Coulombic effects in advection-dominated transport of electrolytes in porous media: Multicomponent ionic dispersion

Massimo Rolle [a,b,*], Muhammad Muniruzzaman [a], Christina M. Haberer [a],
Peter Grathwohl [a]

[a] *Center for Applied Geosciences, University of Tübingen, Hölderlinstr. 12, D-72074 Tübingen, Germany*
[b] *Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, CA 94305, USA*

Abstract

We study the influence of Coulombic effects on transport of charged species in saturated porous media in advection-dominated flow regimes. We focus on transverse hydrodynamic dispersion and we performed quasi two-dimensional flow-through experiments to investigate transport of dilute electrolyte solutions. The experiments were repeated for two average flow velocities (1.5 and 6 m/day) representing advection-dominated and strongly advection-dominated flow conditions, respectively. Numerical transport simulations have been conducted to quantitatively interpret the experimental results. The adopted modeling approach is based on a multicomponent formulation and on the accurate description of transverse dispersion. The latter entails a non-linear dependence of the transverse dispersion coefficient on the flow velocity as well as a compound-specific dependence on the molecular diffusion of the transported solute. These dependencies hold true at low and also at high flow velocities. Our experimental and modeling results show that Coulombic cross-coupling of dispersive fluxes of charged species in porous media significantly affects the lateral displacement of charged species in flow-through systems. Such effects are remarkable not only in diffusion-dominated but also in advection-dominated flow regimes. Their accurate description requires a multicomponent modeling approach and the recognition of the key role of molecular diffusion for both the pore diffusion and the mechanical dispersion terms of hydrodynamic dispersion.
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1. INTRODUCTION

Diffusive and dispersive mass transfer in natural porous media are important for many processes including diagenesis (Wang and Van Cappellen, 1996; Boudreau, 1997), exchange of gases and volatile compounds between the atmosphere and the subsurface (e.g., McCarthy and Johnson, 1993; Holocher et al., 2002; Haberer et al., 2011, 2012), geological carbon sequestration (e.g., Zhang et al., 2010; Molins et al., 2012), solute transport in sediments and groundwater (e.g., Kitanidis, 1994; Haggerty and Gorelick, 1995), and subsurface biogeochemical transformations (e.g., Thullner et al., 2005; Rolle et al., 2008; Bauer et al., 2009; Steefel and Maher, 2009). In particular, molecular diffusion controls transport in aquatic sediments, in low permeability materials such as silt and clay, and determines the sorption/desorption kinetics and the overall rate of many geochemical and biological reactions (e.g., Grathwohl, 1998). The diffusive fluxes of neutral species in dilute solutions can be described by Fick's law in which the flux is proportional to the concentration gradient, and the molecular diffusion coefficient (corrected by the tortuosity in porous media) is the constant of proportionality. When dissolved species are charged, the interactions between diffusing molecules and electrochemical migration terms need to be considered. This has led to the formulation of multi-

* Corresponding author at: Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, CA 94305, USA. Tel.: +1 6507211118.

E-mail addresses: mrolle@stanford.edu, massimo.rolle@uni-tuebingen.de (M. Rolle).

component diffusion models (e.g., Ben-Yaakov, 1972; Lasaga, 1979; Felmy and Weare, 1991; Van Cappellen and Gaillard, 1996; Boudreau et al., 2004; Liu, 2007; Appelo and Wersin, 2007; Steefel and Maher, 2009). These models have been used to describe the multicomponent diffusion effects in laboratory (e.g., Vinograd and McBain, 1941; Ben-Yaakov, 1972; Felmy and Weare, 1991) and field observations (e.g., Giambalvo et al., 2002; Appelo and Wersin, 2007; Appelo et al., 2008). Only a few contributions have addressed the coupling between multicomponent ionic diffusion and other physical and chemical processes in porous media. Notable examples include the works of Giambalvo et al. (2002), Maher et al. (2006), Li et al. (2008), Appelo et al. (2010) and Liu et al. (2011).

The goal of the present study is to investigate the role of multicomponent ionic interactions during transport in saturated porous media at different flow velocities. In particular, we consider flow regimes where advection is the dominant mass-transfer process. The motivation has been provided by recent multitracer laboratory experiments and pore-scale simulations (e.g., Chiogna et al., 2010; Rolle et al., 2010, 2012; Hochstetler et al., 2013) which have shown that transverse dispersion is compound-specific even at high groundwater flow velocities because of pore-scale diffusion limitations. Furthermore, high-resolution field observations and numerical simulations also indicated that the effects of diffusion in groundwater systems are still important at the larger field scale (e.g., LaBolle and Fogg, 2001; Liu and Ball, 2002; Chiogna et al., 2011; Rasa et al., 2011; Van Breukelen and Rolle, 2012). We performed flow-through laboratory experiments in saturated porous media to investigate transport of different electrolytes and to identify and quantify the effects of charge interactions on transverse dispersion. We show that Coulombic cross-coupling of dispersive fluxes is significant not only at low but also at high groundwater flow velocities. The experimental results are quantitatively interpreted with a model based on a multicomponent ionic formulation of diffusive/dispersive fluxes.

2. THEORETICAL BACKGROUND

The theory of multicomponent diffusion has been derived following two different approaches based on the pragmatic extension of Fick's law and on first principles from the theory of non-equilibrium thermodynamics (Boudreau et al., 2004). In this study we follow the first approach which has been adopted by a number of authors in the geochemical and water research literature (e.g., Ben-Yaakov, 1972; Lasaga, 1979; Van Cappellen and Gaillard, 1996; Giambalvo et al., 2002; Boudreau et al., 2004; Liu et al., 2004, 2011; Appelo and Wersin, 2007). Detailed derivations can be found in the above-mentioned studies; in the present section we only summarize the fundamental steps leading to the governing equations of multicomponent diffusion. The starting point is the recognition that interactions among charged species can be captured by including an electrochemical migration term to the description of diffusive fluxes. Therefore, the diffusive flux of an ionic species i in solution depends on a chemical and an electrical potential

gradient. In dilute solutions, the chemical potential gradient can be approximated by the concentration gradient and the diffusive flux can be written as (Cussler, 2009):

$$J_i = -D_i \nabla C_i - D_i \frac{z_i F}{RT} C_i \nabla \psi \quad i = 1, 2, \ldots, n \tag{1}$$

where D_i is the self-diffusion coefficient, z_i is the charge and C_i is the concentration of the ionic species i, F is the Faraday constant, R is the gas constant, T is the temperature, ψ is the electrical potential and n the number of species. In the absence of electrical current (i.e., zero net flow of electrical charge: $\sum_{i=1}^{n} z_i J_i = 0$), the electrical potential gradient can be written as (e.g., Lasaga, 1979):

$$\nabla \psi = \frac{\sum_{i=1}^{n} z_i D_i \nabla C_i}{\sum_{i=1}^{n} (z_i^2 F D_i C_i)/RT} \tag{2}$$

Substituting Eq. (2) into the expression of the diffusive flux (Eq. (1)) yields:

$$J_i = -D_i \nabla C_i + \frac{z_i D_i C_i}{\sum_{j=1}^{n} (z_j^2 D_j C_j)} \sum_{k=1}^{n} z_k D_k \nabla C_k \tag{3}$$

which explicitly represents the dependence of the diffusive flux of the charged species i not only on its concentration gradient but also on the concentration gradients of the other species in solution. Eq. (3) can be further rearranged to:

$$J_i = -\sum_{j=1}^{n} D_{ij} \nabla C_j \tag{4}$$

where D_{ij} is the matrix of inter-diffusion coefficients coupling the flux of ion i and the gradient of ion j:

$$D_{ij} = \delta_{ij} D_i - \frac{z_i z_j D_i D_j C_i}{\sum_{k=1}^{n} (z_k^2 D_k C_k)} \tag{5}$$

in which δ_{ij} is the Kronecker delta that is equal to 1 if $i = j$ and equal to 0 if $i \neq j$. Replacing the diffusive flux (Eq. (3)) in the mass balance equation yields the governing equation of multicomponent diffusion, which for non-reactive species reads as:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot \left(\sum_{j=1}^{n} D_{ij} \nabla C_j \right) \tag{6}$$

3. EXPERIMENTAL SETUP

Laboratory bench-scale experiments were performed to investigate ionic interactions under flow-through conditions. The experiments were carried out in a quasi two-dimensional setup (Fig. 1) with inner dimensions 100 cm × 19 cm × 1 cm (L × H × W). We established a uniform horizontal flow field by connecting two high-precision peristaltic pumps (IPC-N24 Ismatec, Glattbrugg, Switzerland) at the inlet and outlet of the flow-through chamber. Twenty-three and 24 ports, spaced 5 mm apart, were used at the inlet and outlet of the system, respectively. The small spacing between the ports allowed us sampling the tracers and the ambient solutions at high spatial resolution. All injection and extraction ports were made of Alltech rubber septa pierced by hollow needles. The needles