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Modeling wall effects in capillary electrochromatography

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ABSTRACT

A volume averaging technique for modeling electroosmotic and pressure driven flow in microchannels is applied to a packed capillary electrochromatography column. This model can be applied to fluid flow in both porous and open channels and can account for porosity variation in the column due to packing and zeta potential mismatches between the wall and the packing material. Numerical results are presented and compared with experimental results from the literature. Several different porosity models are shown to produce similar concentration profiles and allow the model to reproduce wall effects observed in experimental columns.

1. Introduction

It is well known that wall effects in high performance liquid chromatography (HPLC) and in capillary electrochromatography (CEC) can impact the efficiency of these techniques [1]. In columns packed with spherical beads, packing inefficiencies increase the porosity near the column wall. This region of higher porosity (and larger pore size) can increase the velocity of the fluid near the column wall. In CEC, this effect is compounded by the possibility of a zeta potential mismatch between the packing material and the column wall.

An analytical model for the fluid velocity developed by Rathore and Horvath [2] took into consideration the possible effects of a zeta potential mismatch for thin double layers, but neglected the effect of an increase in porosity near the wall [3]. An analytical expression taking both effects into account was derived for fluid flow through a column with two different regions of porosity [4]. However, the porosity variation seen in practice is actually an oscillating function of position that decays exponentially away from the column wall [3]. This cannot be easily modeled analytically, and thus must be considered using a numerical approach [5,6]. In this work, the model is first validated by comparison with average flow velocity measurements of Liapis and Grimes [7]. Effects of porosity variation are then considered using the finite element method, and compared to the published experimental results of Tallarek et al. [8], who used magnetic resonance imaging to investigate wall effects in CEC columns.

2. Background

2.1. Generalized porous medium equation

The model employed utilizes a formulation of a generalized porous medium equation that incorporates electroosmotic forces [4]. This model is based upon a scaling of the Navier–Stokes equations, with additional terms that account for the resistance provided by the packing material.

In this model a porous medium is conceptualized as a solid medium filled with hollow, tortuous (winding) capillaries. It can be described geometrically in terms of its void volume fraction, or porosity ε, its pore winding factor, or tortuosity τ, and its average pore size a_p.

For an array of N_p cylindrical pores, the external porosity can be expressed as

$$\varepsilon = \frac{V_{void}}{V_{total}} = \frac{N_p \pi a_p^2 l}{AL} \quad (1)$$

where l is the length of the cylinder, A is the cross-sectional area of the porous medium, and L is the length of the porous medium. The tortuosity can be defined as [9]

$$\tau = \left(\frac{l}{L}\right)^2 \quad (2)$$

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For a bed of N_p packed spheres, the porosity can be defined as

$$\varepsilon = \frac{AL - N_p \pi d_p^3/6}{AL} \tag{3}$$

where d_p is the particle diameter. A commonly used definition for the effective solid particle diameter is [10]

$$d_p = 6\frac{V_s}{A_s} \tag{4}$$

where V_s and A_s are the volume and surface area of the solid phase, respectively. This can be used to relate the solid particle diameter to an effective pore size a_p through Eq. (1), resulting in

$$d_p = 3a_p \frac{1-\varepsilon}{\varepsilon} \tag{5}$$

In this work, the model employed will be a generalized porous medium equation that is based upon the volume-averaged scaling of the Navier–Stokes equations. The volume-averaged velocity, $\bar{u}$, is the average volume flow per unit area of the porous medium, which is the apparent velocity with which the fluid flows through a cross-section of material to account for the total volume flow, U. This must be contrasted with the intrinsic average velocity of the fluid, u_{ave}, which is the actual average velocity at which the fluid is moving inside the winding pores that make up only a fraction of the cross-sectional area of the porous medium. The two can be related by

$$u_{ave} = \bar{u}\frac{A}{A_e} = \bar{u}\frac{\sqrt{\tau}}{\varepsilon} \tag{6}$$

where the effective cross-sectional area A_e can be defined as

$$A_e = N_p \pi a_p^2 = \frac{\varepsilon}{\sqrt{\tau}}A \tag{7}$$

This distinction will be important when comparing theory with experimental data, as different techniques are often used to estimate the average velocity. The average velocity could be inferred, for example, either by measuring an increase in fluid volume over time, or by monitoring the time required for a dye in the fluid to travel a certain distance. The first example would be an estimate of the average volume flow $\bar{u}$, while the second would be an estimate of the intrinsic average velocity in the pores u_{ave}.

The volume-averaged model for flow in porous media can be expressed using the generalized porous medium equation as

$$\frac{\sqrt{\tau}}{\varepsilon}\frac{\partial \bar{u}}{\partial t} + \frac{\sqrt{\tau}}{\varepsilon}\bar{u}\cdot\nabla\left(\frac{\bar{u}}{\varepsilon}\right) = -\frac{\nabla P}{\sqrt{\tau}\rho_w} + \frac{\eta}{\sqrt{\tau}}\nabla^2\left(\frac{\bar{u}}{\varepsilon}\right) - \frac{\rho_{eff}\nabla\phi}{\sqrt{\tau}\rho_w} + F \tag{8}$$

$$\nabla\cdot\bar{u} = 0 \tag{9}$$

where P is the applied pressure, ϕ is the applied potential, η is the fluid kinematic viscosity, ρ_{eff} is the effective charge density, ρ_w is the mass density of the fluid and F is the drag force. The drag presented by the solid portion of the medium, F_d, is usually taken into consideration by adding a Forchheimer force, described in terms of the permeability, K of the medium, to the Navier–Stokes equations. The Forchheimer force can be expressed using Ergun's relations [11], as

$$F = -\frac{\eta_e \bar{u}}{K} - \frac{F_\varepsilon \bar{u}\left|\bar{u}\right|}{\sqrt{K}} \tag{10}$$

The constant η_e is the effective viscosity of the fluid in the porous medium, and is often considered to be the same as η. The permeability is

$$K = \frac{\varepsilon m^2}{k_o\sqrt{\tau}} \tag{11}$$

where the mean hydraulic radius $m = \varepsilon/S$ with S equal to the surface area per unit volume of the medium, and the shape factor $k_o = 2$ for most cases. For a bed of packed spheres, S can be written as

$$S = \frac{N_p \pi d_p^2}{AL} \tag{12}$$

which after inserting Eq. (3) for the porosity simplifies to

$$S = \frac{6(1-\varepsilon)}{d_p} \tag{13}$$

Inserting this into the definition of permeability results in the Carman–Kozeny permeability [12]

$$K = \frac{\varepsilon^3\ \mathrm{d}_p^2}{36k_o\sqrt{\tau}(1-\varepsilon)^2} \tag{14}$$

The remaining constant in Eq. (10) is given by

$$F_\varepsilon = \frac{1.75}{\sqrt{36\varepsilon^3 k_o\sqrt{\tau}}} \tag{15}$$

The effective charge density, ρ_{eff}, can be shown to be given by [4]

$$\rho_{eff} = \frac{\varepsilon\varepsilon_w\psi_o}{\sqrt{\tau}K}\left(\frac{\int\int \psi(r)\ \mathrm{d}A_p}{\psi_o A_p} - 1\right) \tag{16}$$

where ψ_o is the zeta potential of the pores, ε_w is the permittivity of the fluid, and the integral is over the cross-sectional area of the pore, A_p. If the double layers are thin, this reduces to

$$\rho_{eff} = -\frac{\varepsilon\varepsilon_w\psi_o}{\sqrt{\tau}K} \tag{17}$$

The above Eqs. (8)–(15) are valid for incompressible fluid flow in both porous and open channels. If the porosity and tortuosity approach unity, the permeability grows towards infinity, and the generalized porous medium equation reduces to the Navier–Stokes equations. This makes the above model suitable for modeling the effect of an oscillating porosity that approaches unity near the wall.

It can be shown that, if the flow is steady, and the velocity is small enough, the nonlinear terms can be neglected and the generalized porous medium equation reduces to a variation of Brinkman's equation, but with electroosmotic forces included:

$$\frac{\eta}{\sqrt{\tau}}\nabla^2\left(\frac{\bar{u}}{\varepsilon}\right) - \frac{\eta_e\bar{u}}{K} = \frac{1}{\sqrt{\tau}\rho_w}\left(\nabla P + (\rho(r) + \rho_{eff})\nabla\phi\right) \tag{18}$$

plus the continuity Eq. (9). It is the Brinkman equation that will be used to study wall effects in this work.

Analytical solutions to the Brinkman equation [4] reveal that wall effects are typically constrained to boundary layers defined by the inverse Brinkman screening length λ, analogous to the inverse Debye screening length κ:

$$\lambda = \sqrt{\frac{\varepsilon\sqrt{\tau}}{K}} \tag{19}$$

If the ratio of column radius b to the Brinkman screening length $1/\lambda$ is small, effects at the boundary will become prominent. If the ratio becomes large, boundary layer effects can be neglected. In columns with varying porosity, this ratio will also vary and it becomes more difficult to predict the size of the boundary layer.

The term $\rho(r)$ in Eq. (18) will account for the charge distribution in the column itself due to the charge on the column walls. This will be modeled using the Poisson–Boltzmann equation

$$\frac{\nabla^2\psi(r)}{\tau} = \frac{-\rho(r)}{\varepsilon_w} \tag{20}$$