

Theoretical Analysis of Anion Exclusion and Diffusive Transport Through Platy-Clay Soils

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Abstract. Diffusive transport through geosynthetic clay liners and engineered compacted clay landfill liners is the primary mechanism for mass transport from well-engineered modern landfills. For this reason, accurate estimates of diffusion coefficients for clay soils are essential for the design of engineered liner systems. A long-standing theoretical problem is the role of *anion exclusion* on the estimation of diffusion coefficients for ionic solutes migrating through charged porous media. This paper describes the steady-state solution of a fully coupled set of transport equations modeling ion movement through a permanently charged platy-clay soil. The microscale analysis takes into account the actual diffusion coefficient for each ion species, ion-pairing (as required by electroneutrality of the solution), as well as *anion exclusion* and *cation inclusion*, arising from the permanent charge on clay particles. To render the problem tractable, the theoretical analysis focuses on an extremely small two-dimensional unit cell in an ideal, saturated, two-phase porous medium. The analysis presented here is limited to a particular geometrical example, but this example is sufficiently general for characteristic behaviours of systems of this kind to be identified. Most importantly, new insight is gained into the mechanism of ion migration through a charged platy-clay soil. The numerical results obtained from this study show that the identification of macroscopic transport quantities such as effective diffusion coefficients and membrane potentials from diffusion cell tests using *standard diffusion theory* only hold for a specific system. While *ion exclusion* behaviours are often referred to in the literature, as far as the authors are aware there has been no previous detailed microscale analysis of their role in steady-state diffusion through a charged platy-clay soil.

Key words: anion exclusion, multi-ion transport, Nernst–Planck equation, Gauss’s electrostatic theorem, effective porosity, effective diffusion coefficient, clay soils.

1. Introduction

Following intensive research by geoenvironmental engineers over the last twenty years, the engineering design of compacted clay liners for waste disposal facilities is now well established (see, e.g., Day and Daniel, 1985; Rowe

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et al., 1995; August *et al.*, 1997; Rowe, 2001). A key design aim is to minimize advective transport of solutes through the compacted clay liner by keeping the leachate mound height in the landfill small, and the permeability of the clay low. When this is successfully achieved and advective transport is minimized, the primary mechanism transporting chemicals from the landfill to the surrounding biological environment is diffusion of the chemicals along their electrochemical potential gradients. For this reason, considerable effort has been devoted to estimating diffusion coefficients for solutes transported through compacted and natural clay soils (Rowe *et al.*, 1988; Shackelford and Daniel, 1991a, b; Barone *et al.*, 1992; Rowe, 1998). Whereas experimental data on diffusive transport of uncharged solutes show reasonable good agreement between estimated diffusion coefficients reported from different laboratories, there is a large scatter of estimated diffusion coefficients for charged solutes. Developing a deeper understanding of ion migration through charged platy-clay soils like montmorillonite provides the primary motivation for the present paper.

Beginning with a presentation of the most common approach employed by geoenvironmental engineers for the estimation of diffusion coefficients (Subsection 1.1), we describe some arguments used by different researchers for explaining the observed experimental data. Based on these findings we state the objectives of the present approach (Subsection 1.2) and then describe some of the limitations of the model employed in this paper. Section 2 describes the governing equations, starting with the description of multi-ion transport at the microscale considering chemical and electrical couplings (i.e., the Nernst–Planck equation and the Poisson equation of electrostatics (Subsection 2.1)). The macroscopic governing equations are obtained by (volume) averaging of the microscopic governing equations (Subsection 2.2) leading to the definitions for the apparent and effective diffusion coefficient and membrane potential. The predictive capabilities of the model are investigated on a microscale unit cell representing an assembly of charged clay particles (Section 3). Three different subproblems related to the uncertainties in experimental interpretation (reported in Subsection 1.1) are investigated. The first (Subsection 3.1) deals with diffusive transport of uncharged solutes. The second (Subsection 3.2) investigates the commonly used concept of *effective porosity*. Finally, the third (Subsection 3.3) deals with steady-state diffusion of a binary electrolyte through a permanently charged platy-clay soil.

1.1. CONVENTIONAL APPROACH TO THE DESCRIPTION OF DIFFUSIVE MASS TRANSPORT AND IMPLICATIONS

In the following, only the essential results for the mathematical description of diffusive transport through soils are given. Steady-state diffusion of solutes through water-saturated soil samples is usually described by Fick's first law

(Dutt and Low, 1962; Gillham *et al.*, 1984; Shackelford and Daniel, 1991a; Kozaki *et al.*, 2001)

$$\langle \mathbf{j}_i \rangle = -\mathbf{D}_i \cdot \nabla \langle c_i \rangle, \quad (1)$$

whereas non-steady state conditions are described by Fick's second law (Robin *et al.*, 1987; Shackelford and Daniel, 1991a)

$$\frac{\partial(n\langle c_i \rangle)}{\partial t} = -\nabla \cdot \langle \mathbf{j}_i \rangle. \quad (2)$$

$\langle \cdot \rangle$ denote macroscopic (volume averaged) quantities obtained from a micro-macro transition method or experimental measurements (see Subsection 2 for details). $\langle \mathbf{j}_i \rangle$, \mathbf{D}_i , and $\nabla \langle c_i \rangle$ are the molar flux, the second-order diffusivity tensor, and the concentration gradient of solute i in the soil pore solution, respectively. Given an isotropic material with a diffusion coefficient D_i , the diffusivity tensor can be expressed as, $\mathbf{D}_i = \mathbf{1}D_i$, with $\mathbf{1}$ being the second order unity tensor. D_i is commonly referred to as the *apparent (or soil) diffusion coefficient* and estimated by diffusion cell tests (see, e.g., Dutt and Low, 1962; Kemper and van Schaik, 1966; Gillham *et al.*, 1984; Rowe *et al.*, 1988; Shackelford and Daniel, 1991b; Rowe, 1998 for details). A relation between the apparent diffusion coefficient of the soil and the pore solution diffusion coefficient is given by (Bear and Bachmat, 1991; Dormieux and Lemarchand, 2001):

$$D_i = n\tau D_{0,i} \quad \text{with} \quad n = \frac{V_f}{V_T} = \frac{V_T - V_s}{V_T}, \quad (3)$$

where n denotes the soil porosity and $D_{0,i}$ is the self-diffusion coefficient of solute i in the pore fluid of the soil (see Table I for self-diffusion coefficient of chloride). V_f , V_s , and V_T are the volumes of the fluid phase, the solid phase and the total soil volume, respectively. The (dimensionless) quantity τ is known as the *tortuosity factor* (see Section 2.2 for details). It is noted that the product of τ and $D_{0,i}$ is often defined as the *effective diffusion coefficient*:

$$D_{\text{eff},i} = \tau D_{0,i}. \quad (4)$$

Experimentally observed effective diffusion coefficients for clay soils for some charged solutes are given in Table I (further effective diffusion coefficients of various species can be found in Rowe *et al.* (1995, pp. 223–228)). It should be noted that depending on the definition of diffusion coefficient (i.e., apparent or effective diffusion coefficient) different values may be tabulated. Hence, one must be careful which definition has been chosen for the evaluation of experimental data (see Shackelford and Daniel, 1991a, for further discussion). The theory described above is well established and has been applied with considerable success in geoenvironmental engineering applications (Rowe and Booker, 1984; Shackelford and Daniel, 1991a, b; Rowe *et al.*, 1995; Rowe, 1998, 2001). However, when attempting to estimate the diffusion coefficients

Table I. Experimental data on effective diffusion coefficients and tortuosity factors evaluated from Equation (4)

Species	Soil	D_{eff} ($10^{10} \text{ m}^2/\text{s}$)	n	τ	References
^{36}Cl	Clay	6.10	0.28	0.31	Clarke and Graham (1968)
	Montmorillonite	3.82	0.76	0.19	Kozaki <i>et al.</i> (2001)
	Clay	1.60	–	0.08	Robin <i>et al.</i> (1987)
NaCl	Montmorillonite	4.11	0.90	0.20	Dutt and Low (1962)
	Montmorillonite	3.13	0.85	0.15	Kemper and van Schaik (1966)
Cl^-	Silty clay	5.70	0.10	0.28	Rowe <i>et al.</i> (1988)
	Silty clay	5.60	0.10	0.28	Barone <i>et al.</i> (1992)
	Clayey till	3.00	0.29–0.41	0.15	Desaulniers <i>et al.</i> (1981)
	Silty clay	2.64–6.10	0.21	0.13–0.30	Crooks and Quigley (1984)
	Silty clay	2.03	–	0.10	Quigley <i>et al.</i> (1984)
	Silty clay loam;	1.62–4.47	–	0.08–0.22	Barracough and Tinker (1981)
	Sandy loam	–	–	–	–
	Kaolinite	2.44–10.2	–	0.12–0.5	Shackelford (1988)
	Smectic clay	1.42–4.87	–	0.07–0.24	Shackelford (1988)

The chloride self-diffusion coefficient was taken as $D_{0,\text{Cl}} = 2.03 \cdot 10^{-9} \text{ m}^2/\text{s}$.

for charged solutes in charged porous media a problem is encountered because of so-called *ion exclusion*. Ion exclusion is produced by electrostatic repulsion of ions away from particle surfaces of like charge (for example, anions are typically repelled from the surfaces of clay particles, as the clay particles usually have a permanent negative charge). Because anions are repelled from the negatively charged surface, the *effective porosity* for anions in a clay soil is reduced. This phenomenon is known as *anion exclusion* (Dutt and Low, 1962). When dealing with charged solutes diffusing through a charged porous medium, Fick's first law (1) and Fick's second law (2)) are sometimes modified to account for electrical effects by using the concept of *effective porosity* (Thomas and Swoboda, 1970; Bresler, 1973; Appelt *et al.*, 1975; Bond *et al.*, 1982; Rowe *et al.*, 1995; Shukla *et al.*, 1999). It is usually believed that ion exclusion may be taken into account by replacing the soil porosity (n) in Equation (2) and Equation (3) by a so-called *effective porosity* (n_{eff}). The effective porosity is defined as (Bresler, 1973; Bond *et al.*, 1982; Sposito, 1989)

$$n_{\text{eff}} = \frac{V_f - V_{\text{ex}}}{V_T}, \quad (5)$$

where V_{ex} is the *excluded volume* of the anion. The excluded volume may be estimated by evaluating the integral (Sposito, 1989, pp. 158)

$$V_{\text{ex}} = \int_{V_i} \left(1 - \frac{c_i}{\bar{c}_i} \right) dV. \quad (6)$$

c_i is the concentration of the i th anion in a clay pore solution with a permanent charge and \bar{c}_i is the concentration of the i th anion in an identical clay soil without a permanent charge.

Practically, the effective porosity may be estimated in the laboratory by means of macroscopic measurements on a so-called *batch test*. For a batch test, c_i and \bar{c}_i may be estimated by first separating the solid from the supernatant liquid (for example, by spinning down the solid fraction in a centrifuge), and then measuring c_i in the solid fraction and \bar{c}_i in the supernatant liquid. Estimation of the excluded volume from Equation (6) and substitution of this value in Equation (5) yields an estimate of the effective porosity of the soil (see Sposito, 1989 for details).

In an alternative approach, (Rowe *et al.*, 1995) discusses the estimation of the effective porosity using a diffusion cell test and a conservative anion (i.e., an ion which has no sorption onto the solid phase during transport). In these tests the effective diffusion coefficient and effective porosity for potassium chloride diffusing through a natural clay soil were estimated by back-analysis (i.e., by solving the inverse problem). Rowe *et al.* (1995) concluded that the effective porosity for the chloride anion was close to the actual porosity of the soil (as estimated from the gravimetric moisture content of the soil). However, as a caveat on their finding, they noted that the soil in the test had a low activity (suggesting the permanent charge on the clay particles is small, and consequently the anion exclusion volume is small). However, Rowe *et al.* (1995) notes that other authors have shown the effective porosity to be significantly less than the actual porosity, and so imply that while in their case the effective porosity was close to the actual porosity, in other cases it maybe quite different.

It should be noted that different authors chose different ways of introducing the effective porosity into Equation (1) and Equation (2). While some authors substitute n_{eff} for n on the left hand side of Equation (2) while keeping the total porosity in the definition of D_i (see e.g., Bresler, 1973; James and Rubin, 1986), others use n_{eff} on both sides (see e.g., Shackelford and Daniel, 1991a; Rowe *et al.*, 1995). These discrepancies clearly introduces some additional uncertainties in interpretation of the theoretical results.

Experimental results on steady-state diffusion of different salts through montmorillonite were reported in Dutt and Low (1962) and Kemper and van Schaik (1966). For NaCl diffusing through the clay plug ($n \approx 0.9$) both obtained a nonlinear concentration distribution over the length of the specimen.

Using Equation (1) for estimation of apparent diffusion coefficients leads to a diffusion coefficient depending on the spatial coordinate (measured in the direction of diffusive transport) and, hence, on the salt concentration. According to these experiments the apparent diffusion coefficient increased with decreasing salt concentration (mean values of effective diffusion coefficients are given in Table I). Dutt and Low (1962) justified their findings by a rather elaborate argument based on the increase of the viscosity of the pore fluid in the vicinity of clay particles. On the other hand, Kemper and van Schaik (1966) explained the observed nonlinearity of the concentration distribution across the clay specimen by the development of an osmotically induced flow across the clay plug (from the low concentration side to the high concentration side).

1.2. OBJECTIVES OF THE PRESENT APPROACH

The uncertainties in interpretation of the experimental data described above may stem from measurement errors and/or using a theory based on assumptions which do not hold for the experiments under investigation. Because most of the experiments reported above used rather large sample numbers the measurement uncertainty is an unlikely explanation.

On the other hand, use of Fick's first law (1) is based on the assumption that ions only respond to a gradient of concentration. However, it is well established that charged solutes respond to a gradient of concentration and to any electrical field present. One immediate effect of a charged solute responding to both driving forces is that the *diffusion coefficient* can only be estimated for a particular *ion pair*. If the *partner ion* in the ion-pair is changed (or if other ions are added to the solution), then a different *diffusion coefficient* would be estimated for a particular test using Equation (1). This is one indication that the diffusion coefficients for *individual ions* estimated experimentally for a complex material like clay soil actually represent mass transfer coefficients for a particular system under investigation, rather than fundamental (system independent) quantities such as pore solution diffusion coefficients (see Cussler, 1997 for details).

The ion transport theory employed in the present paper takes into account gradients of concentration and electrical potential together with pore solution diffusion coefficients for each individual ion. Application of this theory to a microscopic unit cell allows for new insight into ion migration through charged porous media, and with suitable upscaling, can allow for the interpretation of macroscopic transport quantities.

However, before proceeding to investigate numerically ion transport through charged platy-clay soil, we first note that the theoretical study described here is based on the following assumptions and limitations: (i) Only a small assembly of clay particles is analysed by the microscale governing

equations. This is necessary because of the complexity of the governing equations and the rather fine discretization of the domain necessary for accurate finite element analyses. A similar approach has been adopted by previous authors for similar reasons (e.g. Quintard and Whitaker, 1993). (ii) The analysis is limited to two spatial dimensions, when in fact the clay particles are three-dimensional structures. Again this is done to simplify the problem, but the two-dimensional model is nevertheless expected to yield useful information. (iii) While it is straight forward to incorporate sorption in the model, as only steady-state diffusive transport is considered here, sorption is not required. (iv) The diffuse double-layer comprising the clay particles and associated counter-ions in solution is approximated by the Gouy–Chapman theory. While more sophisticated models of the diffuse double-layer have been developed (e.g. triple layer models), such refinements are not included because they only complicate the interpretation of the numerical analyses without changing the fundamental system behaviour. (v) Changes in the pore water viscosity within the diffuse double-layer are neglected. According to recent molecular dynamics simulations (Ichikawa *et al.*, 2002) the viscosity of the pore fluid is usually only significantly changed for a distance of one (to possibly two) nanometers for the surface of a strongly charged clay particle like montmorillonite. The length scales of the clay-water system analysed in this paper are significantly greater than one to two nanometers, hence, neglecting of viscosity changes in the pore water is reasonable. (vi) Surface diffusion is neglected. Some authors have reported that surface diffusion on the solid surface is important for the transport of radionuclides (e.g. Berry and Bond, 1992), but this is also neglected for simplicity. (vii) The influence of osmotically induced fluid flows is not considered. While osmotically induced flows often occur in saturated smectitic soils, this effect is more evident at low porosities and are usually negligible when the porosity is large, as in the example problem examined here. It is noted that the absence of osmotically induced flows implies the absence of streaming potentials (Mitchell, 1993).

While these limitations point to obvious improvements that could be made to better reflect the conditions in an actual platy-clay soil, we believe the model described here nevertheless gives important new insights into the steady-state mass transfer properties of charged platy-clay soils (see Section 3).

2. Governing Transport Equations

Diffusive transport of solutes in a porous medium typically takes place in the pores of the material. For clay materials, the pore sizes range between one nanometer up to some microns. Considering the large ratio of pore diameters to the diameter of the ions transported, a continuum description of diffusive

transport of solutes through the (saturated) pores is reasonable, provided the pore size is greater than about 5 nm.

2.1. MICROSACLE MULTI-ION TRANSPORT MODEL

We consider clay as a porous medium defined on a representative volume element (RVE) of several hundreds of nanometers characteristic length. This medium consists of two phases, a micropore space filled with a solution containing solutes and a solid phase consisting of aluminosilicates. In the following, the surface and the solid phase is regarded as non-diffusive (i.e., $D_{\text{surface},i} = 0$, $D_{\text{solid},i} = 0$),¹ we assign every solute a pore solution diffusion coefficient $D_{\text{poresol},i}$. Assuming that the pore fluid of the soil behaves such as an ideal solution, the species self-diffusion coefficient can be substituted for the pore-solution diffusion coefficient, i.e., $D_{\text{poresol},i} = D_{0,i}$ (see $D_{0,\text{Cl}}$ for chloride in Table I). The key constitutive equation describing microscale ion transport in the presence of electrochemical forces is the Nernst–Planck (N–P) equation (Cussler, 1997),

$$\mathbf{j}_i = -D_{0,i} \left(\nabla c_i + \frac{F}{RT} c_i z_i \nabla \psi \right) \quad (7)$$

where \mathbf{j}_i is the molar flux density of the i th ion, c_i the concentration of the i th ion, ∇c_i the concentration gradient of the i th ion in the pore solution; z_i the valence of the i th ion, $\nabla \psi$ the voltage gradient, and F , R and T are the Faraday constant, gas constant, and absolute temperature, respectively.

The first term inside the brackets results in transport of the i th ion species along minus of the concentration gradient.² The second term inside the brackets results in transport along the voltage gradient.³ The Nernst–Planck equation is a generalisation of Fick’s law, taking into account electrical effects on charged solutes. The voltage (ψ) appearing in Equation (7) is made up of two distinct parts. The first part of the voltage arises from any external potential applied to the system (for example, the external voltage may result from the accumulation of excess ions on one side of a clay barrier membrane). The second part of the voltage arises from the potential generated by the diffusion coefficients of the individual ions being different, leading to the formation of ion-pair dipoles.⁴ This second potential is known as the diffusion potential. However, the ions in solution are influenced by the electric

¹While diffusion either on the surface of the solid phase or through the solid phase may occur, these diffusion coefficients are typically several orders of magnitude smaller than the diffusion coefficient of solutes in the pore fluid and for this reason are neglected here.

²More general, ion transport is driven by the gradient of the chemical potential. However, for the case of ideal solutions the gradient of the chemical potential equals the concentration gradient.

³Note that the direction of the transport depends on the charge on the ion (z_i).

⁴Ion pair dipoles are present only in a time-averaged sense.

potential irrespective of its origin, so the two voltages arising from either process may be summed and represented by a single ψ .

The Nernst–Planck equation for ionic species (7), are supplemented by mass conservation equations. Mass conservation for each conservative ion species is expressed by

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{j}_i, \quad (8)$$

where $\nabla \cdot \mathbf{j}_i$ is divergence of the flux of the i th ion, and t is time. Substitution of the flux equation (7) into the mass conservation equation (8) leads to the governing differential equation for mass transport in the clay pore solution. In order to complete this system of equations, one has to define a relationship that couples the transport of all ionic species to one another. Commonly applied constraint equations are:

$$\sum_{i=1}^N z_i c_i = 0 \quad \text{electroneutrality condition,} \quad (9)$$

$$\nabla \psi = \text{const} \quad \text{constant field assumption,} \quad (10)$$

$$\mathbf{i} = F \sum_{i=1}^N z_i \mathbf{j}_i = 0 \quad \text{nil current condition.} \quad (11)$$

Equations (9)–(11) only hold for special situations depending on the problem being investigated.⁵ The most rigorous way is to relate the variation of the electric potential to the spatial distribution of the electric charges. This relationship is given by Gauss's electrostatic theorem (sometimes referred to as the Poisson equation) (Newman, 1991):

$$\nabla \cdot (\varepsilon \nabla \psi) = F \sum_{i=1}^N z_i c_i, \quad (12)$$

where the permittivity ε is the product of the permittivity of free space, ε_0 , and the relative permittivity ε_w (of water). For the special case of a binary monovalent electrolyte (i.e., $N = 2$) the influence of the constraint equations (9) and (10) on the numerical results were discussed in Kato (1995). It was found that the electroneutrality condition (9) and the constant electric field assumption (10) are limiting asymptotic solutions of the Poisson Equation (12) (see Kato, 1995; MacGillivray, 1968 for details).

The system of simultaneous partial differential Equations (7), (8) and (12) must be solved over the domain of the clay particles subject to appropriate

⁵For example electroneutrality is observed in all solutions except in thin double layers near electrodes and charged particles in porous materials.

initial and boundary conditions. The choice of initial and boundary conditions necessary for the problems analyzed are discussed in Section 3.

2.2. MACROSCALE MULTI-ION TRANSPORT MODEL

Equations (7), (8), and (12) describe ion transport driven by gradients of concentration and electrical potential at the microscale. However, most engineering applications deal with the investigation of macroscopic transport properties such as measurement of macroscopic diffusion coefficients, conductivities, and membrane potentials. There are various alternatives to describe diffusive transport quantities for porous media at the macroscale. Macroscopic governing equations derived empirically are often referred to as phenomenological equations. On the other hand, if the underlying behaviour of the system is understood at a deeper level, these equations are derived through a mathematical process known as *up-scaling* or *homogenization*. Up-scaling is a (volume) averaging method (see, e.g., Bear and Bachmat, 1991; Whitaker, 1999), where microscopic quantities are averaged over a representative volume element (RVE) in order to obtain macroscopic quantities. The notion of the RVE forms the basis of the volume averaging method. The RVE must be large enough in order to capture defined material properties (such as porosity, solid fraction, etc.) correctly. In the following, volume averaged quantities are defined as (Whitaker, 1999):

$$\langle \cdot \rangle = \frac{1}{V_T} \int_{V_T} \cdot \, dV, \quad (13)$$

where V_T denotes the total macroscopic volume of the RVE. Integration of the governing equations over the volume V_T leads to the macroscopic transport equations (Samson *et al.*, 1999):

$$\langle \mathbf{j}_i \rangle = -D_i \left(\nabla \langle c_i \rangle + \frac{F}{RT} \langle c_i \rangle z_i \nabla \langle \psi \rangle \right), \quad (14)$$

$$\frac{\partial (n \langle c_i \rangle)}{\partial t} = \nabla \cdot \langle \mathbf{j}_i \rangle, \quad (15)$$

$$\nabla \cdot (\varepsilon_{\text{app}} \nabla \langle \psi \rangle) = nF \sum_{i=1}^N z_i \langle c_i \rangle + nF \omega \langle X \rangle, \quad (16)$$

where ε_{app} denotes the apparent (or soil) permittivity, X denotes the fixed charge concentration, and ω is the sign of the fixed charge concentration (i.e., negative for negatively charged materials).

The apparent solute diffusion coefficient of the soil is given as (compare with Equation (3) and Bear and Bachmat, 1991):

$$D_i = n\tau_i D_{0,i} = nD_{\text{eff},i} \quad (17)$$

τ_i denotes the tortuosity factor of individual ions. Neglecting electrical effects (i.e., setting $\nabla\langle\psi\rangle = 0$) in Equation (14) yields Fick's first law (compare with Equation (1)). In the case of uncharged porous media the tortuosity factor is a purely geometrical quantity characterizing the pore morphology (Bear and Bachmat, 1991). Values of τ_i ranges between 0 (impermeable pores) and 1 (cylindrical pores). For uncharged porous materials the tortuosity is the same for all diffusing species, i.e., $\tau_i = \tau = \text{const}$. For the case of charged porous materials, the pathways of diffusing cations and anions are different depending on the permanent charge on the particles, the charge of the diffusing ion and the salt concentration (see, e.g., Sen, 1989 and Revil, 1999). In the case of negatively charged porous materials, anions are repelled from the charged surface. It is noted that at high salinity, diffuse double-layers are strongly compressed. In this case the dominant paths for diffusive transport are located in the interconnected pore space, and in the limit, the tortuosities for the transport of anions and cations are equal. As the salinity decreases, the dominant paths for diffusion of cations shift and weighted towards the solid-water interface. The reverse happens for the anions, and so the pathways followed by cations and anions are different, and these different pathways are described by different tortuosities (see Sen, 1989; Revil, 1999 for details).

In the next section, the qualitative arguments given by Sen (1989) and Revil (1999) about cation and anion migration pathways in charged porous media will be investigated quantitatively, and rendered visually explicit using detailed *ion distribution maps*. This is possible by solving the governing equations at the microscale (which describes the behaviour of a *unit cell* in the material), for a particular set of boundary conditions. We believe this leads to new insight into ion migration through charged porous media.

Here we note that the macroscopic equations (14)–(16) are only applicable when the gradient of the ion concentrations are small. When the gradients are large, a more general set of flux equations is required. These equations are considerable more complicated than those shown in Equation (14)–(16). Investigation of these equations will be subject of a future paper.

Further, it is noted that the approach described in this paper can be generalised, and an iterative scheme may be developed involving the alternate solution of the macroscale and microscale equations. The advantage of this hierarchical approach is that it is a completely general solution methodology, providing a means for inserting information lost during the homogenization process at selected locations within the domain. The advantage of this scheme is that important non-linear microscale processes that influence macroscale behaviour are included into the analysis, but the problem is kept computationally feasible. While perturbation methods have been successfully applied to identify transport properties (such as the tortuosity) for uncharged porous

media (Auriault and Lewandowska, 1996; Whitaker, 1999; Dormieux and Lemarchand, 2000), this theory has not yet been applied to charged porous media.

3. Numerical Analysis of Electrolyte Diffusion Through a Unit Cell

The example problem analysed here is a two-dimensional spatially periodic unit cell of clay soil saturated with water. The unit cell is taken to be 150 nm wide and 300 nm high. The six clay particles within the unit cell are modelled as identical plates 10 nm in thickness and 100 nm long (such particles may be encountered in montmorillonitic clay (Iwata *et al.*, 1995)). The number of clay particles was chosen such that the porosity of the unit cell ($n = 0.87$) is close to the one used in the experiments conducted by Dutt and Low (1962) and Kemper and van Schaik (1966) (see Table I). The clay platelets are arranged so that there is no obvious preferred orientation of the clay plates (i.e. they are pseudo-randomly oriented, see Figure 1(a)). A Galerkin finite element method is employed to solve the governing equations. Triangular elements with second-order shape functions are used to approximate the trial solution. The mesh employed for all the reported analyses contains of 5056 triangular elements and 2781 nodes (see Figure 1(b)).

This model may represent diffusion across a very thin membrane (or represent transient diffusion at an early time when large concentration gradients occur). While this model offers no special advantage in the investigation of diffusion through an uncharged porous medium (Subsection 3.1), it does offer advantages when the porous medium is charged, as discussed in Subsection 3.3.

The boundary condition for the unit cell were chosen as follows: (i) for the Nernst–Planck Equation (7), concentrations c_1 and c_2 were applied at the upper and lower end of the unit cell, while zero flux was applied through the sides of the unit cell and the solid particles. For investigation of equilibrium states, zero flux was also applied at the lower boundary; (ii) for the Poisson equation (12), voltage boundary conditions (ψ_1 and ψ_2) were prespecified at the upper and lower end of the unit cell. The permanent negative charge in clay crystals was assumed to create a constant surface voltage ψ_s in the millivolt range. At the left and right side of the unit cell electrical insulation symmetry conditions were employed. For investigation of equilibrium states the insulation symmetry condition was also applied to the lower boundary of the unit cell.⁶ For the electric boundary condition study performed in Subsection 3.3, two different cases

⁶It is noted that at least one Dirichlet boundary condition is necessary in order to obtain a unique solution.

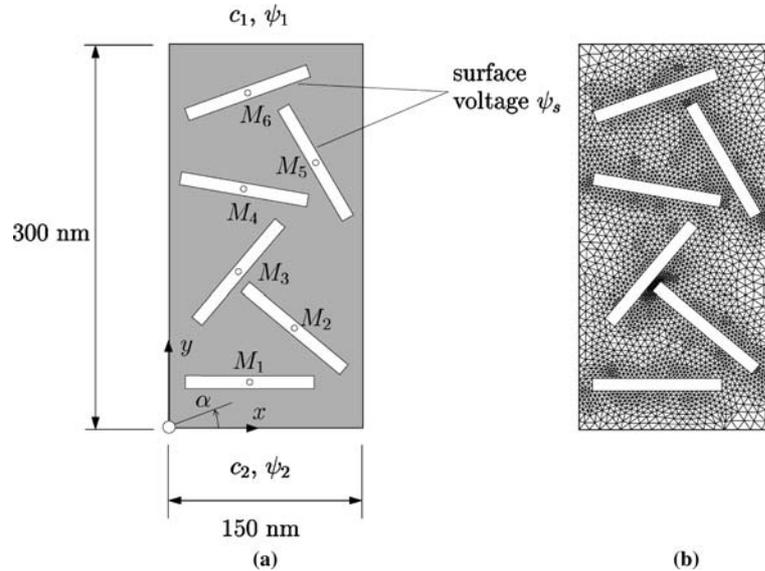


Figure 1. Diffusive transport through a unit cell: (a) geometric dimensions and (b) finite element mesh (mid-point coordinates ($\times 10^{-7}$ m) and rotation angle α : $M_1 = (0.60, 0.35; 0^\circ)$, $M_2 = (0.98, 0.79; -40^\circ)$, $M_3 = (0.55, 1.21; 50^\circ)$, $M_4 = (0.60, 1.86; -10^\circ)$, $M_5 = (1.12, 2.09; -60^\circ)$, $M_6 = (0.59, 2.60; 20^\circ)$).

for the lower boundary condition (ψ_2) were investigated. The first assumed $\psi_1 = \psi_2 = 0$ V, (i.e., allowing no charge to accumulate on either boundary), resulting in an electrical short circuit between the upper and lower boundary. It is noted that practically such an electric short circuit condition can be implemented in the laboratory using a salt bridge. In Subsection 3.3 this case is denoted as the *electric short circuit condition*. The second case involves a boundary condition leading to the nil current condition, given in Equation (11). Assuming a reference voltage ($\psi_1 = 0$ V), ψ_2 can be computed iteratively to satisfy this condition. It is noted that for charged solutes diffusing through soil samples (without applying any external electric field) this condition is the usual one. The voltage difference between the downstream and upstream side of the specimen is commonly referred to as *membrane potential*. The applied boundary condition for all numerical investigations are summarized in Table II. Finally, parameters used for the Nernst–Planck equation are given in Table III.

3.1. STEADY-STATE DIFFUSION OF UNCHARGED SOLUTES

The first case considered is steady-state diffusion of an uncharged solute across the unit cell. The concentration on the upper boundary (c_1) is taken to

Table II. Boundary conditions applied for the numerical analyses

Subsection Nr.	c_1 mol/m ³	c_2 mol/m ³	ψ_1 V	ψ_2 V
3.1	0.001–10	0	– ^a	– ^a
3.2	0.001–10	– ^b	0	– ^c
3.3	0.001–10	0	0	ψ_2 ^d

^a ... uncharged case; ^b ... application of zero flux boundary condition, ^c ... application of insulation symmetry condition; ^d ... $\psi_2 = 0$ for electric short circuit condition or ψ_2 computed to satisfy the nil current condition Equation (11).

Table III. Model parameters used for the numerical analyses

Symbol	Value	Dimension
ϵ_0	8.85×10^{-12}	C ² /(J m)
ϵ_ω	78	–
D_+	1.5×10^{-9}	m ² /s
D_-	1.5×10^{-9}	m ² /s
F	96500	C/mol
T	293	K
R	8.31	J/(K mol)

be 1 mol/m³, and on the lower boundary (c_2) zero (see Table II, Subs. Nr. 3.1 and description of boundary conditions at the beginning of this section). The solute diffusion coefficient is taken to be equal to the salt diffusion coefficient of the anion or cation (see Table III, i.e., $D_{0,\text{solute}} = 1.5 \times 10^{-9} \text{m}^2/\text{s}$).⁷

Figure 2 shows the solute distribution in the unit cell for the applied boundary conditions. Because the solute is uncharged, it is not influenced by surface voltage on the platelets.

The effective diffusion coefficient for the unit cell may be estimated from the mass transfer rate through the unit cell. Volume-averaging (Equation (13)) over the (y -component) of the microscopic flux j_{solute} leads a macroscopic flux as $2.46 \cdot 10^{-3} \text{mol}/(\text{s m}^2)$. Applying Equation (14) and using relation (17) leads to an estimate of the effective diffusion coefficient for the uncharged solute $D_{\text{eff},\text{solute}} = 8.49 \cdot 10^{-10} \text{m}^2/\text{s}$. Knowing the solute free-solution diffusion coefficient (i.e., $D_{0,\text{solute}} = 1.5 \cdot 10^{-9} \text{m}^2/\text{s}$) allows the tor-

⁷ The salt diffusion coefficient of a binary electrolyte is given as (Newman, 1991): $D_{\text{salt}} = D_+ D_- (z_+ - z_-) / (z_+ D_+ - z_- D_-)$.

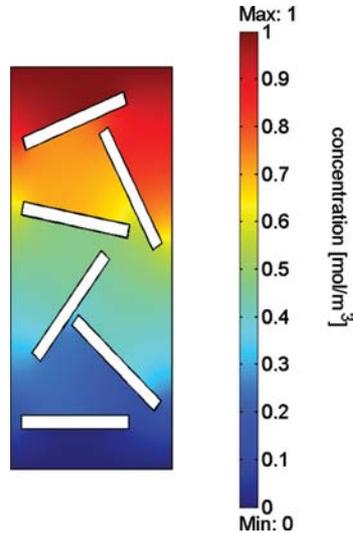


Figure 2. Diffusive transport of an uncharged solute through a platy-clay soil: concentration distribution for $c_1 = 1 \text{ mol/m}^3$ and $c_2 = 0 \text{ mol/m}^3$.

tuosity to be calculated for the uncharged solute as $\tau = D_{\text{eff,solute}}/D_{0,\text{solute}} = 0.56$.

A similar approach has been applied by Dormieux and Lemarchand (2000) in order to compute effective diffusion coefficients for three dimensional unit cells considering spherical and elliptical inclusions, allowing for the investigation of anisotropic effects. Because of the linearity of Fick's first law the size of the domain has no influence on the estimated effective diffusion coefficient, and the effective diffusion coefficient is only a function of the pore geometry (and is independent of the applied concentration gradient). It is mentioned that these findings justify the fundamental assumptions made in perturbation methods, namely, that the boundary conditions chosen for the unit cell or the size of the domain, have no influence on the estimated macroscopic quantity.

3.2. EQUILIBRIUM STATES IN CHARGED POROUS MEDIA

We next consider the equilibrium distribution of ions within the unit cell when the platelets are charged, and calculate the effective porosity ($n_{\text{eff},i}$) for both anions and cations. The experimental method described by Sposito (1989) to estimate the effective porosity is implemented numerically (that is, computing the exclusion volume (Equation (6)) and effective porosity (Equation (5)) for a given set of boundary conditions). In order to establish equilibrium of the system a constant electrolyte concentration $c_1 = c \text{ (mol/m}^3\text{)}$ is applied on the

upper boundary and zero flux on all other boundaries. For the parametric study now undertaken the surface voltage (ψ_s) is assumed to range between -0.01 and -0.05 V while the electrolyte concentration (c) ranges between 0.001 and 10 mol/m³ (see Table II, Subs. Nr. 3.2 and description of boundary condition at the beginning of this section).

The anion and cation distribution for a particular electrolyte concentration $c_l = 1$ mol/m³ with a particular surface voltage at the clay particles of $\psi_s = -0.025$ V is shown in Figure 3. It is clearly apparent that the negative surface voltage results in *exclusion* of anions from the unit cell (note the anion concentration next to the particles is as low as 0.36 mol/m³, see Figure 3(a)). On the other hand, the negative charge on the clay platelets results in *inclusion* of cations within the unit cell (note the cation concentration next to the particle surfaces is as high as 2.71 mol/m³, see Figure 3(b)).

Given the ion distribution for the charged unit cell, Equation. (6) can be applied to compute the exclusion volume V_{ex} and the effective porosity. Figure 4 shows the dependence of the effective porosity of anions and cations on the electrolyte concentration ($c = c_l$) and the surface voltage (ψ_s). Increasing the surface voltage while keeping the electrolyte concentration constant leads to a decrease of the effective porosity of anions ($n_{\text{eff},-}$, see Figure 4(a)) and to an increase of the effective porosity of cations ($n_{\text{eff},+}$, see Figure 4(b)). For the case of high electrolyte concentrations the effective

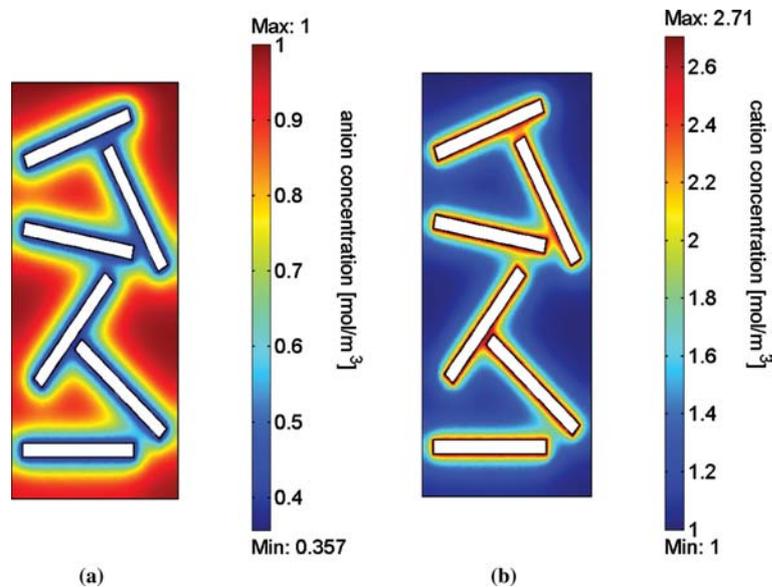


Figure 3. Equilibrium state in a platy-clay soil: concentration of (a) anion and (b) cation ($c_l = 1$ mol/m³ and $\psi_s = -0.025$ V).

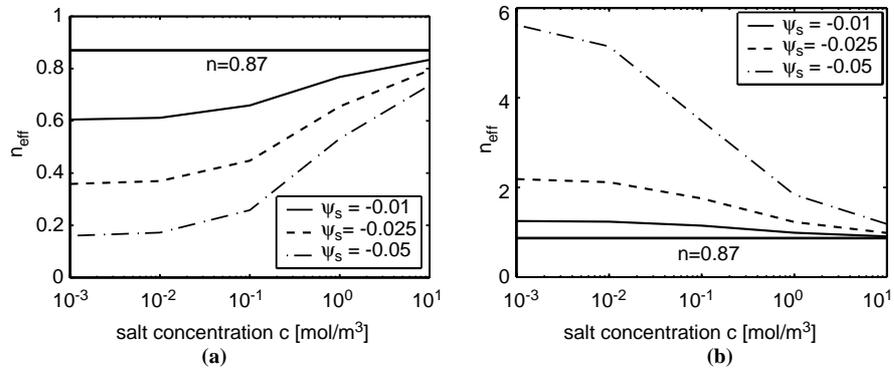


Figure 4. Equilibrium state in a platy-clay soil: dependence of effective porosity on the salt concentration c for (a) anions ($n_{\text{eff},-}$) and (b) cations ($n_{\text{eff},+}$) for various surface voltages ψ_s (semi-logarithmic scale).

porosity of anions and cations converge to the value of the porosity in the uncharged case, i.e., $n = 0.87$ (thick curve in Figure 4).

The influence of electrolyte concentration on the effective porosity of anions and cations can be best explained by looking at the voltage distribution. Figure 5 shows the voltage distribution for $\psi_s = -0.025$ V at

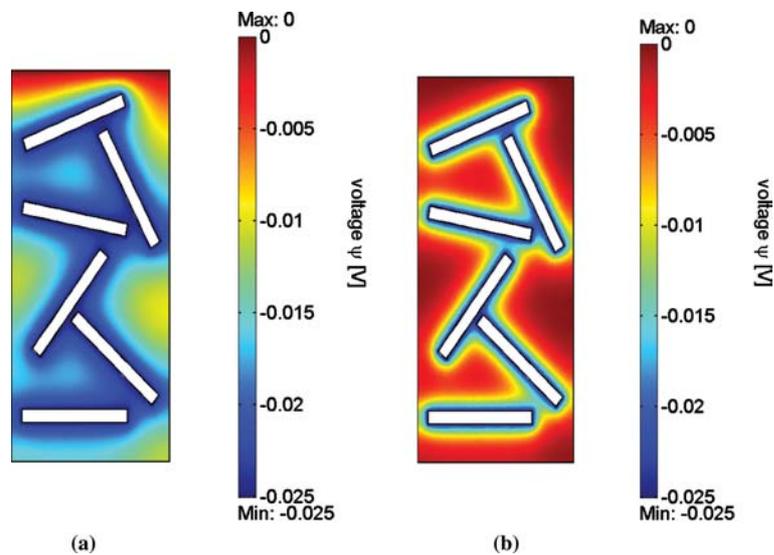


Figure 5. Equilibrium state in a platy-clay soil: voltage distribution for electrolyte concentrations of (a) $c = 0.01$ mol/m³ and (b) $c = 1$ mol/m³ for applied surface voltage $\psi_s = -0.025$ V.

concentrations of $c = 0.01 \text{ mol/m}^3$ and $c = 1 \text{ mol/m}^3$. Comparing the thickness of the electric double-layers, i.e., the (normal) distance from a charged surface at which the voltage reduces to $1/e$ (≈ 0.37) of the surface voltage indicates that for a rather low concentration of $c = 0.01 \text{ mol/m}^3$, the double layer thickness is in the range of 45 nm, while for $c = 1 \text{ mol/m}^3$ the double-layer thickness is only about 10 nm (see Figure 5(a) and (b)). This indicates that increasing the electrolyte concentration leads to a compression of the diffuse double-layer. At very high concentrations the double-layers are highly compressed, hence the effective porosities are almost equal to that for the uncharged case (see Figure 4 for high concentrations).

The numerical results show that the effective porosity strongly depends on the surface voltage on the platelets and on the electrolyte concentration. Thus using a constant effective porosity in Fick's first and/or second law (Equations (1) and (2)) is highly questionable (see arguments in Subsection 1.1). Further, it is noted that the above observations indicate that standard perturbation methods used for up-scaling cannot be used because the properties of the unit cell depend nonlinearly on the boundary conditions applied at the unit cell, thereby invalidating the basic assumption of perturbation theory (see Subsection 2.2).

3.3 STEADY-STATE DIFFUSION OF CHARGED SOLUTES

In this section, steady-state diffusive transport of a binary monovalent electrolyte across the unit cell is investigated. As mentioned previously, this can represent diffusion across a very thin membrane. The advantage of analysing this case is that all effects encountered in charged membranes can be made visually explicit by producing ion distribution maps showing preferential transport pathways, concentration effects on the double layers of the charged particles, and membrane potentials.

We consider two types of boundary conditions for the Poisson equation. First the electric short circuit condition, and second, the nil current condition (see Table II, Subs. Nr. 3.3 and description of boundary conditions at the beginning of this section). We start by investigating the transport behaviour for a particular concentration gradient and surface voltage (i.e., $\Delta c = 1 \text{ mol/m}^3$, $\psi_s = -0.025 \text{ V}$) and then perform a parametric study at the end of this subsection.

Figure 6 shows the voltage distribution and ion map distributions for the cations and anions obtained for the case of an electric short circuit condition.

Comparing the voltage distribution obtained for diffusive transport (Figure 6(a)) with the one obtained for the equilibrium state (Figure 5(b)) indicates a quite different voltage distribution within the unit cell. The thickness of the diffuse double-layer now increases steadily with distance

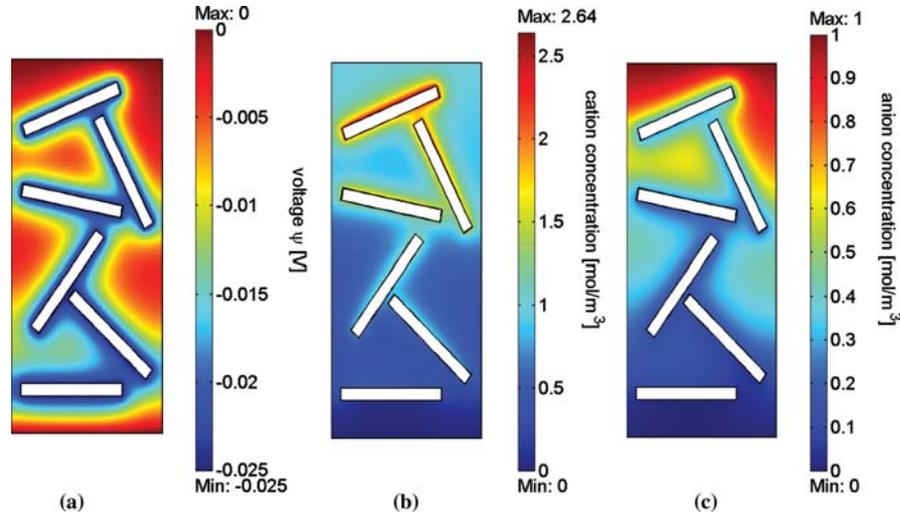


Figure 6. Diffusive transport of binary electrolyte through a platy-clay soil: distribution of (a) voltage, (b) cation concentration, and (c) anion concentration for electric short circuit condition ($\Delta c = 1 \text{ mol/m}^3$, $\psi_s = -0.025 \text{ V}$).

from the top boundary (whereas the concentration of ions in the pore fluid decreases to zero concentration at the bottom boundary). The cation distribution map (Figure 6(b)) clearly indicates that cations are attracted to the negatively charged platelets, and reveals that the diffuse double-layer around the platelets provides a *preferential transport pathway* for the cations. Comparison of the actual cation gradient close to the platelets and the nominal concentration gradient between the boundaries indicates an almost 2.5 fold increase of the concentration gradient (Figure 6(b)). This would suggest that the effective diffusion coefficient of the cations using Fick's first law (1), would be considerable greater than the effective diffusion coefficient for an uncharged solute ($D_{\text{eff,solute}} = 8.49 \cdot 10^{-10} \text{ m}^2/\text{s}$) using the same theory. On the other hand, anions are repelled from the negatively charged clay platelets, serving as a deterrent to the flow of anions (Figure 6(c)).

There is observed to be a very steep anion gradient immediately inside the upper boundary, which greatly reduces the anion gradient over the remainder of the unit cell. This leads to an effective diffusion coefficient for anions much smaller than for an uncharged solute. As mentioned previously, the calculation of effective diffusion coefficients at this stage is not straight forward and so will be the subject of a future paper.

Figure 7 shows the voltage distribution, and ion map distributions of cations and anions obtained by application of the nil current condition.

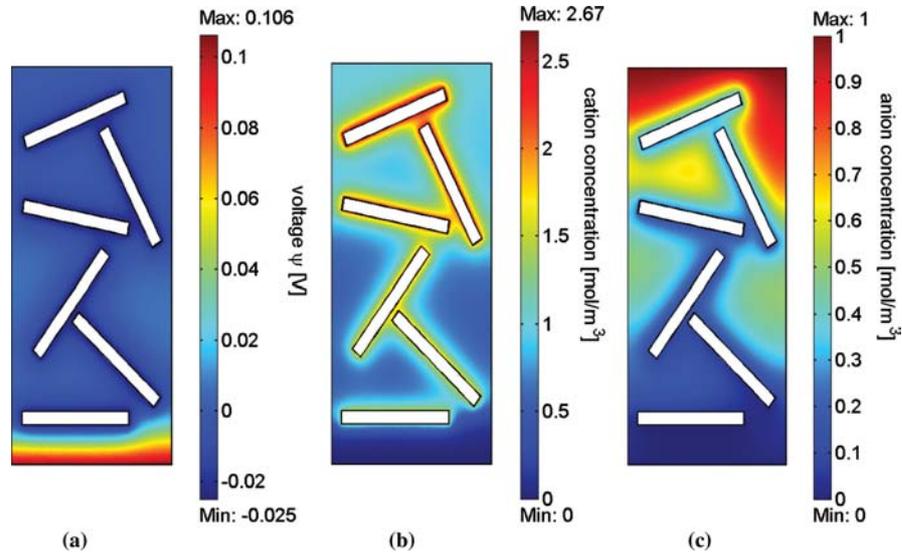


Figure 7. Diffusive transport of binary electrolyte through a platy-clay soil: distribution of (a) voltage, (b) cation concentration, and (c) anion concentration for nil current condition ($\Delta c = 1 \text{ mol/m}^3$, $\psi_s = -0.025 \text{ V}$).

The voltage distribution in the unit cell indicates a sharp voltage change near the lower boundary (see Figure 7(a)). However, this change is restricted to a rather small area near the boundary. The cation distribution clearly shows that the positive voltage on the lower boundary serves to repel cations (i.e., restraining their free exit) across the lower boundary (Figure 7(b)). This *dam effect* serves to increase the cation concentration on all upstream platelets (compare with Figure 6(b): note yellow shading now extends over all platelets). The anion concentration distribution indicates that anions are electrically attracted to the lower boundary by means of the positive voltage, hence anion transport is hastened by this *drag effect* due to the electric field (Figure 7(c)). The nil current requirement enforces the cation and anion flux to be equal (although the transport pathways through the porous medium of cations and anions are different).

Finally, we investigate the dependence of ion fluxes on the concentration gradient and the surface voltage. Figure 8 shows the cation and anion fluxes for the electric short circuit condition and the nil current condition.

For a particular concentration, the electric short circuit condition leads to an increase of the cation flux with increasing surface voltage, whereas the anion flux decreases with increasing surface voltage (Figure 8(a)).

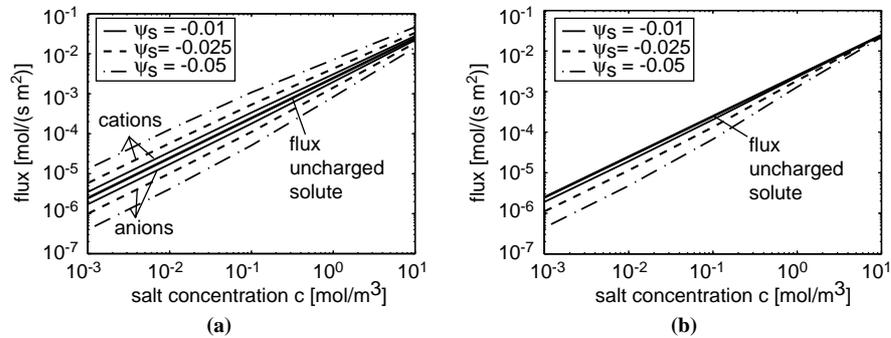


Figure 8. Diffusive transport of binary electrolyte through a platy-clay soil: cation and anion fluxes obtained from (a) electric short circuit condition and (b) nil current condition (double-logarithmic scale).

While the cation fluxes are higher than the flux obtained for an uncharged solute (thick line in Figure 8(a)), the opposite is true for the anions. It is observed that for high concentration gradients (i.e., compressed diffuse double-layers) the fluxes of cations and anions converge to that of the uncharged case. On the other hand, for the nil current condition the fluxes of cations (anions) are smaller than the flux of an uncharged solute (Figure 8(b)). This result is not obvious based on the individual ion behaviour in the electric short circuit condition. The parametric study makes it clear that the nil current condition results in ion fluxes that are much closer to the zero charge flux than either of the individual cation and anion fluxes in the electric short circuit case (i.e. for the nil current condition, the decrease in anion flux is offset against the increase in cation flux).

The dependence of the membrane potential ($\psi_2 - \psi_1$) on the concentration (gradient) and the surface voltage is shown in Figure 9.

The numerical results obtained in this section clearly show that the ion flux, the effective diffusion coefficient, and the membrane potential are functions of the ion concentration gradient and the surface voltage on the clay platelets.

Furthermore, it is noted that these quantities also depend on the size of the domain. These findings indicate that it is impossible to define a single (constant) effective diffusion coefficient (membrane potential) for an ionic species diffusing through a platy-clay soil. Only in the case of high ionic concentration (compressed diffuse double-layers) does the effective diffusion coefficient and the membrane potential become independent of the boundary conditions (i.e., the ion concentration and the surface voltage)

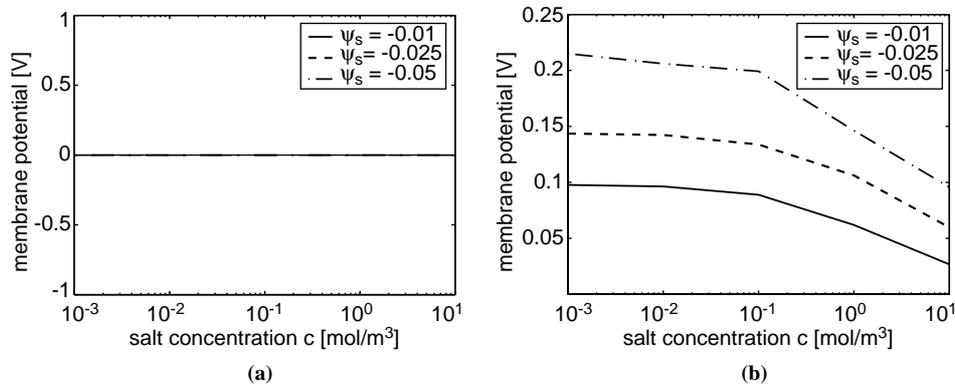


Figure 9. Diffusive transport of binary electrolyte through a platy-clay soil: membrane potentials obtained from (a) electric short circuit condition and (b) nil current condition (semi-logarithmic scale).

and the size of the domain. For this special situation use of a constant effective diffusion coefficient is justified.

4. Summary and Conclusions

From the numerical results obtained on the basis of the Nernst–Planck and Poisson system of equations applied to a unit cell the following conclusions can be made:

- (1) The concept of using effective porosity based on anion exclusion combined with a standard diffusion analysis (i.e. using Fick's first law) has been shown to be of little value in the interpretation of diffusive transport quantities of charged solutes through a charged porous medium. Even in the short circuit case, the distribution of ions within the diffuse double-layer is a function of the pore fluid composition, and so the estimated effective porosity of the charged porous medium is a function of the boundary conditions (i.e., the surface voltage ψ_s and the background electrolyte concentration c). Though not discussed in the example problem, the effective porosity will also be a function of the permittivity of the solvent and the valence of the ions in solution.
- (2) For uncharged solutes, the estimation of effective diffusion coefficients was found to depend only on the pore space geometry, and so is independent of the boundary conditions and size of the unit cell. On the other hand, for charged solutes diffusing through a charged porous medium, the effective diffusion coefficient strongly depends on the electrolyte

concentration and the particle surface voltage. These findings indicate that an effective diffusion coefficient employed in Fick's first law is system specific, and so this parameter is more properly considered an effective mass transfer coefficient. It has also been shown that in the case of high electrolyte concentrations the influence of the surface voltage becomes less pronounced because of the compression of the diffuse double-layer. Only for this special case is the concept of effective diffusion coefficients useful.

- (3) Application of the microscale governing equations allows the calculation of mass transfer properties of a charged porous medium based on diffusion coefficients. This approach can be practically employed at the microscale to reveal the behaviour of a unit cell. By means of this approach, detailed ion distribution maps have afforded important new insights into ionic transport through a charged platy-clay soil at the nanoscale. These maps have revealed a *dam effect* and a *drag effect*, both arising from charge accumulation on one side of a barrier membrane. It has been noted that modelling the complete macroscopic system using the microscale equations is for practical purposes currently unachievable. To make this problem tractable, it has been suggested that a hierarchical modelling approach can be employed.

Finally it is concluded that the mass transfer of ions through a charged porous medium cannot be simply represented by the same formalism as that adopted for the transport of an uncharged solute through a porous medium. The theory presented here allows for a detailed understanding of microscale ion transport, and provides for the first time, a detailed picture of ion transport through a charged porous medium. However, further experimental and theoretical investigations of ion transport through charged porous media are warranted for a more complete understanding of the system behaviour. Of particular interest are the macroscopic field equations in the presence of large concentration gradients, the effect of viscosity changes in the pore fluid close to the particle surface, the influence of advective transport, the generalization of the model to three spatial dimensions, and the development of a hierarchical modelling approach.

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Appendix: Notation

The following notation is used in this paper.

c_i	= concentration of ions in pore solution in mol/m ³
c_1, c_2	= electrolyte concentration on upstream and downstream side in mol/m ³
\bar{c}_i	= concentration of ion i in clay soil without permanent charge in mol/m ³
$D_{\text{eff},i}$	= effective diffusion coefficient of ion i in m ² / s
D_i	= apparent diffusion coefficient of ion i in m ² / s
\mathbf{D}_i	= second order apparent (i.e., homogenized) diffusion tensor of ion i (coefficients in m ² / s)
$D_{\text{poresol},i}$	= ion diffusion coefficient of pore solution in m ² / s
D_{salt}	= salt diffusion coefficient in m ² / s
$D_{\text{solid},i}$	= ion diffusion coefficient of solid phase of the soil in m ² / s
$D_{\text{surface},i}$	= surface diffusion coefficient in m ² / s
$D_{0,i}$	= self-diffusion coefficient of ion i in m ² / s
$D_{0,-}, D_{0,+}$	= self-diffusion coefficient of anion and cation in m ² / s
$D_{0,\text{solute}}$	= self-diffusion coefficient of uncharged solute in m ² / s
F	= Faraday constant in C/mol
\mathbf{i}	= current density in C/(m ² s)
\mathbf{j}_i	= molar mass flux density of ion i in pore solution of the soil in mol/(m ² s)
n	= total porosity of soil
n_{eff}	= effective porosity of soil
$n_{\text{eff},-}, n_{\text{eff},+}$	= effective anion and cation porosity of soil
R	= universal gas constant in J/(K mol)
t	= time variable in s
T	= absolute temperature in K
$V_f; V_s; V_T$	= volumes of the fluid phase, the solid phase, and the total volume of soil in m ³
V_{ex}	= excluded/included volume of the anion/cation in m ³
X	= fixed charge concentration mol/m ³
x, y	= spatial coordinates in m
z_i	= valence of ion i
ϵ	= permittivity of the medium in C ² /(J m)
ϵ_{app}	= apparent (or soil) permittivity in C ² /(J m)
ϵ_w	= relative permittivity of water (dimensionless)
ϵ_0	= permittivity of free space in C ² /(J m)
ψ	= voltage in V
ψ_s	= surface voltage on charged particles in V
ψ_1, ψ_2	= voltage applied on upstream and downstream side in V
τ	= tortuosity factor of uncharged solutes (dimensionless)

τ_i	= tortuosity factor of charged solutes in charged porous media (dimensionless)
ω	= sign of fixed charge concentration X
$\langle \cdot \rangle$	= macroscopic (volume averaged) quantities

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