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Research Article

Dispersion of charged solute in charged micro- and nanochannel with reversible sorption

We study dispersion of a charged solute in a charged micro- and nanochannel with reversible sorption and derive an analytical solution for mass fraction in the fluid, transport velocity and dispersion coefficient. Electrical double layer formed on the charged surface gives rise to a charge-dependent solute transport by modifying the transverse distribution of the solute. We discuss the effect of sorption and electrical double layer on solute transport and show that the coupling between sorption and electrical double layer gives rise to charge-dependent transport even for a thin double layer. However, in this case, it can be reduced to a simple non-charge-dependent case by introducing the intrinsic sorption equilibrium constant.

Keywords:
Charged channel / Dispersion / Reversible sorption / Thin layer model
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1 Introduction

Dispersion of a solute refers to the overall spreading process of the solute around their mean position. Typically, the solute dissolved in the liquid is charged due to the solvation effect. Understanding dispersion of charged solute such as ionic species, colloids or macromolecules [1] in a micro- and nanochannel is of fundamental importance in lab-on-a-chip devices for analyte separation [2, 3]. In addition, the information of band broadening by dispersion also can be used to determine diffusion coefficients [4], monitor electric current [5], measure flow velocity, and infer liquid viscosity [6].

In general, solute dispersion can be caused by (i) inhomogeneous flow fields, (ii) solute wall interaction, (iii) a force field normal to channel walls [7]. The interaction of inhomogeneous flow field and solute Brownian motion leads to the well-known Taylor dispersion [8] and it has been discussed in numerous papers [9–12]. The solute wall interaction refers to the sorptive process commonly met in chromatography. Sorption can be irreversible or reversible depending on the nature of the solute and the wall. Due to the continuous mass lost onto the wall surface, irreversible sorption is generally of less interest than reversible sorption. Moreover, force fields, such as electrical, magnetic and thermal fields normal to channel walls will have an influence on dispersion in an inhomogeneous flow field by modifying the solute distribution. In a charged micro- or nanochannel, the electrical double layer (EDL) generated at the solid-liquid interface gives rise to a spontaneous normal force field. Due to the dependence on charge valence, this effect can be used as a separation method for charged solutes, called the autogenous electric field-flow fractionation [13].

The expression for the dispersion coefficient either in a sorptive channel or a charged channel is well established. To deal with sorption on the surface, Golay [14] extended the Taylor theory by deriving a dispersion coefficient depending on partition coefficient, which is the ratio of adsorbed mass over aqueous mass. The effect of EDL on the dispersion of ionic solutes in a charged nano-scale capillary has been studied by De Leebeeck and Sinton [15]. Recently, Zhang, Hesse, et al. [16] obtained a transient solution for solute dispersion in a sorptive, uncharged channel by combining the Method of Moments [17] and Laplace transform. However, to the authors' knowledge, a general expression for dispersion in a *charged* channel with *sorption* has never been obtained. In this work, we derive a general solution for dispersion coefficient in a charged channel with reversible sorption using the Method of Moments. We show that the previous results in Golay [14] and De Leebeeck, and Sinton [15] are limiting cases of our general solution.

2 Mathematical formulation and analytical solution

As shown in Fig. 1A, we consider transport of a charged solute in a charged, infinitely long channel. The solute is immersed in an electrolyte solution with bulk concentration

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Abbreviations: EDL, Electrical double layer; **PB**, Poisson-Boltzmann

Color online: See the article online to view Figs. 1–3 in color.

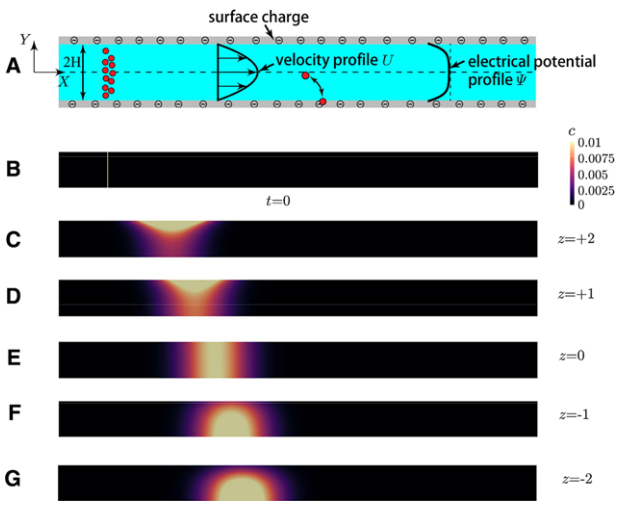

Figure 1. In a charged, infinitely long channel, a slender strip of charged solute with valence z migrates and undergoes reversible sorption on the wall. (A) Physical model and (B–G) color map of solute concentration obtained by numerical simulation for upper half of the channel at (B) $t = 0$ and (C–G) $t = 50$ for $z = \pm 2, \pm 1, 0$. The simulation system consists of a 8000 × 40 mesh with a large aspect ratio of 200:1 to mimic an infinitely long channel, but the results shown in Fig. 1B–G is compressed to a ratio of 20:1 for demonstration.

C_b and initially released as a transversely uniform, small strip with concentration C_0. Figure 1B–G demonstrates the color map of concentration by direct numerical simulation for upper half of the channel at times $t = 0$ (Fig. 1B) and $t = 50$ (Fig. 1C–G) for ionic species with different charge valences. In this work, we focus on the development of the analytical solution, and details of the numerical method can be found in Zhang and Wang [18] and Zhang, Hesse, et al. [16].

Next, we formulate the mathematical model for this problem and derive the analytical solution for transport properties of the ionic species. The transport equation of the charged solute is given by

$$\frac{\partial C}{\partial T} + U\frac{\partial C}{\partial X} = D\left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2}\right) + zM\frac{\partial}{\partial Y}\left(C\frac{\partial \Psi}{\partial Y}\right), \quad (1)$$

where C is the concentration of charged solute ([mol/L]), U is the effective velocity driven by pressure or an applied external electrical field, Ψ is the electrical potential related to EDL on the surface. Here D, M, and z are constants that denote the diffusion coefficient, electrical mobility and charge valence of the charged solute, respectively. According to Einstein-Stokes relation, $M = De/k_B T_K$, where k_B, e, and T_K denoting the Boltzmann constant, the elementary charge and the absolute temperature, respectively. For the infinitely long channel considered here, the flow U and the EDL potential Ψ are uniform along the channel and only vary in the transverse direction. In general, the flow velocity can be written as

$$U = U_p + U_{eof} + U_{ep}, \quad (2)$$

where U_p is the pressure-driven velocity, U_{eof} is the electroosmotic velocity and U_{ep} is the electrophoretic velocity. In Section 3, we will mainly talk about the purely pressure-driven flow, but our analytical results are generally valid for any pressure-driven or electrically-driven flow, which is discussed in Section 4.

Assuming the concentration of solute is much smaller than the bulk concentration and the dominant electrolyte is 1:1 type (e.g., KCl), the EDL potential is determined by the 1D Poisson-Boltzmann (PB) equation

$$\varepsilon\frac{d^2\Psi}{dY^2} = 2eC_b\sinh\left(\frac{\Psi e}{k_B T_K}\right), \quad (3)$$

where ε is the permittivity of the electrolyte solution.

Charged solute may adsorb on the surface, either physically (e.g., electrical interaction for protein adsorption) or chemically (e.g., surface complexation for ionic species). The law of mass action for reversible sorption gives

$$K_d = \frac{S}{C}, \quad (4)$$

where K_d is the apparent equilibrium constant of sorption and S is the sorbed solute concentration ([M/L^2]). Mass balance of the solute on the surface gives

$$\frac{\partial S}{\partial T} = -D\frac{\partial C}{\partial n} - zMC\frac{\partial \Psi}{\partial n}, \quad (5)$$

where n is the normal vector pointing outwards. Substitution of (4) into (5) gives the boundary condition of solute on the wall

$$K_d\frac{\partial C}{\partial T} = -D\frac{\partial C}{\partial n} - zMC\frac{\partial \Psi}{\partial n}, \quad (6)$$

We choose the following characteristic quantities to nondimensionalize the system,

$$c = C/C_0,\ x = X/H,\ y = Y/H,\ t = T/\left(H^2/D\right)$$
$$u = U/U_0,\ \psi = \Psi/\left(k_B T_K/e\right), \quad (7)$$

where the characteristic velocity U_0 is mean flow velocity. Then the dimensionless version of the transport equation, the PB equation and the corresponding boundary conditions follow as

$$\frac{\partial c}{\partial t} + Pe\,u\frac{\partial c}{\partial x} = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial}{\partial y}\left(\mu c\frac{\partial \psi}{\partial y}\right), \quad (8)$$

$$k_d\frac{\partial c}{\partial t} = -\frac{\partial c}{\partial y} - zc\frac{\partial \psi}{\partial y} \quad y = \pm 1, \quad (9)$$

$$\frac{d^2\psi}{dy^2} = \kappa^2\sinh(\psi), \quad (10)$$

$$\psi = \zeta \qquad y = \pm 1, \quad (11)$$

where ζ is the dimensionless zeta potential of the EDL. The main dimensionless parameters are the Peclet number $Pe = U_0 H/D$, the dimensionless partition coefficient $k_d = K_d/H$ and $\kappa = H/\lambda_D$ with $\lambda_D = \sqrt{\frac{\varepsilon k_B T_K}{2000 N_A C_b e^2}}$ the Debye screening length. The ratio of the channel width over the EDL thickness is given by κ. Due to the symmetry of the channel, only the upper half of the channel needs to be studied and the lower

boundary condition is replaced by the symmetric boundary conditions

$$\frac{\partial c}{\partial y} = 0 \quad y = 0, \tag{12}$$

$$\frac{\mathrm{d}\psi}{\mathrm{d}y} = 0 \quad y = 0. \tag{13}$$

Note that here we ignore the effect of sorption on surface charge and assume that the channel is homogeneously charged. More generally, the surface charge (also, zeta potential) can be modified by sorption and rely on the local chemistry of the electrolyte solution. For example, Ghosal [19] proposed a phenomenological model for electro-osmosis with protein adsorption modifying surface charge. For ionic species, surface complexation models are used to incorporate chemistry-dependent surface charge [20, 21].

In Zhang, Hesse, et al. [16], the authors derived a series solution for transport velocity and dispersion coefficient for solute transport in a *soprtive, uncharged* channel by combining the Method of Moments and Laplace transform. In this case, the same method cannot be applied to seek a transient solution due to the complexity introduced by the electrical interaction. However, it is still possible to obtain the equilibrium solution after the transport process reaches equilibrium, when the transport velocity and dispersion coefficient become constants. For long channels typically met in chromatography, the transient period is short compared with the entire operation time and thus the equilibrium solution is of more interest. The detailed derivation of the solution is given in the appendix and we show the main results of this work by presenting the analytical solution for the mass of the solute in the fluid M_0, the transport velocity V and the dispersion coefficient D_L:

$$M_0 = \frac{1}{1 + k_\mathrm{int}}\ , \tag{14}$$

$$V = Pe\ \frac{\beta}{1 + k_\mathrm{int}}, \tag{15}$$

$$D_\mathrm{L} = D_\mathrm{diff} - \frac{Pe^{\,2}}{\langle\mathcal{B}\rangle\,(1 + k_\mathrm{int})} \int_0^1 \mathcal{B}\,(y)\,(u - V/\,Pe)\mathcal{K}\,(y)\,\mathrm{d}y + \frac{Pe^{\,2}\beta k_\mathrm{int}}{(1 + k_\mathrm{int})^2}\mathcal{K}\,(1), \tag{16}$$

where

$$k_\mathrm{int} = k_\mathrm{d}\ \alpha, \tag{17}$$

$$\mathcal{B}\,(y) = \exp\left(-z\psi\right), \tag{18}$$

$$\alpha = \exp\left(-z\zeta\right)/\langle\mathcal{B}\rangle, \tag{19}$$

$$\beta = \langle u\mathcal{B}\rangle/\langle\mathcal{B}\rangle, \tag{20}$$

$$\mathcal{K}\,(y) \ = \int_0^y \mathcal{B}^{-1}\left(y'\right)\int_0^{y'} (u - V/\,Pe)\,\mathcal{B}\left(y''\right)\mathrm{d}y''\mathrm{d}y', \tag{21}$$

$$D_\mathrm{diff} = 1/\left(1 + k_\mathrm{int}\right), \tag{22}$$

where $\langle\cdot\rangle$ is the cross-sectional averaging operator and $\mathcal{B}(y)$ is a Boltzmann factor characterizing EDL interaction on charged solute and can be generalized to other interactions such as thermal potential. The intrinsic equilibrium constant is k_int and will be discussed later. Here, α and β are the coefficients dependent on the EDL and $\mathcal{K}(y)$ is a kernel function dependent on both velocity distribution and EDL. $D_\mathrm{diff} = 1/(1 + k_\mathrm{int}\alpha)$ is the contribution of molecular diffusion to dispersion [16]. Besides, dispersion can be generated by shear flow and surface sorption, which corresponds to the first and second part in D_L, respectively. Note that the interaction due to EDL modifies both of them. Furthermore, we define the normalized transport velocity $\mathcal{V}$ and dispersion coefficient $\mathcal{D}$ to avoid the dependence on Pe and D_diff,

$$\mathcal{V} \ = \frac{V}{Pe} = \frac{\beta}{1 + k_\mathrm{int}}\ , \tag{23}$$

$$\mathcal{D} \ = \frac{D_L - D_\mathrm{diff}}{D_\mathrm{Taylor}} = -\frac{105}{2\langle\mathcal{B}\rangle\,(1 + k_\mathrm{int})} \int_0^1 \mathcal{B}\,(y)\,(u - V)\,\mathcal{K}\,(y)\,\mathrm{d}y + \frac{\beta k_\mathrm{int}}{(1 + k_\mathrm{int})^2}\mathcal{K}\,(1)\ , \tag{24}$$

where $D_\mathrm{Taylor} = 2\ Pe^{\,2}/105$ denotes the classical Taylor dispersion coefficient without sorption and EDL [8].

The electrical potential distribution ψ is determined by solving the 1D PB Eq. (10), which only has an approximate solution in the thin double layer limit, i.e., $\kappa H \gg 1$, but has no general solution when the EDL overlaps. Hence, we solve the PB equation numerically by linearizing the right-hand-side term and discretizing the derivative term by a central difference scheme. We have done a convergence test for the solver and it is shown to be converged by ensuring the relative error for electrical potential smaller than 10^{-10}. The computational cost of the numerical procedure is very low as it only takes <0.01s to get the solution for a 1000-grid mesh on a 4 core laptop.

3 Discussion

The general solution for M_0, $\mathcal{V}$, and $\mathcal{D}$ can be reduced to several limiting cases studied previously. If the channel is not charged, i.e., $\psi = 0$, then $\mathcal{B} = 1$, $\alpha = 1$, $k_\mathrm{int} = k_\mathrm{d}$, $\beta = 1$, $\mathcal{V} = \frac{1}{1+k_\mathrm{d}}$, $\mathcal{K}(y) = \int_0^y \int_0^{y'} (u - \mathcal{V})\mathrm{d}y''\mathrm{d}y'$. For a purely pressure-driven flow with velocity profile

$$u \ = \frac{3}{2}\ \left(1 - y^2\right), \tag{25}$$

it can be shown that

$$M_0 = \frac{1}{1 + k_d}\ , \tag{26}$$

$$\mathcal{V} \ = \frac{1}{1 + k_\mathrm{d}}\ , \tag{27}$$

$$\mathcal{D} = -\frac{105}{2\left(1+k_{\mathrm{d}}\right)}\int_0^1 \left(u-\mathcal{V}\right)\mathcal{K}\left(\gamma\right)\mathrm{d}\gamma + \frac{k_{\mathrm{d}}}{\left(1+k_{\mathrm{d}}\right)^2}\mathcal{K}\left(1\right)$$
$$= \frac{1+9k_{\mathrm{d}}+25.5k_{\mathrm{d}}^2}{\left(1+k_{\mathrm{d}}\right)^3}. \tag{28}$$

This was first obtained by Golay [14] using Laplace transform.

If there is no sorption, i.e., $k_{\mathrm{d}} = 0$, then

$$M_0 = 1, \tag{29}$$

$$\mathcal{V} = \frac{\langle u\mathcal{B}\rangle}{\langle\mathcal{B}\rangle}, \tag{30}$$

$$\mathcal{D} = -\frac{105}{2\langle\mathcal{B}\rangle}\int_0^1 \mathcal{B}\left(\gamma\right)\left(u-\mathcal{V}\right)\int_0^{\gamma}\mathcal{B}^{-1}\left(\gamma'\right)$$
$$\int_0^{\gamma'}\left(u-\mathcal{V}\right)\mathcal{B}\left(\gamma''\right)\mathrm{d}\gamma''\mathrm{d}\gamma'\mathrm{d}\gamma, \tag{31}$$

which is given by De Leebeeck and Sinton [15] following the analysis of the flux pioneered by Taylor [8].

As shown in Fig. 2, the analytical solution is in good agreement with the direct numerical simulation results using lattice Boltzmann method [16,18] for an EDL with $\kappa = 5$ and pressure-driven flow with $Pe = 1$. When sorption gets stronger, the mass of the solute in the fluid decreases and the transport slows downs, but the dispersion coefficient has a peak, the position of which depends on the charge valence of the solute. This is because sorption increases dispersion by the continuous removal of the solute from the concentration front and release of the solute at the tail. At the same time, sorption also decreases dispersion by storing mass in the immobile surface layer. These competing effects of sorption on dispersion give rise to the peak in Fig. 2C. What's more, because of the electrical interaction from the negatively-charge surface, counterions(coions) are accumulated(depleted) near the surface region with lower flow velocity so that in average, counterions(coions) move slower(faster) compared to the mean flow, as shown in Fig. 1C–G. This is the fundamental principle for the autogenous electric field-flow fractionation [13].

The effect of the EDL on the solute transport relies on its thickness, given by κ^{-1}, as shown in Fig. 3. When the EDL thickness is much larger than the channel width, i.e., $\kappa H \ll 1$, the two EDLs on both walls fully overlap and the electrical potential gradient vanishes, leading to negligible electrical interaction, as indicated by the merging of the different curves when $\kappa H \to 0$. Contrarily, in the limit of thin double layer (TDL), i.e., $\kappa H \gg 1$, the electrical interaction is confined in a very thin region near the surface. In this case, $\langle\mathcal{B}\rangle \to 1$, $\alpha \to \exp(-z\zeta')$, $\beta \to \langle u\rangle$, $\mathcal{K} \to \int_0^{\gamma}\int_0^{\gamma'}(u-\mathcal{V})\mathrm{d}\gamma''\mathrm{d}\gamma'$. Therefore, the transport parameters (14–16) reduce to

$$M_{0,\mathrm{TDL}} = \frac{1}{1+k_{\mathrm{int}}}, \tag{32}$$

$$\mathcal{V}_{\mathrm{TDL}} = \frac{1}{1+k_{\mathrm{int}}}, \tag{33}$$

$$\mathcal{D}_{\mathrm{TDL}} = -\frac{105}{2\left(1+k_{\mathrm{int}}\right)}\int_0^1 \left(u-\mathcal{V}\right)\mathcal{K}\left(\gamma\right)\mathrm{d}\gamma + \frac{k_{\mathrm{int}}}{\left(1+k_{\mathrm{int}}\right)^2}\mathcal{K}\left(1\right) \tag{34}$$

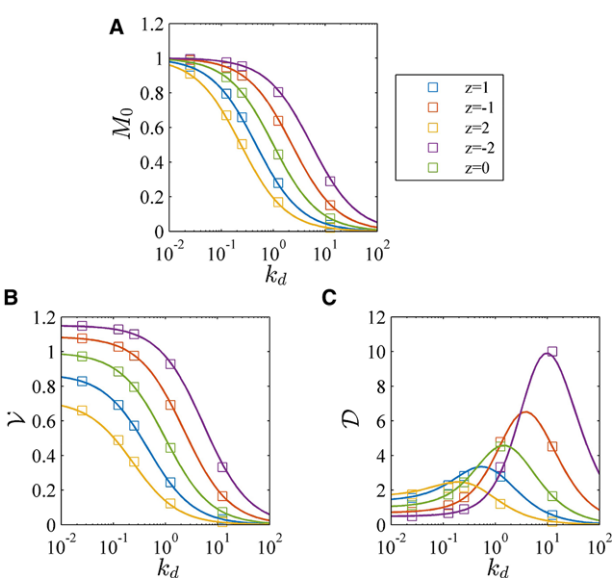

Figure 2. Comparison between the analytical solution (solid lines) and the numerical simulation (squared symbols) for (A) mass fraction in the fluid M_0, (B) normalized transport velocity $\mathcal{V}$ and (C) normalized dispersion coefficient $\mathcal{D}$ as function of k_d for ions with different valence z. In this case, the flow is purely pressure-driven and $Pe = 1$, $\zeta = -1$, $\kappa = 5$.

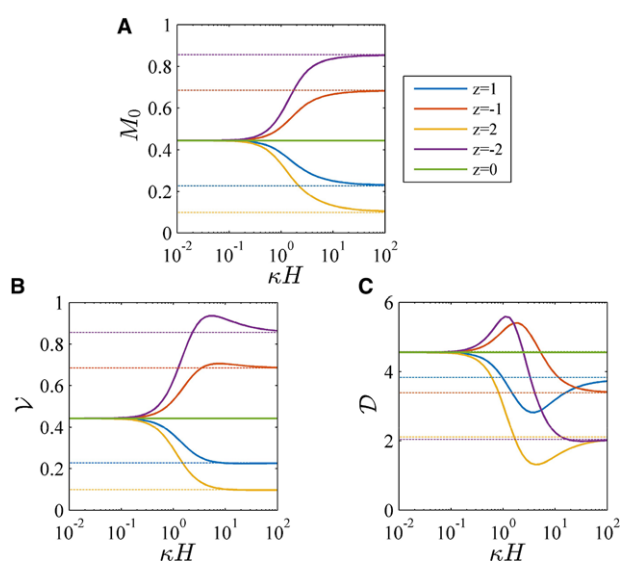

Figure 3. (A) Mass fraction in the fluid M_0, (B) normalized transport velocity $\mathcal{V}$ and (C) normalized dispersion coefficient $\mathcal{D}$ as function of the dimensionless EDL thickness κH. In this case, the flow is purely pressure-driven and $Pe = 1$, $\zeta = -1$, $k_{\mathrm{d}} = 1.25$. The dashed lines are limiting solutions for thin double layer given by Eqs (32–34).

Note that these are identical to Eqs. (26–28) if k_d is replaced by k_{int}. Physically, it means that the EDL is so thin that it can be treated as an adsorption layer with a potential drop ζ. The intrinsic equilibrium constant k_{int} accounts for this potential drop and the resulting difference between the concentration inside and outside the EDL. In fact, α is the electrostatic correction factor introduced in the surface complexation theory for ions [22]. Sometimes, column flood or microfluidic experiments, where TDL limit is generally valid, are used to infer the sorptive behavior of the solute by measuring the transport parameters. Here, we show that it is the intrinsic equilibrium constant k_{int}, rather than the apparent equilibrium constant k_{d}, that is directly inferred from the experiments. Besides, because the thickness of the EDL is dependent on the bulk electrolyte concentration C_{b}, it suggests that C_{b} can be tuned to achieve a better separation efficiency.

4 Concluding remarks

In summary, we study dispersion in a charged channel with reversible sorption on the surface and derive a general analytical solution, which recovers to previous results as limiting cases. It is shown that because of the attraction/repulsion effect of the EDL on the charged solute, the mass fraction, transport velocity and dispersion coefficient of the solute transport is highly dependent on its charge valence, i.e., a charge-dependent transport process. This can be used to separate solutes with different charges and the separation efficiency of the process can be further controlled by tuning the sorption equilibrium constant (e.g., using different sorptive materials) and salinity of the electrolyte solution.

Here we show the effects of sorption and EDL on dispersion for pressure-driven flow, but our analytical solution can be used for electrokinetic flow. For example, if the flow is purely driven by external electrical field, the flow velocity of the ionic species is a superposition of the electro-osmotic velocity U_{eof} and the electrophoretic velocity U_{ep}. The electro-osmotic velocity can be determined by the similarity between electrical field and the flow field [23], while the electrophoretic velocity is the product of the external electrical field and the mobility of the ionic species. By substituting the electrokintic flow velocity for the general flow velocity u, our analytical solution (14–16) still apply. In this case, however, the effect of streaming potential [24] and the dependence of the surface charge on sorption [19] are assumed to be negligible, and shall be studied in the future work.

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Appendix

Analytical solution by method of moments

We show the detailed derivation of the analytical solution (14–16) in this section by using Method of Moment [17] and method of undermined coefficients. Firstly, the transport Eq. (8) and the boundary conditions (9) and (12) are integrated in the longitudinal direction to obtain the moment equation with corresponding boundary conditions for n^{th} longitudinal

moment in a filament $c_n^* = \int_{-\infty}^{\infty} x^n c \, dx$. For the lowest three moments we mostly care,

$$\frac{\partial c_0^*}{\partial t} = \frac{\partial^2 c_0^*}{\partial y^2} + \frac{\partial}{\partial y}\left(z c_0^* \frac{\partial \psi}{\partial y}\right), \tag{A.1}$$

$$\frac{\partial c_1^*}{\partial t} - Pe\ u\ c_0^* = \frac{\partial^2 c_1^*}{\partial y^2} + \frac{\partial}{\partial y}\left(z c_1^* \frac{\partial \psi}{\partial y}\right), \tag{A.2}$$

$$\frac{\partial c_2^*}{\partial t} - 2\ Pe\ u\ c_1^* = 2c_0^* + \frac{\partial^2 c_2^*}{\partial y^2} + \frac{\partial}{\partial y}\left(z c_2^* \frac{\partial \psi}{\partial y}\right) \tag{A.3}$$

with boundary conditions

$$\frac{\partial c_n^*}{\partial y} = 0 \quad y = 0, \tag{A.4}$$

$$k_d \frac{\partial c_n^*}{\partial t} = -\frac{\partial c_n^*}{\partial y} - z c_n^* \frac{\partial \psi}{\partial y} \quad y = 1, \tag{A.5}$$

for $n = 0, 1, 2$. The longitudinal moments of the solution distribution is defined as

$$m_n = \int_{-1}^{1} c_n^* \, dy \tag{A.6}$$

and the mass fraction of solute in the fluid M_0, the transport velocity V and the dispersion coefficient D_L are computed as

$$M_0 = \frac{m_0}{m_t}, \tag{A.7}$$

$$V = \frac{d(m_1/m_0)}{dt}, \tag{A.8}$$

$$D_L = \frac{1}{2}\frac{d\left(m_2/m_0 - (m_1/m_0)^2\right)}{dt}, \tag{A.9}$$

where m_t is the total mass in the system. A general transient solution to the moment Eqs. (A.1–A3) relies on the initial condition and is intractable, but a late-time solution after an initial equilibrium time is workable. Noting that at equilibrium M_0, V, D_L are constants, we assume that c_0^*, c_1^*, c_2^* have the following forms

$$c_0^* = A_0\, \mathcal{B}(y), \tag{A.10}$$

$$c_1^* = A_1\, \mathcal{B}(y)\, t + B_1(y), \tag{A.11}$$

$$c_2^* = A_2\, \mathcal{B}(y)\, t^2 - 2\ Pe\ A_1 f(y)\, \mathcal{B}(y)\, t + B_2(y), \tag{A.12}$$

where A_0, A_1, A_2, $B_1(y)$, $B_2(y)$ and $f(y)$ are unknown constants or functions to be determined by matching the Eqs. (A.1–3) and boundary conditions (A.4) and (A.5).

Since c_0^* does not rely on t, equation (A.1) reduces to an ordinary differential equation. Combined with the boundary conditions (A.4), (A.5), c_0^* is solved as

$$c_0^* = A_0\, \mathcal{B}(y), \tag{A.13}$$

where A_0 is a constant to be determined by initial condition. It follows that the zeroth moment, i.e., the mass in the fluid is

$$m_0 = 2A_0\langle \mathcal{B}\rangle. \tag{A.14}$$

At the initial moment, i.e., $t = 0$, $m_0 = m_t$ so that $A_0 = m_t/2\langle B\rangle$. The adsorbed mass is

$$m_{ads} = 2\int_{-\infty}^{\infty} s\, dx = 2k_d \int_{-\infty}^{\infty} c|_{y=1}\, dx = 2k_d c_0^*|_{y=1} = 2k_d A_0 \exp(-z\zeta). \tag{A.15}$$

Then, the fraction of solute mass in the fluid is

$$M_0 = \frac{m_0}{m_0 + m_{ads}} = \frac{1}{1 + k_d \alpha} = \frac{1}{1 + k_{int}}, \tag{A.16}$$

i.e., Eq. (14).

Since V is a constant at equilibrium, we assume c_1^* has the following form

$$c_1^* = A_1\, \mathcal{B}(y)\, t + B_1(y), \tag{A.17}$$

where the Boltzmann factor $\mathcal{B}(y)$ is introduced to cancel the dependence on t on the right-hand-side of equation (A.2). Substitute c_1^* into (A.2) gives an equation of $B_1(y)$ and it can be solved as

$$B_1(y) = \mathcal{B}(y)\left(B_{1,m} - A_0\ Pe\ \mathcal{K}(y)\right), \tag{A.18}$$

where $B_{1,m}$ is a parameter to be determined by initial condition and the kernel function is given as

$$\mathcal{K}(y) = \int_0^{y'} \mathcal{B}^{-1}(y') \int_0^{y'} \left(u - \frac{A_1}{A_0\ Pe}\right) \mathcal{B}(y'')\, dy''\, dy'. \tag{A.19}$$

Meanwhile, substitution of c_1^* in the sorptive boundary condition (A.5) gives

$$A_1 = A_0\ Pe\ \frac{\langle u\mathcal{B}\rangle}{\langle \mathcal{B}\rangle + k_d \exp(-z\zeta)} = A_0\ Pe\ \frac{\beta}{1 + k_{int}}. \tag{A.20}$$

Replacing A_1 in $\mathcal{K}(y)$ gives Eq. (21) in the main text. Then c_1^* can be integrated in the y-direction to obtain the first moment

$$m_1 = 2A_1\langle \mathcal{B}\rangle t + 2B_{1,m}\langle \mathcal{B}\rangle - 2A_0\ Pe \int_0^1 \mathcal{B}(y)\, \mathcal{K}(y)\, dy. \tag{A.21}$$

Initially, the center of the mass of the solute is kept at $x = 0$, i.e., $m_1(t = 0)/m_0 = 0$, so that

$$B_{1,m} = \frac{A_0\ Pe}{\langle \mathcal{B}\rangle} \int_0^1 \mathcal{B}(y)\, \mathcal{K}(y)\, dy. \tag{A.22}$$

The transport velocity V is obtained as

$$V = \frac{d(m_1/m_0)}{dt} = \frac{A_1}{A_0} = Pe\ \frac{\beta}{1 + k_{int}}, \tag{A.23}$$

i.e., Eq. (15).

Similarly, we assume c_2^* has the following form

$$c_2^* = A_2\, \mathcal{B}(y)\, t^2 - 2\ Pe\ A_1 f(y)\, \mathcal{B}(y)\, t + B_2(y), \tag{A.24}$$

where A_2 is a constant and $f(y)$, $B_2(y)$ are functions to be determined. Since the dispersion coefficient is a constant at equilibrium, the quadratic term in c_2^* has to be cancelled by c_1^* and c_0^*, which gives $A_2 = A_1^2/A_0$ based on the definition

(A.9). Substitute c_0^*, c_1^* and c_2^* into the second-order moment Eq. (A.3),

$$(A_2 - 2\ Pe\ u(\gamma)\ A_1)\,\mathcal{B}(\gamma)\,t - 2\ Pe\ A_1 f(\gamma)\,\mathcal{B}(\gamma) - 2\ Pe\ u(\gamma)\ B_1(\gamma) - 2A_0\mathcal{B}(\gamma) = \frac{\partial}{\partial\gamma}\left(-2\ Pe\ A_1\mathcal{B}(\gamma)\frac{\partial f}{\partial\gamma}\right)t + \frac{\partial}{\partial\gamma}\left(\frac{\partial B_2}{\partial\gamma} + zB_2\frac{\partial\psi}{\partial\gamma}\right). \quad (A.25)$$

To remove the time dependence, $f(\gamma)$ has to satisfy

$$\frac{\partial}{\partial\gamma}\left(\mathcal{B}(\gamma)\frac{\partial f}{\partial\gamma}\right) + \left(\frac{A_2}{A_1\ Pe} - u(\gamma)\right)\mathcal{B}(\gamma) = 0. \quad (A.26)$$

Further substitution of c_2^* into the symmetric boundary condition (A.4) gives

$$\frac{\partial f}{\partial\gamma} = 0 \quad \gamma = 0. \quad (A.27)$$

Equation (A.26) and (A.27) are solved to obtain $f(\gamma)$ as

$$f(\gamma) = \mathcal{K}(\gamma) + f_2, \quad (A.28)$$

where f_2 is a constant to be determined. Replace f_2 in (A.25) by (A.28) and solve $B_2(\gamma)$ as

$$B_2(\gamma) = \mathcal{B}(\gamma)\left(B_{2,\mathrm{m}} + \int_0^{\gamma}\mathcal{B}^{-1}(\gamma')\int_0^{\gamma'}(\mathcal{F}(\gamma'') - 2\ Pe\ A_1 f_2)\mathcal{B}(\gamma'')\mathrm{d}\gamma''d\gamma'\right), \quad (A.29)$$

where

$$\mathcal{F}(\gamma) = 2\ Pe^{\ 2}A_0(u - \mathcal{V})\mathcal{K}(\gamma) - 2\ Pe\ uB_{1,m} - 2A_0. \quad (A.30)$$

$B_{2,m}$ is the value of B_2 at $\gamma = 0$, which depends on the initial condition, but doesn't affect the final expression of dispersion coefficient. Then, substitute c_2^* into the sorptive boundary condition (A.5) with $f(\gamma)$ given by (A.28) and $B_2(\gamma)$ given by (A.29), f_2 is determined as

$$f_2 = -\frac{1}{Pe^2\beta} + \frac{1}{\beta\langle\mathcal{B}\rangle}\int_0^1\mathcal{B}(\gamma)(u - V/Pe)\mathcal{K}(\gamma)\,\mathrm{d}\gamma - \frac{1}{\langle\mathcal{B}\rangle} \times \int_0^1\mathcal{B}(\gamma)\mathcal{K}(\gamma)\,\mathrm{d}\gamma - \frac{k_{\mathrm{int}}}{(1 + k_{\mathrm{int}})}\mathcal{K}(1) \quad (A.31)$$

Finally, according to the definition of the dispersion coefficient, we obtain

$$D_L = \frac{1}{2}\left(\frac{-2\ Pe\ A_1\int_{-1}^1 f(\gamma)\mathcal{B}(\gamma)\,\mathrm{d}\gamma}{2A_0\langle\mathcal{B}\rangle}\right) = \frac{Pe^{\ 2}\beta}{\langle\mathcal{B}\rangle(1 + k_{\mathrm{int}})}\left(-\int_0^1\mathcal{B}(\gamma)\mathcal{K}(\gamma)\,\mathrm{d}\gamma - f_2\langle\mathcal{B}\rangle\right) = \frac{1}{1 + k_{\mathrm{int}}} - \frac{Pe^2}{\langle\mathcal{B}\rangle(1 + k_{\mathrm{int}})}\int_0^1\mathcal{B}(\gamma)(u - V/Pe)\mathcal{K}(\gamma)\,\mathrm{d}\gamma + \frac{Pe^{\sim 2}\beta k_{\mathrm{int}}}{(1 + k_{\mathrm{int}})^2}\mathcal{K}(1), \quad (A.32)$$

i.e., Eq. (A.16).

