Palencia 1980) to upscale the microscopic model to the macroscale. The kaolinite is then idealized as a bounded domain characterized by a periodic structure and two characteristic length scales; the characteristic microscopic scale ℓ of the order of the square root of the permeability $\ell = \sqrt{\kappa}$ and the macroscopic length scale L. Within the framework of homogenization introduce the perturbation parameter $\varepsilon = l/L$ and adopt the assumption of scale separation so that $\varepsilon \ll 1$. The family of perturbed models, referred herein to as ε-models, consist of properly scaled equations posed in the macroscopic domain Ω^{ε}, considered the union of disjoint fluid and solid sub-domains Ω^{ε}_{f} and Ω^{ε}_{s} along with scaled boundary conditions on the interface $\Gamma^{\varepsilon}_{fs}$. The perturbed domain Ω^{ε} is reconstructed periodically by replication of a micro cell Y^{ε}. In a similar fashion the sub-domains Ω^{ε}_{f} and Ω^{ε}_{s} along with the interface $\Gamma^{\varepsilon}_{fs}$ are given by the union of adjacent cell sub-domains Y^{ε}_{f} and Y^{ε}_{s} and $\partial Y^{\varepsilon}_{fs}$ interfaces, respectively. Each cell is congruent to a standard unitary parallelepiped period Y composed of sub-domains Y_f and Y_s with common boundary ∂Y_{fs}. Our starting point $\varepsilon = 1$ corresponds to our microscopic model. The basic problem consists of investigating the asymptotics as $\varepsilon \to 0$ and obtain the homogenized limit as the scale of the heterogeneity tends to zero.

4.1 Dimensionless Form of the Governing Equations

To capture the correct physics in the process of up-scaling the coefficients of the microscopic model must be properly scaled in powers of ε. This as accomplished by pursuing the procedure proposed in Auriault (1991) which consists in estimating the dimensionless quantities which appear in the local description. To write the dimensionless form of the microscopic governing equations we begin by normalizing the unknowns with respect to reference values denoted by the superscript "ref". By designating the dimensionless variables with respect to the reference values by the superscript "$*$", we have

$$x^* = \tfrac{x}{L}; \quad \nabla^* = L\nabla; \quad \mathbf{v}^* = \tfrac{\mathbf{v}}{V_{\text{ref}}}; \quad p^* = \tfrac{p}{p_{\text{ref}}}; \quad C^*_{\text{Na}_\text{b}^+} = \frac{C_{\text{Na}_\text{b}^+}}{C^{\text{ref}}_{\text{Na}}};$$
$$C^*_{\text{H}_\text{b}^+} = \frac{C_{\text{H}_\text{b}^+}}{C^{\text{ref}}_{H}}; \quad t^* = \tfrac{t}{t_{\text{ref}}}; \quad \phi^* = \tfrac{\phi}{\phi_{\text{ref}}}; \quad \zeta^* = \tfrac{\zeta}{\phi_{\text{ref}}}; \quad \widehat{D}^*_{\text{H}} = \tfrac{\widehat{D}_{\text{H}}}{D_{\text{H}^+}};$$

Denoting $L^{\text{ref}}_{D} := \left(\widetilde{\epsilon}_0 \widetilde{\epsilon}_r RT/2F^2 C_b\right)^{1/2}$, introducing the dimensionless numbers

$$Q_L = \frac{\mu_f V_{\text{ref}}}{p_{\text{ref}} L}; \quad D^{\star} = \frac{D_{\text{Na}^+}}{D_{\text{H}^+}}; \quad \hat{D}^{\star}(C_{\text{H}_\text{b}^+}) = 1 + \frac{D_{\text{OH}^-} K_w}{D_{\text{H}^+} C^2_{\text{H}_\text{b}^+}};$$
$$Pe_{\text{Na}} = \frac{V_{\text{ref}} L}{D_{\text{Na}^+}}; \quad Pe_{\text{H}} = \frac{V_{\text{ref}} L}{D_{\text{H}^+}}; \quad B^* = \frac{B C^{\text{ref}}_{\text{H}_\text{b}^+}}{A C^{\text{ref}}_{\text{Na}_\text{b}^+}}; \quad C^* = \frac{C}{A C^{\text{ref}}_{\text{Na}_\text{b}^+}} \tag{25}$$

and choosing $p_{\text{ref}} = 2RTC^{\text{ref}}_{b}$, $t_{\text{ref}} = L^2/D_{\text{Na}^+}$ and $V_{\text{ref}} = \ell^2 p_{\text{ref}}/L\mu_f$ the microscopic Eq. 23 can be rewritten in dimensionless form as

$$\begin{cases} \nabla^* \cdot \mathbf{v}^* = 0 \\ Q_L \triangle^* \mathbf{v}^* - \nabla^* p^* = 0 \\ \dfrac{\partial C^*_{\mathrm{Na}^+_\mathrm{b}}}{\partial t^*} + Pe_{\mathrm{Na}} \nabla^* \cdot \left(C^*_{\mathrm{Na}^+_\mathrm{b}} \mathbf{v}^* \right) = \nabla^* \cdot \left[D^\star \left(\nabla^* C^*_{\mathrm{Na}^+_\mathrm{b}} + C^*_{\mathrm{Na}^+_\mathrm{b}} \nabla^* \overline{\phi} \right) \right] \\ \dfrac{\partial \left(\Theta C^*_{\mathrm{H}^+_\mathrm{b}} \right)}{\partial t^*} + Pe_{\mathrm{H}} \nabla^* \cdot \left(\Theta C^*_{\mathrm{H}^+_\mathrm{b}} \mathbf{v}^* \right) = \nabla^* \cdot \left[\widehat{D}^* \left(\nabla^* C^*_{\mathrm{H}^+_\mathrm{b}} + C^*_{\mathrm{H}^+_\mathrm{b}} \nabla^* \overline{\phi} \right) \right] \\ \nabla^* \cdot \left(\nabla^* C^*_{\mathrm{Na}^+_\mathrm{b}} + B^* \nabla^* C^*_{\mathrm{H}^+_\mathrm{b}} + C^* \nabla^* \overline{\phi} \right) = 0 \end{cases} \tag{26}$$

The number Q_L quantifies the ratio between viscous forces and macroscopic pressure gradient in the Stokes problem. Its estimate follows from the well known derivation of Darcy's law which gives $Q_L = O(\epsilon^2)$ (Auriault 1991). The Péclet numbers Pe_i ($i =$Na, H) quantify the ratio between convective and diffusive effects for each solute. Assume these of same order of magnitude so that $Pe_{\mathrm{Na}} = Pe_H = O(1)$. In addition, since the diffusivities have same order of magnitude this yields $D^* = \hat{D}^* = B^* = C^* = O(1)$.

We now consider the dimensionless form of the boundary conditions. To this end we begin by rewriting the two latter equations in (24) as

$$D_{\mathrm{Na}^+} \left(\nabla C_{\mathrm{Na}^+_\mathrm{b}} + C_{\mathrm{Na}^+_\mathrm{b}} \nabla \overline{\phi} \right) \cdot \mathbf{n} = \frac{\partial \alpha C_{\mathrm{Na}^+_\mathrm{b}}}{\partial t}; \quad \widehat{D}_{\mathrm{H}} \left(\nabla C_{\mathrm{H}^+_\mathrm{b}} + C_{\mathrm{H}^+_\mathrm{b}} \nabla \overline{\phi} \right) \cdot \mathbf{n} = \frac{\partial \beta C_{\mathrm{H}^+_\mathrm{b}}}{\partial t}$$

where by invoking the constitutive laws (11) and (16b) for Γ_i and γ_{H^+} the coefficients α and β are given by

$$\alpha = \Gamma_{\mathrm{Na}^+} / C_{\mathrm{Na}^+_\mathrm{b}} \quad \beta = \left(\gamma_{\mathrm{H}^+} + \Gamma_{\mathrm{H}^+} - \Gamma_{\mathrm{OH}^-} \right) / C_{\mathrm{H}^+_\mathrm{b}} \tag{27}$$

Thus, introducing the numbers $U_L = K_E^{\mathrm{ref}} \phi_{\mathrm{ref}} / V_{\mathrm{ref}} L$, $Da_{\mathrm{N}} = \alpha / L$ and $Da_H = D_{\mathrm{Na}^+} \beta / D_{\mathrm{H}^+} L$ the dimensionless interface conditions read as

$$\begin{aligned} &\mathbf{v}^* \cdot \boldsymbol{\tau} = U_L \overline{\zeta} \nabla^* \overline{\phi} \cdot \boldsymbol{\tau}; \quad D^\star \left(\nabla^* C^*_{\mathrm{Na}^+_\mathrm{b}} + C^*_{\mathrm{Na}^+_\mathrm{b}} \nabla^* \overline{\phi} \right) \cdot \mathbf{n} = \frac{\partial}{\partial t^*} \left(Da_{\mathrm{N}} C^*_{\mathrm{Na}^+_\mathrm{b}} \right) \\ &\mathbf{v}^* \cdot \mathbf{n} = 0; \quad \mathbf{I}^*_f \cdot \mathbf{n} = 0; \quad \widehat{D}^* \left(\nabla^* C^*_{\mathrm{H}^+_\mathrm{b}} + C^*_{\mathrm{H}^+_\mathrm{b}} \nabla^* \overline{\phi} \right) \cdot \mathbf{n} = \frac{\partial}{\partial t^*} \left(Da_{\mathrm{H}} C^*_{\mathrm{H}^+_\mathrm{b}} \right) \end{aligned} \tag{28}$$

Recalling that $\ell = O(10 L_D)$ we have the estimate

$$U_L = \frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r R^2 T^2}{\mu_f F^2 L V_{\mathrm{ref}}} = \frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r R^2 T^2}{\mu_f \ell^2 p_{\mathrm{ref}}} = \frac{2 L_D^2 R T C_b}{\ell^2 p_{\mathrm{ref}}} = \frac{L_D^2}{\ell^2} = O(1) \tag{29}$$

4.2 Numerical Estimates of the Damköhler Numbers

A crucial issue underlying the multiscale method proposed herein are the estimates of the dimensionless quantities Da_i ($i =$Na, H) which play the role of non-linear Damköhler numbers that quantify the ratio between sorption and diffusion effects at the interface (Auriault and Lewandowska 1996). The numerical constitutive law of the Damköhler numbers can be obtained by revisiting the nanoscopic modeling in (11) and (16b). Numerically $|Da_{\mathrm{N}}| < 10^{-5} |Da_{\mathrm{H}}| < 3.5\, 10^{-2}$ in the investigated range of Na^+ concentration and pH. For simplicity we adopt an averaged estimate for both Da_{N} and Da_{H} with magnitude dictated by the higher concentration of the sodium, chosen of $O(\epsilon)$.

To summarize, by collecting the aforementioned estimates, the ε-model is rephrased below including a ε^n scaling factor in front of each coefficient

$$\begin{cases} \nabla \cdot \mathbf{v}^\varepsilon = 0 \\ \varepsilon^2 \mu_f \triangle \mathbf{v}^\varepsilon - \nabla p^\varepsilon = 0 \\ \dfrac{\partial C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+}}{\partial t} + \nabla \cdot \left(C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} \mathbf{v}^\varepsilon \right) = \nabla \cdot \left[D_{\mathrm{Na}^+} \left(\nabla C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} + C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} \nabla \overline{\phi}^\varepsilon \right) \right] = 0 \\ \dfrac{\partial \left(\Theta^\varepsilon C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} \right)}{\partial t} + \nabla \cdot \left(\Theta^\varepsilon C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^\varepsilon \right) = \nabla \cdot \left[\widehat{D}^\varepsilon_H \left(\nabla C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} + C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} \nabla \overline{\phi}^\varepsilon \right) \right] = 0 \\ \nabla \cdot \left(A \nabla C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} + B^\varepsilon \nabla C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} + C^\varepsilon \nabla \overline{\phi}^\varepsilon \right) = 0 \end{cases} \tag{30}$$

and

$$\begin{array}{ll} \mathbf{v}^\varepsilon \cdot \boldsymbol{\tau} = \dfrac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^\varepsilon}{\mu_f} \nabla \phi^\varepsilon \cdot \boldsymbol{\tau} & D_{\mathrm{Na}^+} \left(\nabla C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} + C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} \nabla \overline{\phi}^\varepsilon \right) \cdot \mathbf{n} = \varepsilon \dfrac{\partial \left(\alpha^\varepsilon C^\varepsilon_{\mathrm{Na}_\mathrm{b}^+} \right)}{\partial t} \\ \mathbf{v}^\varepsilon \cdot \mathbf{n} = 0 \quad \mathbf{I}^\varepsilon_f \cdot \mathbf{n} = 0 & \widehat{D}^\varepsilon_\mathrm{H} \left(\nabla C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} + C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} \nabla \overline{\phi}^\varepsilon \right) \cdot \mathbf{n} = \varepsilon \dfrac{\partial \left(\beta^\varepsilon C^\varepsilon_{\mathrm{H}_\mathrm{b}^+} \right)}{\partial t} \end{array} \tag{31}$$

4.3 Matched Asymptotic Expansions

To upscale the microscopic model to the macroscale we adopt the formal homogenization procedure based on perturbation expansions (Auriault 1991; Sanchez-Palencia 1980). Within this framework each property is considered dependent on both global and local length scales in the form $f = f(\mathbf{x}, \mathbf{y})$, where $\mathbf{x}$ and $\mathbf{y}$ denote the macroscopic and microscopic coordinates, respectively. Up to a translation $\mathbf{x}$ and $\mathbf{y}$ are related by $\mathbf{y} = \mathbf{x}/\varepsilon$. By the chain rule the differential operator is replaced by $\nabla = \nabla_x + \varepsilon^{-1} \nabla_y$. The usual procedure to obtain the homogenized problem consists in postulating asymptotic expansions for the unknowns $f^\varepsilon(\mathbf{x}, \mathbf{y}) = \sum_{k=0}^{\infty} \varepsilon^k f^k(\mathbf{x}, \mathbf{y})$ with the functions $f^i = f^i(\mathbf{x}, \mathbf{y})$ $(i = 0, 1, 2 \ldots)$$\mathbf{y}$-periodic. In the subsequent notation we adopt the superscripts “0” and “1” to designate the zero and first-order components of the Taylor series expansion. Inserting the ansatz into the microscopic governing Eqs. 30–31 and collecting powers of ε we obtain the following successive equations at different orders:

$$\nabla_y \cdot \left[D_{\mathrm{Na}^+} \left(\nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + C^0_{\mathrm{Na}_\mathrm{b}^+} \nabla_y \overline{\phi}^0 \right) \right] = 0 \tag{32}$$

$$\nabla_y \cdot \left[\widehat{D}^0 \left(\nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0_{\mathrm{H}_\mathrm{b}^+} \nabla_y \overline{\phi}^0 \right) \right] = 0 \tag{33}$$

$$\nabla_y \cdot \left(A \nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + B^0 \nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0 \nabla_y \overline{\phi}^0 \right) = 0 \tag{34}$$

$$\nabla_y \cdot \mathbf{v}^0 = 0 \tag{35}$$

$$\nabla_y p^0 = 0 \tag{36}$$

$$\nabla_y \cdot \left(C^0_{\mathrm{Na}_\mathrm{b}^+} \mathbf{v}^0 \right) + \nabla_x \cdot \left[D_{\mathrm{Na}^+} \left(\nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + C^0_{\mathrm{Na}_\mathrm{b}^+} \nabla_y \overline{\phi}^0 \right) \right] + \nabla_y \cdot \mathbf{J}^0_{\mathrm{Na}^+} = 0 \tag{37}$$

$$\nabla_y \cdot \left(\Theta^0 C^0_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^0\right) + \nabla_x \cdot \left[\widehat{D}^0 \left(\nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0_{\mathrm{H}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right)\right] + \nabla_y \cdot \mathbf{J}^0_{\mathrm{H}^+} = 0 \tag{38}$$

$$\nabla_x \cdot \left(A \nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + B^0 \nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0 \nabla_y \overline{\phi}^0\right) + \nabla_y \cdot \mathbf{I}^0_f = 0 \tag{39}$$

$$\begin{aligned}\mathbf{J}^0_{\mathrm{Na}^+} &= -D_{\mathrm{Na}^+} \left[\left(\nabla_x C^0_{\mathrm{Na}_\mathrm{b}^+} + \nabla_y C^1_{\mathrm{Na}_\mathrm{b}^+}\right) + C^0_{\mathrm{Na}_\mathrm{b}^+} \left(\nabla_x \overline{\phi}^0 + \nabla_y \overline{\phi}^1\right)\right. \\ &\quad \left. + C^1_{\mathrm{Na}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right]\end{aligned} \tag{40}$$

$$\begin{aligned}\mathbf{J}^0_{\mathrm{H}^+} &= -\widehat{D}^0 \left[\left(\nabla_x C^0_{\mathrm{H}_\mathrm{b}^+} + \nabla_y C^1_{\mathrm{H}_\mathrm{b}^+}\right) + C^0_{\mathrm{H}_\mathrm{b}^+} \left(\nabla_x \overline{\phi}^0 + \nabla_y \overline{\phi}^1\right) + C^1_{\mathrm{H}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right] \\ &\quad - \widehat{D}^1 \left(\nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0_{\mathrm{H}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right)\end{aligned} \tag{41}$$

$$\begin{aligned}\mathbf{I}^0_f &= A \left(\nabla_x C^0_{\mathrm{Na}_\mathrm{b}^+} + \nabla_y C^1_{\mathrm{Na}_\mathrm{b}^+}\right) + B^0 \left(\nabla_x C^0_{\mathrm{H}_\mathrm{b}^+} + \nabla_y C^1_{\mathrm{H}_\mathrm{b}^+}\right) \\ &\quad + C^0 \left(\nabla_x \overline{\phi}^0 + \nabla_y \overline{\phi}^1\right) + B^1 \nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^1 \nabla_y \overline{\phi}^0\end{aligned} \tag{42}$$

$$\nabla_x \cdot \mathbf{v}^0 + \nabla_y \cdot \mathbf{v}^1 = 0 \tag{43}$$

$$\mu_f \triangle_{yy} \mathbf{v}^0 - \nabla_y p^1 = \nabla_x p^0 \tag{44}$$

$$\begin{aligned}&\frac{\partial C^0_{\mathrm{Na}_\mathrm{b}^+}}{\partial t} + \nabla_x \cdot \left(C^0_{\mathrm{Na}_\mathrm{b}^+} \mathbf{v}^0\right) + \nabla_y \cdot \left(C^0_{\mathrm{Na}_\mathrm{b}^+} \mathbf{v}^1 + C^1_{\mathrm{Na}_\mathrm{b}^+} \mathbf{v}^0\right) \\ &\quad + \nabla_x \cdot \mathbf{J}^0_{\mathrm{Na}^+} + \nabla_y \cdot \mathbf{J}^1_{\mathrm{Na}^+} = 0\end{aligned} \tag{45}$$

$$\begin{aligned}&\frac{\partial \left(\Theta^0 C^0_{\mathrm{H}_\mathrm{b}^+}\right)}{\partial t} + \nabla_x \cdot \left(\Theta^0 C^0_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^0\right) + \nabla_y \cdot \left[\Theta^0 \left(C^0_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^1 + C^1_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^0\right) + \Theta^1 C^0_{\mathrm{H}_\mathrm{b}^+} \mathbf{v}^0\right] \\ &\quad + \nabla_x \cdot \mathbf{J}^0_{\mathrm{H}^+} + \nabla_y \cdot \mathbf{J}^1_{\mathrm{H}^+} = 0\end{aligned} \tag{46}$$

$$\nabla_x \cdot \mathbf{I}^0_f + \nabla_y \cdot \mathbf{I}^1_f = 0 \tag{47}$$

whereas the successive orders of the interface conditions read as

$$\left[D_{\mathrm{Na}^+} \left(\nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + C^0_{\mathrm{Na}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right)\right] \cdot \mathbf{n} = 0 \tag{48}$$

$$\left[\widehat{D}^0 \left(\nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0_{\mathrm{H}_\mathrm{b}^+} \nabla_y \overline{\phi}^0\right)\right] \cdot \mathbf{n} = 0 \tag{49}$$

$$\left(A \nabla_y C^0_{\mathrm{Na}_\mathrm{b}^+} + B^0 \nabla_y C^0_{\mathrm{H}_\mathrm{b}^+} + C^0 \nabla_y \overline{\phi}^0\right) \cdot \mathbf{n} = 0 \tag{50}$$

$$\mathbf{v}^0 \cdot \mathbf{n} = 0 \quad \mathbf{v}^1 \cdot \mathbf{n} = 0 \tag{51}$$

$$\mathbf{v}^0 \cdot \boldsymbol{\tau} = \frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r}{\mu_f} \left[\zeta^0 \left(\nabla_x \phi^0 + \nabla_y \phi^1\right) + \zeta^1 \nabla_y \phi^0\right] \cdot \boldsymbol{\tau} \tag{52}$$

$$\mathbf{J}^0_{\mathrm{Na}^+} \cdot \mathbf{n} = 0 \quad \mathbf{J}^0_{\mathrm{H}^+} \cdot \mathbf{n} = 0 \quad \mathbf{I}^0_f \cdot \mathbf{n} = 0 \tag{53}$$

$$\mathbf{J}^1_{\mathrm{Na}^+} \cdot \mathbf{n} = \frac{\partial \left(\alpha^0 C^0_{\mathrm{Na}_\mathrm{b}^+}\right)}{\partial t} \quad \mathbf{J}^1_{\mathrm{H}^+} \cdot \mathbf{n} = \frac{\partial \left(\beta^0 C^0_{\mathrm{Na}_\mathrm{b}^+}\right)}{\partial t} \mathbf{I}^1_f \cdot \mathbf{n} = 0 \tag{54}$$

4.4 Non-Oscillatory Variables

We begin by collecting our set of slow $\mathbf{y}$-independent variables. From (36) we have $p^0(\mathbf{x}, \mathbf{y}, t) = p^0(\mathbf{x}, t)$. In addition, denoting $\Psi^0 := \{C^0_{\mathrm{Na}_\mathrm{b}^+}, C^0_{\mathrm{H}_\mathrm{b}^+}, \phi^0\}$ Eqs. 32–34 together with the Neumann boundary conditions (48–50) can be rewritten in the form

$$\begin{cases} \nabla_y \cdot \left(\mathbf{M}^0 \nabla_y \Psi^0\right) = 0 \text{ in } Y_f \\ \mathbf{M}^0 \nabla_y \Psi^0 \cdot \mathbf{n} = 0 \quad\ \text{ on } \partial Y_{fs} \end{cases} \text{with } \mathbf{M}^0 := \begin{bmatrix} D_{\mathrm{Na}^+} & 0 & D_{\mathrm{Na}^+} C^0_{\mathrm{Na}_\mathrm{b}^+} \\ 0 & \widehat{D}^0 & \widehat{D}^0 C^0_{\mathrm{H}_\mathrm{b}^+} \\ A & B^0 & C^0 \end{bmatrix} \tag{55}$$

The solution of the above homogeneous Neumann problem is simply $C^0_{\mathrm{Na}_\mathrm{b}^+}(\mathbf{x}, \mathbf{y}, t) = C^0_{\mathrm{Na}_\mathrm{b}^+}(\mathbf{x}, t)$, $C^0_{\mathrm{H}_\mathrm{b}^+}(\mathbf{x}, \mathbf{y}, t) = C^0_{\mathrm{H}_\mathrm{b}^+}(\mathbf{x}, t)$ and $\overline{\phi}^0(\mathbf{x}, \mathbf{y}, t) = \overline{\phi}^0(\mathbf{x}, t)$. Moreover, by invoking the definitions of the coefficients we also have $\mathcal{Y}^0(\boldsymbol{x}, \boldsymbol{y}, t) := \{\Theta^0, \widehat{D}^0, B^0, C^0, \zeta^0, \alpha^0, \beta^0, V^0_{\mathrm{slip}}\} = \mathcal{Y}^0(\boldsymbol{x}, t)$. Thus our set of non-oscillatory variables is $\{p^0, C^0_{\mathrm{Na}_\mathrm{b}^+}, C^0_{\mathrm{H}_\mathrm{b}^+}, \overline{\phi}^0, \Theta^0, \widehat{D}^0, B^0, C^0, \zeta^0, \alpha^0, \beta^0, V^0_{\mathrm{slip}}\}$.

4.5 Microscopic Closure Problems

Since $\{C^0_{\mathrm{Na}_\mathrm{b}^+}, C^0_{\mathrm{H}_\mathrm{b}^+}, \phi^0, \Theta^0, \widehat{D}^0\}$ are independent of the fast variable all terms containing their gradient with respect to $\boldsymbol{y}$ vanish. Thus, to establish the local closure problems for $\Psi^1 = \{C^1_{\mathrm{Na}_\mathrm{b}^+}, C^1_{\mathrm{H}_\mathrm{b}^+}, \phi^1\}$ we note that using the local incompressibility condition (35), only the last terms in (37), (38) and (39) survive. When combined with the constitutive laws (40)-(42) and boundary conditions (53) this yields the local Neumann problems

$$\begin{cases} \nabla_y \cdot \left(\mathbf{M}^0 \nabla_y \Psi^1\right) = 0 & \text{in } \ Y_f \\ -\mathbf{M}^0 \nabla_y \Psi^1 \cdot \mathbf{n} = \mathbf{M}^0 \nabla_x \Psi^0 \cdot \mathbf{n} & \text{on } \ \partial Y_{fs} \end{cases}$$

Recalling that the components of the matrix $\mathbf{M}^0$ in (55) are $\boldsymbol{y}$-independent, by linearity the solution can be represented in the form

$$C^1_{i_b}(\mathbf{x}, \mathbf{y}, t) = \mathbf{f}(\mathbf{y}) \cdot \nabla_x C^0_{i_b}(\mathbf{x}, t) + \widetilde{C}_i(\mathbf{x}, t) \tag{56}$$

$$\overline{\phi}^1(\mathbf{x}, \mathbf{y}, t) = \mathbf{f}(\mathbf{y}) \cdot \nabla_x \overline{\phi}^0(\mathbf{x}, t) + \widetilde{\phi}(\mathbf{x}, t) \tag{57}$$

where $i = \mathrm{Na}^+, \mathrm{H}^+$ and the characteristic vectorial function $\mathbf{f} = \mathbf{f}(\mathbf{y})$ satisfies the canonical Neumann problem

$$\begin{cases} \triangle_{yy} \mathbf{f}(\mathbf{y}) = 0 & \text{in } Y \\ \nabla_y \mathbf{f}(\mathbf{y}) \mathbf{n} = -\mathbf{n} & \text{on } \partial Y_{fs} \end{cases} . \tag{58}$$

with $\nabla_y \mathbf{f}$ incorporating the tortuosity effects.

4.6 Macroscopic Transport Equation

To derive the macroscopic transient Nernst-Planck equation for the Na^+ and H^+ transport we begin by introducing the volume and surface average operators over the periodic cell

$$\langle \chi \rangle := \frac{1}{|Y|} \int\limits_{Y_f} \chi \, \mathbf{dy} \quad \langle \chi \rangle_{fs} := \frac{1}{|Y|} \int\limits_{\partial \Gamma_{fs}} \chi \cdot \mathbf{ndy}$$

By averaging (45) and (46) we obtain

$$\left\langle \frac{\partial C^0_{\mathrm{Na}^+_{\mathrm{b}}}}{\partial t} \right\rangle + \left\langle \nabla_x \cdot \left(C^0_{\mathrm{Na}^+_{\mathrm{b}}} \mathbf{v}^0 \right) \right\rangle + \left\langle \nabla_y \cdot \left(C^0_{\mathrm{Na}^+_{\mathrm{b}}} \mathbf{v}^1 + C^1_{\mathrm{Na}^+_{\mathrm{b}}} \mathbf{v}^0 \right) \right\rangle$$
$$+ \left\langle \nabla_x \cdot \mathbf{J}^0_{\mathrm{Na}^+} + \nabla_y \cdot \mathbf{J}^1_{\mathrm{Na}^+} \right\rangle = 0$$
$$\left\langle \frac{\partial \left(\Theta^0 C^0_{\mathrm{H}^+_{\mathrm{b}}} \right)}{\partial t} \right\rangle + \left\langle \nabla_x \cdot \left(\Theta^0 C^0_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{v}^0 \right) \right\rangle + \left\langle \nabla_y \cdot \left[\Theta^0 \left(C^0_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{v}^1 + C^1_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{v}^0 \right) \right.\right.$$
$$\left.\left. + \Theta^1 C^0_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{v}^0 \right] \right\rangle + \left\langle \nabla_x \cdot \mathbf{J}^0_{\mathrm{H}^+} + \nabla_y \cdot \mathbf{J}^1_{\mathrm{H}^+} \right\rangle = 0$$

Recalling that $\{C^0_{\mathrm{Na}^+_{\mathrm{b}}}, C^0_{\mathrm{H}^+_{\mathrm{b}}}, \overline{\phi}^0\}$ are $\mathbf{y}$-independent, defining $\eta := |Y_f|/|Y|$ and $\mathbf{V}^0_D := \langle \mathbf{v}^0 \rangle$ the macroscopic porosity and Darcy´s velocity, respectively, using Gauss theorem and interface conditions (51) and (54a–54b) gives

$$\eta \frac{\partial C^0_{\mathrm{Na}^+_{\mathrm{b}}}}{\partial t} + \nabla_x \cdot \left(C^0_{\mathrm{Na}^+_{\mathrm{b}}} \mathbf{V}^0_D \right) + \nabla_x \cdot \langle \mathbf{J}^0_{\mathrm{Na}^+} \rangle = - \int_{\partial \Gamma_{fs}} \mathbf{J}^1_{\mathrm{Na}^+} \cdot \mathbf{n} d\Gamma$$
$$= - \frac{\partial}{\partial t} \left(\langle \alpha^0 \rangle_{fs} C^0_{\mathrm{Na}^+_{\mathrm{b}}} \right)$$
$$\eta \frac{\partial \left(\Theta^0 C^0_{\mathrm{H}^+_{\mathrm{b}}} \right)}{\partial t} + \nabla_x \cdot \left(\Theta^0 C^0_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{V}^0_D \right) + \nabla_x \cdot \langle \mathbf{J}^0_{\mathrm{H}^+} \rangle = - \int_{\partial \Gamma_{fs}} \mathbf{J}^1_{\mathrm{H}^+} \cdot \mathbf{n} d\Gamma$$
$$= - \frac{\partial}{\partial t} \left(\langle \beta^0 \rangle_{fs} C^0_{\mathrm{H}^+_{\mathrm{b}}} \right)$$

Using the constitutive laws for the fluxes (40) and (41) along with the closure relations in (56)-(57) we obtain the macroscopic equations

$$\frac{\partial \left(R^0_N C^0_{\mathrm{Na}^+_{\mathrm{b}}} \right)}{\partial t} + \nabla_x \cdot \left(C^0_{\mathrm{Na}^+_{\mathrm{b}}} \mathbf{V}^0_D \right) = \nabla_x \cdot \left[\mathbf{D}^{\mathrm{eff}}_{\mathrm{Na}^+} \left(\nabla_x C^0_{\mathrm{Na}^+_{\mathrm{b}}} + C^0_{\mathrm{Na}^+_{\mathrm{b}}} \nabla_x \overline{\phi}^0 \right) \right]$$
$$\frac{\partial \left(R^0_H C^0_{\mathrm{H}^+_{\mathrm{b}}} \right)}{\partial t} + \nabla_x \cdot \left(\Theta^0 C^0_{\mathrm{H}^+_{\mathrm{b}}} \mathbf{V}^0_D \right) = \nabla_x \cdot \left[\widehat{\mathbf{D}}^{\mathrm{eff}} \left(\nabla_x C^0_{\mathrm{H}^+_{\mathrm{b}}} + C^0_{\mathrm{H}^+_{\mathrm{b}}} \nabla_x \overline{\phi}^0 \right) \right]$$

with the effective diffusivities and retardation coefficients defined by

$$\mathbf{D}^{\mathrm{eff}}_{\mathrm{Na}^+} := D_{\mathrm{Na}^+} \left\langle \mathbf{I} + \nabla_y \mathbf{f}(\mathbf{y}) \right\rangle \quad \widehat{\mathbf{D}}^{\mathrm{eff}} := \widehat{D}^0 \left\langle \mathbf{I} + \nabla_y \mathbf{f}(\mathbf{y}) \right\rangle$$
$$R^0_N := \eta + \langle \alpha^0 \rangle_{fs} \qquad R^0_H := \eta \Theta^0 + \langle \beta^0 \rangle_{fs}$$

The novelty in the above homogenized form of Nernst-Planck equation is the appearance of the retardation factors R^0_N and R^0_H which quantify the transient storativity of the Na^+ in the EDL and of $H^+ - \mathrm{OH}^-$ in both EDL and particle surface.

4.7 Macroscopic Conservation of Charge

The effective charge conservation equation can be obtained in a straightforward fashion. By averaging (47) and using boundary condition (54c) we obtain

$$\left\langle \nabla_x \cdot \mathbf{I}_f^0 + \nabla_y \cdot \mathbf{I}_f^1 \right\rangle = \nabla_x \cdot \left\langle \mathbf{I}_f^0 \right\rangle + \frac{1}{|Y|} \int\limits_{\partial Y_{fs}} \mathbf{I}_f^1 \cdot \mathbf{n} d\mathbf{y} = \nabla_x \cdot \mathbf{I}_f^{\text{eff}} = 0. \tag{59}$$

where $\mathbf{I}_f^{\text{eff}} := \left\langle \mathbf{I}_f^0 \right\rangle$ is the effective current.

By combining (56–57) for the fluctuations with (42) we obtain the macroscopic constitutive law

$$\mathbf{I}_f^{\text{eff}} = \mathbf{A}^{\text{eff}} \nabla_x C^0_{\text{Na}_\text{b}^+} + \mathbf{B}^{\text{eff}} \nabla_x C^0_{\text{H}_\text{b}^+} + \mathbf{C}^{\text{eff}} \nabla_x \overline{\phi}^0 \tag{60}$$

with the effective parameters given by $\mathbf{Z}^{\text{eff}} := Z \left\langle \mathbf{I} + \nabla_y \mathbf{f}(\mathbf{y}) \right\rangle$ where $Z = A, B^0, C^0$.

4.8 Macroscopic Darcy Law

To derive the macroscopic form of Darcy´s law we begin by using the closure relation for the electric potential (57) in (52) to obtain for the slip velocity

$$V^0_{\text{slip}} = \frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f} \left(\mathbf{I} + \nabla_y \mathbf{f} \right) \nabla_x \phi^0 \cdot \boldsymbol{\tau}. \tag{61}$$

Combining the above result with the mass balance (35) and the momentum equation (44) we obtain the local Stokes problem formulated in the pair $(\mathbf{v}^0, p^1)$

$$\begin{cases} \mu_f \triangle_{yy} \mathbf{v}^0 - \nabla_y p^1 = \nabla_x p^0 & \\ \nabla_y \cdot \mathbf{v}^0 = 0 & \text{in } Y_f \\ \mathbf{v}^0 \cdot \mathbf{n} = 0 & \\ \mathbf{v}^0 \cdot \boldsymbol{\tau} = \dfrac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f} \left(\mathbf{I} + \nabla_y \mathbf{f} \right) \nabla_x \phi^0 \cdot \boldsymbol{\tau} \text{ on } & \partial Y_{fs} \end{cases}$$

To derive Darcy's Law we proceed in a similar fashion to Murad and Moyne (2008) and decompose velocity and pressure fluctuation into their hydraulic and electroosmotic components $\mathbf{v}^0 = \mathbf{v}^0_P + \mathbf{v}^0_E$ and $p^1 = p^1_P + p^1_E$ with each one satisfying the local cell problems

$$\begin{cases} \mu_f \triangle_{yy} \mathbf{v}^0_P - \nabla_y p^1_P = \nabla_x p^0 \\ \nabla_y \cdot \mathbf{v}^0_P = 0 \\ \mathbf{v}^0_P = 0 \end{cases} \quad \begin{cases} \mu_f \triangle_{yy} \mathbf{v}^0_E - \nabla_y p^1_E = 0 & \\ \nabla_y \cdot \mathbf{v}^0_E = 0 & \text{in } Y_f \\ \mathbf{v}^0_E \cdot \mathbf{n} = 0 & \\ \mathbf{v}^0_E \cdot \boldsymbol{\tau} = \dfrac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f} \left(\mathbf{I} + \nabla_y \mathbf{f} \right) \nabla_x \phi^0 \cdot \boldsymbol{\tau} & \text{on } \partial Y_{fs} \end{cases} \tag{62}$$

The local system (62a) for $\{\mathbf{v}^0_P, p^1_P\}$ is nothing but the classical closure problem which gives rise to the hydraulic conductivity (Auriault 1991). Unlike (62a), the cell problem for $\mathbf{v}^0_E$ is ruled by the slip boundary condition. By invoking the closure problem for the tortuosity function $\mathbf{f}$ one may observe that (62b) admits a solution of the type

$$\mathbf{v}^0_E = -\boldsymbol{\kappa}^0_E \nabla_x \phi^0 \quad \text{with } \boldsymbol{\kappa}^0_E = -\frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f} \left(\mathbf{I} + \nabla_y \mathbf{f} \right). \tag{63}$$

After averaging we obtain the macroscopic Darcy´s law

$$\mathbf{V}_D^0 = -\mathbf{K}_P^{\text{eff}}\nabla_x p^0 - \mathbf{K}_E^{\text{eff}}\nabla_x \phi^0 \quad \text{with } \mathbf{K}_E^{\text{eff}} := -\frac{\widetilde{\epsilon}_0 \widetilde{\epsilon}_r \zeta^0}{\mu_f}\left\langle \mathbf{I} + \nabla_y \mathbf{f} \right\rangle \tag{64}$$

The macroscopic coefficients $\mathbf{K}_P^{\text{eff}}$ and $\mathbf{K}_E^{\text{eff}}$ are nothing but the macroscopic hydraulic and electroosmotic conductivities (Moyne and Murad 2006a,b). It should be noted that since the closure relation for $\mathbf{K}_E^{\text{eff}}$ contains the ζ-potential, by combining the nanoscopic constitutive law (8) and (16) for ζ^0 with (64b) we can build-up numerically the dependency $\mathbf{K}_E^{\text{eff}} = \mathbf{K}_E^{\text{eff}}(C^0_{\text{Na}_\text{b}^+}, C^0_{\text{H}_\text{b}^+})$. Unlike the electroosmotic permeability which depends on the pair $\{C^0_{\text{Na}_\text{b}^+}, C^0_{\text{H}_\text{b}^+}\}$, the hydraulic permeability $\mathbf{K}_P^{\text{eff}}$ is only dictated by the cell geometry and fluid viscosity.

4.9 Macroscopic Mass Balance

The macroscopic mass conservation can easily be obtained by averaging (43) using the divergence theorem along with boundary condition (51b) and the periodicity to obtain

$$\nabla_x \cdot \mathbf{V}_D^0 = \nabla_x \cdot \left\langle \mathbf{v}^0 \right\rangle = -\left\langle \nabla_y \cdot \mathbf{v}^1 \right\rangle = -\frac{1}{|Y|}\int_{\partial Y_{fs}} \mathbf{v}^1 \cdot \mathbf{n}\mathbf{d}\mathbf{y} = 0$$

which when combined with (64) furnishes

$$\nabla_x \cdot \mathbf{V}_D^0 = \nabla_x \cdot \left(\mathbf{K}_E^{\text{eff}} \nabla_x \phi^0 + \mathbf{K}_P^{\text{eff}} \nabla_x p^0 \right) = 0$$

4.10 Summary of the Three Scale Model

We are now ready to formulate our three-scale transient problem. Let Ω be the macroscopic domain occupied by the kaolinite saturated by an aqueous solution containing four monovalent ions $\{\text{Na}^+, \text{H}^+, \text{OH}^-, \text{Cl}^-\}$. Given the set of constants $\{F, \widetilde{\varepsilon}_0, \widetilde{\varepsilon}_r, \mu_f, D_{\text{Na}^+}, D_{\text{H}^+}, D_{\text{Cl}^-}, D_{\text{OH}^-}, K_W\}$, the porosity η, the characteristic function $\mathbf{f}$, solution of (58), the hydraulic permeability $\mathbf{K}_P^{\text{eff}}$, the functions $\{\Theta^0, \widehat{D}^0\}$ depending on $C^0_{\text{H}_\text{b}^+}$, and $\{\zeta^0, \alpha^0, \beta^0\}$ depending on $\{C^0_{\text{H}_\text{b}^+}, C^0_{\text{Na}_\text{b}^+}\}$ solution of the nanoscopic problems (8), (16), (27), find the macroscopic unknowns $\{C^0_{\text{Na}_\text{b}^+}, C^0_{\text{H}_\text{b}^+}, p^0, \phi^0, \mathbf{V}_D^0, \mathbf{J}^{\text{eff}}_{\text{Na}^+}\}$, functions of $(\mathbf{x}, t)$, satisfying

$$\begin{cases} \nabla_x \cdot \mathbf{V}_D^0 = 0 \\ \mathbf{V}_D^0 = -\mathbf{K}_E^{\text{eff}} \nabla_x \phi^0 - \mathbf{K}_P^{\text{eff}} \nabla_x p^0 \\ \dfrac{\partial \left(R_N^0 C^0_{\text{Na}_\text{b}^+} \right)}{\partial t} + \nabla_x \cdot \left(C^0_{\text{Na}_\text{b}^+} \mathbf{V}_D^0 \right) = \nabla_x \cdot \left[\mathbf{D}^{\text{eff}}_{\text{Na}^+} \left(\nabla_x C^0_{\text{Na}_\text{b}^+} + C^0_{\text{Na}_\text{b}^+} \nabla_x \overline{\phi}^0 \right) \right] \\ \dfrac{\partial \left(R_H^0 C^0_{\text{H}_\text{b}^+} \right)}{\partial t} + \nabla_x \cdot \left(\Theta^0 C^0_{\text{H}_\text{b}^+} \mathbf{V}_D^0 \right) = \nabla_x \cdot \left[\widehat{\mathbf{D}}^{\text{eff}} \left(\nabla_x C^0_{\text{H}_\text{b}^+} + C^0_{\text{H}_\text{b}^+} \nabla_x \overline{\phi}^0 \right) \right] \\ \nabla_x \cdot \left(\mathbf{A}^{\text{eff}} \nabla_x C^0_{\text{Na}_\text{b}^+} + \mathbf{B}^{\text{eff}} \nabla_x C^0_{\text{H}_\text{b}^+} + \mathbf{C}^{\text{eff}} \nabla_x \overline{\phi}^0 \right) = 0 \end{cases}$$

with the effective electro-osmotic, electrical conductivity and retardation coefficients $\{\mathbf{K}_E^{\text{eff}}, \mathbf{C}^{\text{eff}}, R^0_{\text{N}}, R^0_{\text{H}}\}$ depending on $\{C^0_{\text{Na}_\text{b}^+}, C^0_{\text{H}_\text{b}^+}\}$, and the parameters $\{\widehat{\mathbf{D}}^{\text{eff}}, \mathbf{B}^{\text{eff}}\}$ depending on $C^0_{\text{H}_\text{b}^+}$ solution of the microscopic closure problems posed in the unit cell

$$\begin{aligned}
\mathbf{K}_E^{\text{eff}} &= -\frac{\widetilde{\epsilon}_0\widetilde{\epsilon}_r\zeta^0}{\mu_f}\left\langle \mathbf{I}+\nabla_y\mathbf{f}\right\rangle \qquad R_N^0 = \eta + \left\langle \alpha^0\right\rangle_{fs} \qquad R_H^0 = \eta\Theta^0 + \left\langle \beta^0\right\rangle_{fs}\\
\mathbf{A}^{\text{eff}} &= F\left\langle \mathbf{I}+\nabla_y\mathbf{f}\right\rangle\left(D_{\mathrm{Na}^+}-D_{\mathrm{Cl}^-}\right)\\
\widehat{\mathbf{D}}^{\text{eff}} &= \widehat{D}^0\left\langle \mathbf{I}+\nabla_y\mathbf{f}(\mathbf{y})\right\rangle \qquad \mathbf{D}_{\mathrm{Na}^+}^{\text{eff}} = D_{\mathrm{Na}^+}\left\langle \mathbf{I}+\nabla_y\mathbf{f}(\mathbf{y})\right\rangle\\
\mathbf{B}^{\text{eff}} &= F\left\langle \mathbf{I}+\nabla_y\mathbf{f}\right\rangle\left[D_{\mathrm{H}^+}-D_{\mathrm{Cl}^-}+\frac{\left(D_{\mathrm{OH}^-}-D_{\mathrm{Cl}^-}\right)K_W}{(C^0_{\mathrm{H}_\mathrm{b}^+})^2}\right]\\
\mathbf{C}^{\text{eff}} &= F\left\langle \mathbf{I}+\nabla_y\mathbf{f}\right\rangle\Bigg[\left(D_{\mathrm{Na}^+}+D_{\mathrm{Cl}^-}\right)C^0_{\mathrm{Na}_\mathrm{b}^+}+\left(D_{\mathrm{H}^+}+D_{\mathrm{Cl}^-}\right)C^0_{\mathrm{H}_\mathrm{b}^+}\\
&\qquad +\frac{\left(D_{\mathrm{OH}^-}-D_{\mathrm{Cl}^-}\right)K_W}{C^0_{\mathrm{H}_\mathrm{b}^+}}\Bigg]
\end{aligned}$$

5 Conclusion

In this study, we developed a three-scale model for transient electrokinetic flow and ion transport in kaolinite clays incorporating ionic solute sorption in the EDL and H^+ bonding at particle surface due to a single protonation/deprotonation chemical reaction (1–pK model).

The main feature of the approach developed herein is the appearance of two retardation parameters R_N and R_H in the effective Nernst-Planck relations for the Na^+ and (H^+–OH^-) transport. Within the framework of homogenization the constitutive responses of these parameters were rigorously derived adopting suitable numerical estimates of the Damköhler numbers which appear in the adsorption boundary conditions at the microscale. The parameter R_N quantities the storativity of the sodium in the EDL whereas R_H the proton binding in both EDL and particle surface. The reconstruction of the adsorption isotherms associated with the three-scale constitutive model for R_N and R_H along with the discretization of the macroscopic model to numerically simulate electrokinetic remediation are addressed in the follow-up article.

The generalization of the present approach to higher pK models involving additional reactions can be accomplished within the same methodology. Moreover, the extension of the multiscale procedure to smectite clays including a secondary nanoporosity level wherein EDLs overlap can also be accomplished by combining the current model with the dual porosity approach proposed by Murad and Moyne (Murad and Moyne 2008).

The model proposed herein exploits the Boltzmann distributions of the EDL that give rise to the Poisson–Boltzmann problem whose accuracy is restricted to monovalent ionic species, wherein ion-ion correlation effects are of small magnitude. The extension of the theory to higher valence ions incorporating correlation effects can be included in the nanoscopic description within the framework of modified Poisson Boltzmann theories or integral equation based approaches (see, e.g. McQuarrie 2000).

Acknowledgements Supported by FAPERJ Cientistas do Nosso Estado Grant Number 100.581/2007, CNPq Edital Universal Grant Number 470511/2008-7 and GDR MoMaS CNRS.

References

Acar, Y.B., Alshawabkeh, A.N.: Principles of electrokinetics remediation. Environ. Sci. Technol. **27**, 2638–2647 (1993)

Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M., Parker, R.: Electrokinetic remediation: basic and technology status. J. Hazard. Mater. **40**, 117–137 (1995)

Auriault, J.L.: Heterogeneous media: is an equivalent homogeneous description always possible?. Int. J. Eng. Sci. **29**, 785–795 (1991)

Auriault, J.L., et Lewandowska, J.: Diffusion/adsorption/advection macrotransport in soils. Eur. J. Mech. A **15**, 681–704 (1996)

Avena, M.J., De Pauli, C.P.: Modeling the interfacial properties of an amorphous aluminosilicate dispersed in aqueous NaCl solution. Colloids Surf. A **118**, 75–87 (1996)

Avena, M.J., Mariscal, M.M., De Pauli, C.P.: Proton binding at clay surface in water. Appl. Clay Sci. **24**, 3–9 (2003)

Basu, S., Shrarma, M.M.: An improved space–charge model for flow through charged microporous membranes. J. Membr. Sci. **124**, 77–91 (1997)

Bolland, M.D.A., Posner, A.M., Quirk, J.P.: Surface charge on kaolinites in aqueous suspension. Aus. J. Soil Res. **14**, 197–216 (1976)

Brady, P.V., Cygan, R.T., Nagy, K.L.: Molecular control on kaolinite surface charge. J. Colloid Interface Sci. **183**, 356–364 (1996)

Casagrande, I.L.: Electro-osmosis in soils. Geotechnique **1**(3), 159–177 (1949)

Chi, M., Eggleton, R.A.: Cation exchange capacity of kaolinite. Clays Clay Miner **47**(2), 174–180 (1999)

Chorover, J., Sposito, G.: Surface charge characteristics of kaolinite tropical soils. J. Geochimica Et Cosmochimica Acta **59**, 875–884 (1995)

Dormieux, L., Barboux, P., Coussy, O., Dangla, P.: A macroscopic model of the swelling phenomenon of a saturated clay. Eur. J. Mech. A **14**(6), 981–1004 (1995)

Edwards, D.A.: Charge transport through a spatially periodic porous medium: electrokinetic and convective dispersion phenomena. Phil. Trans. Roy. Soc. Lond. **A353**, 174–180 (1995)

Ganor, J., Cama, J., Metz, V.: Surface protonation data of kaolinite-reevaluation based on dissolution experiments. J. Colloid Interface Sci. **264**, 67–75 (2003)

Hlushkou, D., Morgenstern, A.S., Tallarek, U.: Numerical analysis of electroosmotic flow in dense regular and random arrays of impermeable nonconductiong spheres. Langmuir **21**, 6097–6112 (2005)

Huertas, F.J., Chou, L., Wollast, R.: Mechanism of kaolinite dissolution at room temperature an in pressure: part 1. Surface speciation. Geochimica Et Cosmochimica Acta **62**, 417–431 (1997)

Hunter, R.J.: Introduction to Modern Colloid Science. Oxford University Press, Oxford (1994)

Lemaire, T., Moyne, C., Stemmelen, D.: Modelling of electro-osmosis in clayey materials including pH effects. Phys. Chem. Earth **32**, 441–452 (2007)

Lima, S.A., Murad, M.A., Moyne, C., Stemmelen, D.: A three scale model for pH-dependent steady flows in 1:1 clays. Acta Geotechnica **3**, 153–174 (2008)

McQuarrie, D.A.: Statistical Mechanics. University Science Books, New York (2000)

Mitchell, J.: Fundamentals of Soil Behavior. Wiley, New York (1993)

Moyne, C., Murad, M.: A two-scale model for coupled electro-chemo-mechanical phenomena and onsager's reciprocity relations in expansive clays: I. Homogenization analysis. Transp. Porous Media **62**(3), 333–380 (2006a)

Moyne, C., Murad, M.: A Two-scale model for coupled electro-chemo-mechanical phenomena and onsager's reciprocity relations in expansive clays: II. Computational validation. Transp. Porous Media **63**(1), 13–56 (2006b)

Murad, M.A., Moyne, C.: A dual-porosity model for ionic solute transport in expansive clays. Comput. Geosci. **12**, 47–82 (2008)

Samson, E., Marchand, J., Robert, J.-L., Bournazel, J.-P.: Modelling ion diffusion mechanisms in porous media. Int. J. Numer. Methods Eng. **46**, 2043–2060 (1999)

Sanchez-Palencia, E.: Non-Homogeneous Media and Vibration Theory, Lectures Notes in Physics. Springer Verlag, Berlin (1980)

Sasidhar, V., Ruckenstein, E.: Electrolyte osmosis through capillaries. J. Colloid Interface Sci. **82**(2), 439–457 (1981)

Schroth, B.K., Sposito, G.: Surface charge properties of kaolinite. Clays Clay Miner. **45**(1), 85–91 (1997)

Sherwood, J.D.: A model for the flow of water and ions into swelling shale. Langmuir **10**, 2480–2486 (1994)

Van Olphen, H.: An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists, and Soil Scientists. Wiley, New York (1977)

Zemaitis, J.F., Clark, D.M., Rafal, M., Scrivner, N.C.: Handbook of Aqueous Electrolyte Thermodynamics: Theory and Application. Wiley-AICHE, New York (1986)