# Hydrodynamic Dispersion of a Neutral Non-Reacting Solute in Electroosmotic Flow

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## ABSTRACT

To investigate hydrodynamic dispersion in electroosmotic flow, we have derived an asymptotic series solution for the problem of two-dimensional species transport in a tube or channel. This solution is applicable to the late-time diffusive and advective transport of a neutral non-reacting species in an incompressible fluid having uniform and constant electrical and transport properties. We find that the axial dispersion is proportional to the square of the Peclet number based on the characteristic transverse dimension of the tube or channel when the Debye length is large. When the Debye length is small, the dispersion varies as the square of the Peclet number based on the Debye length.

**Keywords:** dispersion, electroosmotic, electrokinetic, flow, transport

## INTRODUCTION

Chromatographic separations using electric fields to drive electroosmotic flow are usually performed in packed columns. The role of the packing is to provide a large surface area for solute adsorption and thereby to improve column performance. However, recent advances in manufacturing methods now enable the fabrication of electrochromatographic columns having characteristic transverse dimensions in the micron to sub-micron range. Because the inherent specific surface area of a tube or channel is inversely proportional to its size, such columns may perform well even without an auxiliary packing. Moreover, the separation performance of micro-scale columns with no packing may exceed that of a packed column of comparable surface area since solute dispersion in open columns is generally much smaller than in packed beds.

Axial dispersion is important in chromatographic processes because it tends to spread solute peaks. As a result, closely spaced peaks cannot be resolved when dispersion is excessive. Estimating the magnitude of the dispersion and identifying the conditions leading to minimum dispersion are thus important to optimizing these processes.

As a solute is convected in an open column, transverse variations in the velocity field produce transverse variations in the solute concentration. At the same time, transverse diffusion tends to reduce these induced concentration gradients. At sufficiently late times, advective transport in the axial direction is just balanced by diffusive transport in the transverse direction. This is the phenomenon of hydrodynamic dispersion [1]. Such dispersion yields a mean axial profile of the solute concentration that is consistent with diffusive transport alone, although the apparent diffusivity is larger than the actual value.

## GOVERNING EQUATIONS

Here we consider two-dimensional planar or axisymmetric transport of a neutral non-reacting species. The flow is assumed incompressible and transport properties are assumed constant. Under these restrictions, the time-dependent concentration field is governed by

$$\frac{\partial c}{\partial t} + \mathbf{u}\cdot\nabla c = D\nabla^2 c \tag{1}$$

where $c$ is the local solute concentration, $t$ is time, $\mathbf{u} = u\mathbf{i} + v\mathbf{j}$ is the local fluid velocity, and $D$ is the coefficient of diffusion. Further assuming that the flow is steady and that inertial effects are small, the momentum equation may be written as

$$\mu\nabla^2\mathbf{u} = \rho_e\nabla\phi \tag{2}$$

where $\mu$ is the fluid viscosity, $\rho_e$ is the net local charge density, and $\phi$ is the local electric potential. Finally, for a dielectric constant, $\epsilon$, that does not vary with position, the Poisson equation governing the electric field is

$$\epsilon\,\nabla^2\phi = -\rho_e \tag{3}$$

and the local charge density may be related to the electric potential through the Boltzmann distribution given by $\rho_e = -2Fzc_e\sinh(zF\phi/RT)$, where $F$ is the Faraday constant, $z$ is the ion charge number, $c_e$ is the bulk fluid ion concentration, $R$ is the universal gas constant, and $T$ is the temperature.

To solve generally for the concentration field, we now introduce a set of dimensionless variables. The new normalized dependent variables are taken as $c^* = c/c_o$, $\mathbf{u}^* = \mathbf{u}/U$ and $\phi^* = \phi/\zeta$, where $c_o$ is some reference concentration yet to be specified, $U$ is the mean axial fluid speed spatially averaged across the tube or channel, and $\zeta$ is the electric potential on the tube or channel wall. The new independent variables are $x^* = (x - Ut)/a$, $y^* = y/a$ and $t^* = Dt/a^2$, where $x$ and $y$ are the axial

and transverse coordinates, and $a$ is the tube radius or channel half-height. This normalization leads to three new parameters, the normalized Debye length,

$$\lambda^{*2} = \frac{1}{\kappa^{*2}} = \left(\frac{\lambda}{a}\right)^2 = \frac{\epsilon RT}{2F^2 z^2 c_e a^2} \tag{4}$$

the normalized wall potential, $\zeta^* = zF\zeta/RT$, and the Peclet number, $Pe = Ua/D$, indicating the relative importance on advective and diffusive transport.

Boundary conditions for the fluid velocities are $du^*/dy^* = 0$ at $y^* = 0$ and $u^* = 0$ at $y^* = 1$. Those for the electric potential are $\partial\phi^*/\partial y^* = 0$ at $y^* = 0$ and $\phi^* = 1$ at $y^* = 1$.

The momentum equation (2) possesses closed-form solutions for the case in which $\zeta^*$ is small, corresponding to the well-known Debye-Hückel approximation. Recognizing that incompressible flow in a long column must be one dimensional, and further recognizing that the second derivative of the electric potential in the axial direction is small compared to that in the transverse direction, the axial fluid speed for a channel is given by,

$$u^* = \frac{\cosh(y^*/\lambda^*) - \cosh(1/\lambda^*)}{\lambda^* \sinh(1/\lambda^*) - \cosh(1/\lambda^*)} \tag{5}$$

while that for a tube is

$$u^* = \frac{I_0(y^*/\lambda^*) - I_0(1/\lambda^*)}{2\lambda^* I_1(1/\lambda^*) - I_0(1/\lambda^*)} \tag{6}$$

The latter expression was derived by Whitehead [2].

## METHOD OF SOLUTION

To solve Eq. (1) we now introduce one more transformation of the axial coordinate, $\eta = x^*/2\sqrt{t^*}$. Introducing this new variable into the diffusion-advection equation yields

$$\frac{\partial^2 c^*}{\partial \eta^2} + 2\eta \frac{\partial c^*}{\partial \eta} = 2\sqrt{t^*} Pe\big(u^* - 1\big)\frac{\partial c^*}{\partial \eta} + 4t^* \left[\frac{\partial c^*}{\partial t^*} - \frac{1}{y^{*n}}\frac{\partial}{\partial y^*}\left(y^{*n}\frac{\partial c^*}{\partial y^*}\right)\right] \tag{7}$$

The parameter $n$ in Eq. (7) is used to describe either the planer or axisymmetric geometries by taking $n = 0$ or 1, respectively. Note that the left of Eq. (7) yields a homogeneous solution of the form $c^* \propto \mathrm{erfc}(\eta)$. This is the well known solution for a translating interface with either no flow, $Pe \to 0$, or a uniform axial fluid speed, $u^* - 1 = 0$. Under the same restrictions, solutions for the case of an instantaneous plane source are obtained from the left of Eq. (7) along with the term $4t^*\partial c^*/\partial t^*$ on the right. The solution in this case has the form $c^* \propto e^{-\eta^2}/\sqrt{t^*}$.

Based on Taylor's observation [1] that the transverse variation in solute concentration is proportional to the axial concentration gradient, we now seek a solution to Eq. (7) of the form

$$c^* t^{*m/2} = f + \sum_{j=1}^{\infty} \frac{Pe^j}{2^j\, t^{*j/2}} \frac{d^j f}{d\eta^j}\, g_j \tag{8a}$$

where

$$f = f_0 + \sum_{j=1}^{\infty} \frac{f_j}{2^j\, t^{*j/2}} \tag{8b}$$

The function $g_j$ depend only on the transverse position, $y^*$, while the functions $f_j$ depend only on the axial position, $\eta$. Values of the parameter $m = 0$ or $m = 1$ identify the case of an initial interface or instantaneous source, respectively.

Boundary conditions for the functions $f_j$ are $f_0 \to 0$ as $\eta \to \infty$ and $f_0 \to 1$ as $\eta \to -\infty$ for the case of a translating interface, and $f_0 \to 0$ as $\eta \to \pm\infty$ for the instantaneous plane source. For this latter case, we additionally require that integral over the domain of $f_0$ is unity such that the initial source strength is properly normalized. Boundary conditions for higher-order functions for both cases are $f_j \to 0$ as $\eta \to \pm\infty$. In addition, since the total solute mass must be invariant with time, integrals over the domain of the higher-order functions $f_j$ must vanish. Boundary conditions for the functions $g_j$ are $dg_j/dy^* = 0$ at $y^* = 0$ and $y^* = 1$.

Now substituting Eq. (8) into Eq. (7) and grouping like powers of time yields a set of equations involving both functions $f_j$ and $g_k$. Noting, however, that $df_0/d\eta$ cannot be everywhere zero, the order $\sqrt{t^*}$ equation requires that

$$g_1'' + n\,\frac{g_1'}{y} - (u^* - 1) = 0 \tag{9}$$

Further noting that $f_0$ is a function of $\eta$ only and the $g_1$ is a function of $y^*$ only, necessary conditions for the existence of a solution in the form of Eq. (8) are

$$g_2'' + n\,\frac{g_2'}{y^*} - (u^* - 1)\, g_1 = \alpha_0 \tag{10}$$

$$\big(1 + \alpha_0\, Pe^2\big)\, f_0'' + \; 2\,\eta f_0' + 2m f_0 = 0 \tag{11}$$

where $\alpha_0$ is some yet unknown separation constant or eigenvalue. Similarly, we find that the third-order function $g_3$ and first-order function $f_1$ must satisfy

$$g_3'' + n\,\frac{g_3'}{y^*} - (u^* - 1)\, g_2 - \alpha_0\, g_1 = \alpha_1 \tag{12}$$

$$\big(1 + \alpha_0\, Pe^2\big)\, f_1'' + 2\,\eta f_1' + 2(m+1) f_1 = -\,\alpha_1 Pe^3 f_0''' \tag{13}$$

Note that the form of Eq. (8) is critical to satisfying all of the necessary integral and boundary conditions

on the functions $g_j$. If the function $f(\eta)$ were taken as simply $f_0$, then only the single eigenvalue $\alpha_0$ ever appears in the problem. As a result, this simpler form of the solution can not satisfy the condition $dg_3/dy^*=0$ at $y^*=0$. Instead, the result is simply a constant which cannot be made to vanish.

The functions $g_j$ are unusual in that they are governed by second-order equations but must satisfy two boundary conditions on their first derivatives. In general such a system of equations cannot be solved since only one constant of integration is available to satisfy the two boundary conditions. Here this problem is solved by appropriate choices for the eigenvalues, $\alpha_k$. From the governing equation and the condition $g_1'=0$ at $y^*=0$, the derivative at the tube or channel wall automatically satisfies $g_1'=0$ at $y^*=1$. For the higher-order terms, the conditions $g_2'(1)=0$ and $g_3'(1)=0$ require that

$$\alpha_0 = -(n+1)\int_0^1 \left[(u^*-1)\,g_1\right] y^{*n} dy^* \tag{14}$$

$$\alpha_1 = -(n+1)\int_0^1 \left[(u^*-1)\,g_2 + \alpha_0 g_1\right] y^{*n} dy^* \tag{15}$$

respectively. The eigenvalues for this problem are thus uniquely determined by the two boundary conditions $dg_j/dy^*=0$ at $y^*=0$ and $y^*=1$.

Given the eigenvalues $\alpha_0$ and $\alpha_1$, Eqs. (11) and (13) can be solved to obtain the functions $f_0$ and $f_1$ describing axial variation of the solute concentration. For $m=0$, the case of a translating interface, these are

$$f_0 = \frac{1}{2}\operatorname{erfc}\eta' \tag{16}$$

$$\text{and} \qquad f_1 = \alpha_1 \frac{1-2\eta'^2}{2\sqrt{\pi\left(1+\alpha_0 Pe^2\right)^7}}\, e^{-\eta'^2} Pe^3 \tag{17}$$

$$\text{where} \qquad \eta' = \frac{\eta}{\sqrt{1+\alpha_0 Pe^2}} \tag{18}$$

For $m=1$, the case of a instantaneous plane source of unit strength, the zeroth-order contribution is

$$f_0 = \frac{1}{\sqrt{\pi(1+\alpha_0 Pe^2)}}\, e^{-\eta'^2} \tag{19}$$

Noting the definition of $\eta$ given above, we see that Eqs. (16) and (19) describe a diffusion process in which the diffusivity, $D$, is replaced by an effective diffusivity $D'=D(1+\alpha_0 Pe^2)$. This observation confirms that late-time dispersion yields a mean axial concentration profile resembling that due to diffusion alone.

## RESULTS

Equation (9) governing the function $g_1$ possesses closed-form solutions satisfying all required boundary conditions and integral constraints. For species transport and dispersion in a tube, the solution is

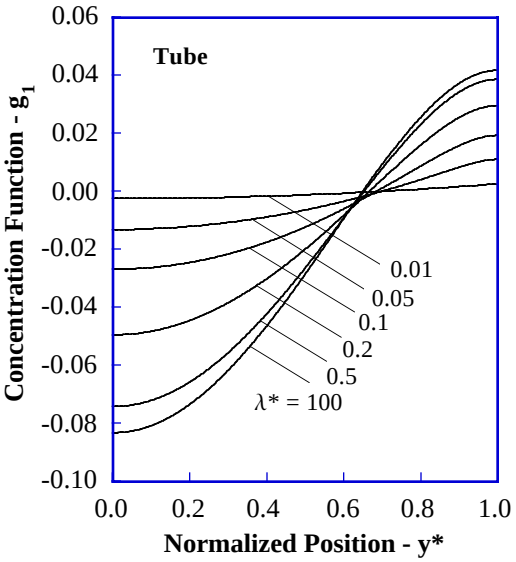


**Figure 1.** First-order correction describing the transverse variation in species concentration for electroosmotic flow in a tube.

$$\frac{4g_1}{\lambda^*} = \frac{4\lambda^* I_0(\kappa^* y^*) - \left(2y^{*2} + 8\lambda^{*2} - 1\right) I_1(\kappa^*)}{2\lambda^* I_1(\kappa^*) - I_0(\kappa^*)} \tag{20}$$

where $\kappa^* = 1/\lambda^*$. This result is plotted in Fig. 1 for a range of values of $\lambda^*$. The corresponding zeroth-order eigenvalue for this problem is

$$\frac{\alpha_0}{\lambda^{*2}} = \frac{\left(3+16\lambda^{*2}\right) I_1^2(\kappa^*) - 4\lambda^* I_0(\kappa^*)\, I_1(\kappa^*) - 2I_0^2(\kappa^*)}{2\left[2\lambda^* I_1(\kappa^*) - I_0(\kappa^*)\right]^2} \tag{21}$$

This second result is equivalent to that obtained by McEldoon and Datta using integral methods for the case of no surface reactions [3]. Although this expression is valid over the full range of $\lambda^*$, it is difficult to evaluate numerically outside the range $0.1 < \lambda^* < 10$ due to the exponential growth of the Bessel functions when $\lambda^*$ is very small and due to indeterminancy of the expression when $\lambda^*$ is very large. To avoid these problems, we have developed a fit to this expression that is based on the asymptotic limits of Eq. (21) for both small and large $\lambda^*$. The result is

$$\frac{4}{\alpha_0} \approx 192 + \frac{4}{\lambda^{*3/2}} + \frac{8}{\lambda^{*2}} \tag{22}$$

This approximation agrees with the results of Eq. (21) to within 2% over the full range of $\lambda^*$. Note that the common factor of four on the left of this expression is intentionally left in place since the Peclet number employed here is that based on the tube radius or channel

half-height. Thus the appropriate expression for $\alpha_0$ for a Peclect number based on the diameter or full-height is obtained simply by replacing this four by a one. Also note that the limiting behavior of $\alpha_0 = 1/48$ for large $\lambda^*$ is the result obtained by Taylor for pressure-driven flow in a tube [1].

The parallel results for electroosmotic flow in a channel are shown in Fig. 2 and given by

$$\frac{6g_1}{\lambda^*} = \frac{6\lambda^*\cosh(\kappa^* y^*) - \left(3y^{*2} + 6\lambda^{*2} - 1\right)\sinh(\kappa^*)}{2\lambda^*\sinh(\kappa^*) - \cosh(\kappa^*)} \quad (23)$$

and

$$\frac{\alpha_0}{\lambda^{*2}} = \frac{\left(2+12\lambda^{*2}\right)\sinh^2(\kappa^*) - 9\lambda^*\sinh(\kappa^*)\cosh(\kappa^*) - 3}{6\left[\lambda^*\sinh(\kappa^*) - \cosh(\kappa^*)\right]^2} \quad (24)$$

This last result is again difficult to evaluate for very small or large values of $\lambda^*$. In this case, the fit based on asymptotic behavior for small and large $\lambda^*$ is

$$\frac{4}{\alpha_0} \approx 210 + \frac{5}{\lambda^{*3/2}} + \frac{12}{\lambda^{*2}} \quad (25)$$

Again, this approximation agrees with the results of Eq. (24) to within 2% over the entire range of $\lambda^*$. Note that the limiting behavior of $\alpha_0 = 2/105$ for large $\lambda^*$ is the same as that obtained by Wooding for pressure-driven flow in a channel [4].

Finally, these results are useful in estimating the condition for minimum dispersion during transport over a fixed distance. This condition is equivalent to the condition for minimum theoretical plate height. The axial extent of spreading in a given time $t$ due to both diffusion and dispersion is given by $\delta = 2\sqrt{D' t}$. By expressing the time in terms of the travel distance $\ell$, $t = \ell/U = a\ell/PeD$, the extent of spreading may be rewritten as $\delta = 2[a\ell(1+\alpha_0 Pe^2)/Pe]^{1/2}$. This expression exhibits a minimum for the condition $Pe = \sqrt{1/\alpha_0}$ and the corresponding extent of spreading is $\delta = 2\alpha_0^{1/4}\sqrt{2a\ell}$.

## SUMMARY

Using analytical methods, we have determined the zeroth-order coefficient of axial dispersion of a neutral non-reacting solute in an incompressible electroosmotic flow. Here, in contrast to previous approaches, the dispersion is calculated by directly solving the governing transport equations. Using a late-time series to describe the full concentration field, the coefficient of dispersion arises naturally from a necessary condition for satisfying all required boundary conditions in transformed spatial and temporal coordinates.

Solutions based on the Debye-Hückel approximation are presented for both a circular tube and a channel of infinite width. These results recover the well-known solutions for dispersion in pressure-driven flows when the Debye length is very large. In this limit, the axial dispersion is proportional to the square of the Peclet number based on the characteristic transverse dimension of the tube or channel. In the limit of very small Debye lengths, we find that the dispersion varies as the square of the Peclet number based on the Debye length. Simple approximations to the dispersion as a function of the Debye length and Peclet number are also presented.

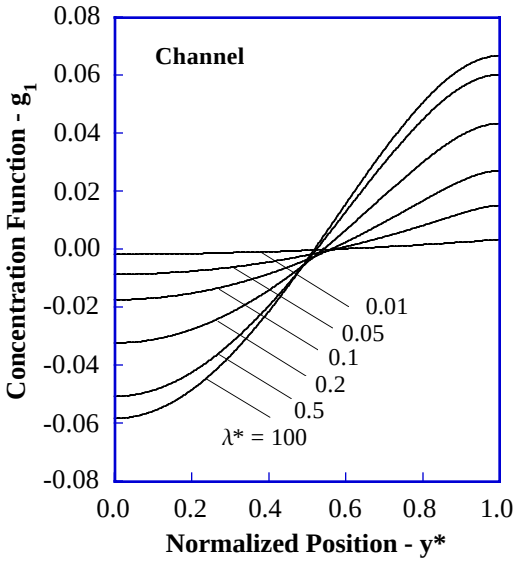


**Figure 2.** First-order correction describing the transverse variation in species concentration for electroosmotic flow in a channel.

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