Streaming Potential Effects on Solute Dispersion in Nanochannels

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This correspondence presents a theoretical analysis of the effects of streaming potential on the hydrodynamic dispersion of solutes in pressure-driven flow. The induced electroosmotic backflow is shown to significantly decrease the solute dispersion in slit nanochannels. The dispersion coefficient as traditionally defined may be significantly increased or decreased by streaming potential effects. These influences are sensitive to the solute charge, and found to be mainly dependent on an electrokinetic "figure of merit".

Recently, Pennathur and Santiago[1] and Garcia et al.[2] reported a separation of charged solutes in electroosmotic flow along nanochannels. This separation stems partially from the transverse solute distribution produced by the inherent electric field in the electric double layer.[3−5] More recently, Griffiths and Nilson,[6] and Xuan and Li[7] proposed that such charge-based separation could also be implemented in pressure-driven nanochannel flows. The mean speed and the hydrodynamic dispersion of charged solutes in both types of flows have been studied.[1−8] However, the effects of streaming potential on these two parameters in pressure-driven flow have been neglected. In nanoscale channels, the flow-induced streaming potential field is known to generate a strong electroosmotic backflow giving rise to the so-called electroviscous effects.[9−12] While the streaming potential effects on solute retention are relatively small,[7] they were found to reduce the dispersion of neutral solutes by up to 25% in nanochannels with even a small surface potential.[13] In this correspondence, we develop an analytical model to study the effects of streaming potential on the hydrodynamic dispersion of charged solutes in slit nanochannels with an arbitrary value of surface potential.

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THEORY

Solute Transport and Dispersion in Electrokinetic Flow. The local solute (neutral or charged) speed u_i in a general electrokinetic flow, viz., a combined pressure-driven and electroosmotic flow, is expressed as

$$u_i = u_p + u_e + v_i z_i F E \tag{1}$$

where u_p is the pressure-driven fluid velocity, u_e the electroosmotic fluid velocity, v_i the solute mobility, z_i the solute charge number, F the Faraday's constant, and E the axial electric field (e.g., the streaming potential field in pressure-driven flow). The two fluid velocity components in a slit channel are given by[9,11,13]

$$u_p = \frac{a^2}{2\mu}(1 - y^2)P \quad \text{and} \quad u_e = -\frac{\epsilon\zeta}{\mu}\left(1 - \frac{\Psi}{\zeta^\star}\right)E \tag{2}$$

where a is the channel half-height, μ the fluid viscosity, y the transverse coordinate normalized by a, P the pressure drop per unit channel length, ϵ the fluid permittivity, and $\zeta^\star = F\zeta/RT$, the nondimensional zeta potential with R the universal gas constant and T the fluid temperature.

The nondimensional double layer potential in eq 2, $\Psi = F\psi/RT$, is solved from the Poisson−Boltzmann equation[14]

$$d^2\Psi/dy^2 = \kappa^{\star\,2}\sinh(\Psi) \tag{3}$$

where $\kappa^\star = \kappa a$ is the normalized channel height and $\kappa = (2F^2 c_b/\epsilon RT)^{1/2}$ is the inverse of the so-called Debye length with c_b being the ionic concentration of the bulk fluid. Note that a symmetric electrolyte with unit charge has been assumed here for simplicity. The analytical solution of Ψ to eq 3 is expressed in terms of the Jacobian elliptical function[15−17]

$$\Psi = \Psi_0 + 2\ln\left(\text{JacCD}\left(\frac{\kappa^\star y}{2}e^{-\Psi_0/2}\middle|e^{2\Psi_0}\right)\right) \tag{4}$$

where Ψ_0 denotes the potential at the channel center ($y = 0$) and can be determined from the known zeta potential $\zeta^\star$ at the channel wall ($y = 1$).

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As analyzed previously,[1–8] the mean solute speed $\bar{u}_i$ in an electrokinetic flow is given by

$$\bar{u}_i = \bar{u}_{ip} + \bar{u}_{ie} + v_i z_i FE \tag{5}$$

$$\bar{u}_{ip} = \frac{\langle u_p B_i \rangle}{\langle B_i \rangle} \quad \text{and} \quad \bar{u}_{ie} = \frac{\langle u_e B_i \rangle}{\langle B_i \rangle} \tag{6}$$

where $\bar{u}_{ip}$ and $\bar{u}_{ie}$ denote, respectively, the mean solute speed in a pure pressure-driven flow ($E = 0$) and a pure electroosmotic flow ($P = 0$), $\langle \cdots \rangle = \int_0^1 \ldots dy$ signifies the area-average over the channel cross section, and $B_i = \exp(-z_i \Psi)$ characterizes the Boltzmann distribution of charged solutes in the transverse direction. For neutral solutes ($z_0 = 0$), it is straightforward to obtain $\bar{u}_{0p} = \langle u_p \rangle$ and $\bar{u}_{0e} = \langle u_e \rangle$, where $\langle u_p \rangle$ and $\langle u_e \rangle$ are the area-averaged fluid velocities.

As u_p and u_e vary over the channel cross section, they both contribute to the spreading of solutes along the flow direction, which is termed hydrodynamic dispersion or Taylor dispersion.[18,19] The general formula for calculating the dispersion of solutes[20]

$$K_i = \frac{a^2}{D_i} \frac{\langle B_i^{-1} [\int_0^y (u_i - \bar{u}_i) B_i \, dy']^2 \rangle}{\langle B_i \rangle} \tag{7}$$

is then specified as

$$K_i = \frac{a^2}{D_i} (F_{ip} \langle u_p \rangle^2 + F_{ipe} \langle u_p \rangle \langle u_e \rangle + F_{ie} \langle u_e \rangle^2) \tag{8}$$

$$F_{ip} = \langle B_i^{-1} [\int_0^y (u_p^* - \bar{u}_{ip}^*) B_i \, dy']^2 \rangle \langle B_i \rangle^{-1},$$
$$F_{ie} = \langle B_i^{-1} [\int_0^y (u_e^* - \bar{u}_{ie}^*) B_i \, dy']^2 \rangle \langle B_i \rangle^{-1} \text{ and}$$
$$F_{ipe} = 2\langle B_i^{-1} [\int_0^y (u_p^* - \bar{u}_{ip}^*) B_i \, dy'] [\int_0^y (u_e^* - \bar{u}_{ie}^*) B_i \, dy'] \rangle \langle B_i \rangle^{-1} \tag{9}$$

where D_i is the molecular diffusivity, $u_m^* = u_m / \langle u_m \rangle$, and $\bar{u}_{im}^* = \bar{u}_{im} / \langle u_m \rangle$ ($m = p$ and e). For the cases of a pure pressure-driven flow and a pure electroosmotic flow, eq 8 is reduced, respectively, to

$$K_{ip} = F_{ip} a^2 \langle u_p \rangle^2 / D_i \quad \text{and} \quad K_{ie} = F_{ie} a^2 \langle u_e \rangle^2 / D_i \tag{10}$$

both of which have been discussed in detail recently.[6,8] In a combined pressure-driven and electroosmotic flow, however, an additional dispersion due to the coupling of these two flows arises,[13,21–23] that is, the second term in the bracket of eq 8.

Streaming Potential Field in Pressure-Driven Flow. In a pressure-driven flow with no externally applied electric field, downstream accumulation of counterions results in the development of a streaming potential field.[14] This induced electric field

E_{st} can be determined from the zero current condition. The electric current density j for electrokinetic flow in a slit channel is given by[11,13]

$$j = -\frac{\epsilon RT}{a^2 F} \frac{d^2 \Psi}{dy^2} (u_p + u_e) + c_b \lambda_b \cosh(\Psi) E \tag{11}$$

where λ_b is the molar conductivity of the bulk fluid. Note that the contribution of surface conductance to electric current has been considered through the cosine hyperbolic function.[11,13] Substituting u_p and u_e in eq 11 with eq 2 and then area-averaging the new equation yield (see the Supporting Information for the derivation)

$$E_{st} = \frac{\zeta^* g_1}{4 c_b F[(1 + \beta/4) g_3 - \cosh(\Psi_0)]} P \tag{12}$$

$$g_1 = 1 - \langle \Psi/\zeta^* \rangle \quad \text{and} \quad g_3 = \langle \cosh(\Psi) \rangle \tag{13}$$

where $\beta = \lambda_b \mu / \epsilon RT$, termed the Levine number by Griffiths and Nilson,[24] is a combination of fluid properties and spans only the range $2 < \beta < 10$ for aqueous solutions.[25]

Then, replacing the electric field E in the expression of u_e in eq 2 with E_{st} and area-averaging u_p and u_e lead to

$$\langle u_e \rangle / \langle u_p \rangle = -Z \tag{14}$$

where Z, previously termed electrokinetic "figure of merit",[26] is expressed as (see the Supporting Information for the derivation)

$$Z = \frac{3 \zeta^{*2} g_1^2}{2 \kappa^{*2} [(1 + \beta/4) g_3 - \cosh(\Psi_0)]} \tag{15}$$

This Z is the key parameter in the optimal performance of electrokinetic devices including electroosmotic pumps and electrokinetic generators.[27] Apparently Z depends on three nondimensional parameters, that is, β, κ^*, and ζ^*. Moreover, a smaller β results in a higher Z. The dependence of Z on the latter two parameters are, however, not as straightforward as we see in eq 15 because g_1, g_3, and Ψ_0 are all associated with κ^* and ζ^*. It is also important to note that Z is unconditionally positive and less than unity.[27]

Solute Dispersion in Pressure-Driven Flow with Streaming Potential Effects. Combining eqs 8, 10, and 14 provides a measure of the solute dispersion in pressure-driven flow with streaming potential effects as compared to that of pressure-driven flow alone

$$K_i / K_{ip} = 1 - \delta_2 Z + \delta_3 Z^2 \tag{16}$$

$$\delta_2 = F_{ipe} / F_{ip} \quad \text{and} \quad \delta_3 = F_{ie} / F_{ip} \tag{17}$$

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As we have discussed recently on the dispersion of neutral solutes with streaming potential effects,[13] both δ_2 and δ_3 approach zero in the high limit of κ^* (widest channel) because the induced electroosmotic backflow u_e is negligible.[28] In the limit of low κ^* (narrowest channel), δ_2 approaches 2 while δ_3 approaches 1 because pressure-driven flow and electroosmotic flow both own a parabolic profile in very narrow nanochannels.[13,29] (There is a factor 2 in front of the integration in F_{ipe}, see eq 9, which should help understanding why δ_2 approaches 2 while δ_3 approaches 1 in the limit of low κ^*.) Therefore, streaming potential always reduces the solute dispersion regardless of its charge, $K_i/K_{ip} < 1$, which will be illustrated shortly. As seen from eqs 15 and 16, K_i/K_{ip} is a function of β, κ^*, ζ^*, and z_i, but independent of the molecular diffusivity D_i. The influence of β is straightforward; that is, a smaller β results in a higher Z and thus a larger K_i/K_{ip}. The influences of κ^*, ζ^*, and z_i on K_i/K_{ip} are, however, much more complicated because of the dispersion ratio's exponential dependence on these parameters.

Solute dispersion K_i is often expressed in terms of a dispersion coefficient χ_i,[13,19,21−23,30−33]

$$K_i = \chi_i Pe_i^2 D_i \qquad (18)$$

where the Peclet number Pe_i may be based either on the mean solute speed, $Pe_i = \bar{u}_i a/D_i$,[6] or on the area-averaged fluid velocity, $Pe_i = (\langle u_p \rangle + \langle u_e \rangle)a/D_i$.[8] With the solute speed-based Pe_i, χ_i becomes dependent on the solute diffusivity D_i if electroosmotic flow is present, because the solute mobility v_i appearing in $\bar{u}_i$ (see eq 5) is coupled to D_i via the Nernst−Einstein relation, $v_i = D_i/RT$. This dependence does not occur if χ_i is defined with the fluid velocity-based Pe_i. Here, we use the latter definition of Pe_i, in keeping with the dispersion studies of neutral solutes.[13,19,21−23,30−33] The dispersion coefficient χ_i in pressure-driven flow with streaming potential effects can thus be obtained from eq 8 as

$$\chi_i = F_{ip} \frac{1 - \delta_2 Z + \delta_3 Z^2}{(1 - Z)^2} \qquad (19)$$

As compared to the dimensional K_i (in unit of D_i, see eq 8), χ_i is nondimensional and independent of solute speed.

If streaming potential effects are ignored, that is, $Z = 0$ for a pure pressure-driven flow, the dispersion coefficient in eq 19 reduces to $\chi_{ip} = F_{ip}$, yielding

$$\frac{\chi_i}{\chi_{ip}} = \frac{1 - \delta_2 Z + \delta_3 Z^2}{(1 - Z)^2} \qquad (20)$$

This formula holds the same form as that we derived recently for neutral solutes ($z_0 = 0$),[13] where $\chi_{0p} = 2/105$ is the familiar

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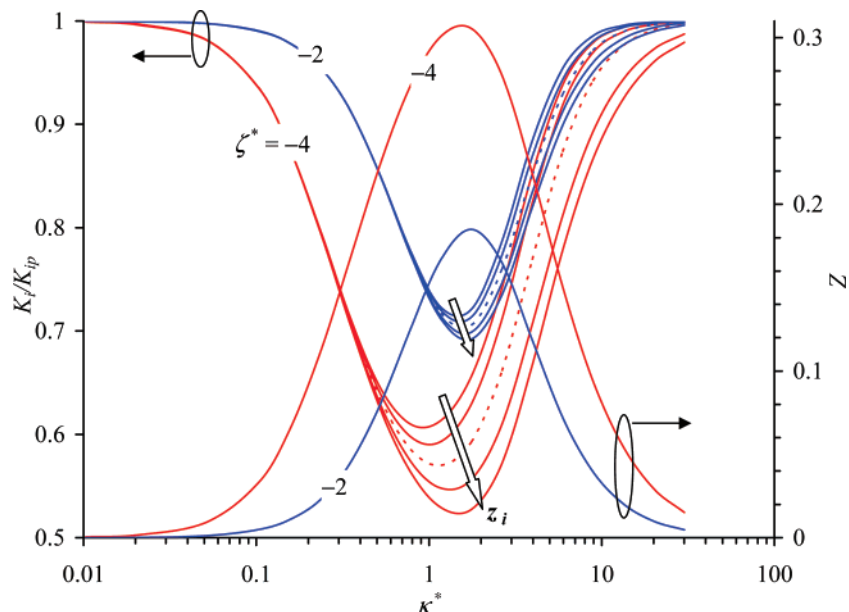(33) Wooding, R. A. *J. Fluid Mech.* **1960**, *7*, 501−515.

dispersion coefficient for pure pressure-driven flow in a slit channel.[33] Apparently the dispersion coefficient ratio χ_i/χ_{ip} differs from the dispersion ratio K_i/K_{ip} (see eq 16) only by the square of the so-called apparent viscosity ratio, $\gamma = \langle u_p \rangle/\langle u_p + u_e \rangle = 1/(1 − Z)$, which is no less than 1 and provides a measure of the streaming potential induced electroosmotic backflow, that is, electroviscous effects.[14,28] As γ is independent of the solute charge z_i, it is expected that the variation of χ_i/χ_{ip} with respect to z_i will be identical to that of K_i/K_{ip}. Other than z_i, χ_i/χ_{ip} also depends on β, κ^*, and ζ^*, just like K_i/K_{ip} does.

RESULTS AND DISCUSSION

A MATLAB program was developed to evaluate the effects of streaming potential on solute dispersion (coefficient) in nanochannels. An iterative method was first employed to determine the double layer potential Ψ_0 from eq 4. Specifically, an initial guess for Ψ_0 was used in eq 4 to calculate Ψ at the channel wall ($y = 1$). The resulting value of $\Psi(1)$ did not necessarily satisfy the required boundary condition, $\Psi(1) = \zeta^*$, so an improved value of Ψ_0 was computed based on the discrepancy between the observed and required boundary values. This process was repeated to convergence. Then, a direct numerical integration approach was applied to calculate in turn the streaming potential, "figure of merit", solute dispersion and dispersion coefficient. Typical values of the Levine number, $\beta = 5$, and of the diffusion coefficient (actually no use as alluded to above), $D_i = 10^{-11}$ m²/s, were chosen in the calculations. The nondimensional zeta potential ζ^* was fixed to -2 and -4 corresponding to a zeta potential of about -50 and -100 mV. The value of the normalized channel height κ^* was varied between 0.01 and 30. The charge number z_i was varied from -4 to $+4$ covering negative, neutral and positive solutes. (It is acknowledged that solute species with $z_i = \pm 4$ may not exist in practice. These two values are only used for demos.)

Figure 1 shows the solute dispersion ratio K_i/K_{ip} (refer to the left ordinate) at $\zeta^* = -2$ and -4 as a function of the normalized channel height κ^*. As expected, K_i/K_{ip} is less than 1 in all circumstances, indicating that streaming potential decreases the solute dispersion K_i as a consequence of the induced electroosmotic backflow. Such reduction of K_i is greater at $\zeta^* = -4$, which is attributed to the corresponding higher value of "figure of merit" Z as demonstrated in Figure 1 (refer to the right ordinate). When the charge number z_i is increased from -2 to $+2$ (indicated by the block arrows in Figure 1), K_i/K_{ip} is decreased and deviates further away from 1 over the whole range of κ^* for both values of ζ^*. For example, at $\kappa^* = 4$, streaming potential effects reduce the dispersion for z_{-2} solutes by only 15% while reducing that for z_{+2} solutes by 33%. The optimum κ^* at which K_i/K_{ip} is minimized increases with z_i at each value of ζ^* but is smaller than that at which Z is maximized. This κ^* decreases with the rise of ζ^* for all solutes though it becomes unobvious for positively charged solutes. These trends are attributed to the nonlinear dependence of K_i/K_{ip} on κ^*, ζ^*, and z_i, as noted earlier. In both the low and high limits of κ^*, Z becomes essentially zero, indicating negligible streaming potential effects, and so K_i/K_{ip} reduces to 1 as expected.

Figure 2 shows the dispersion coefficient ratio χ_i/χ_{ip} at $\zeta^* = -4$ (refer to the left ordinate) as a function of κ^*. In contrast to the decrease in solute dispersion K_i (refer to the left ordinate), which has also been included in Figure 2 for a better comparison, the dispersion coefficient χ_i is increased by the effects of streaming

Figure 1. Solute dispersion ratio K_i/K_{ip} (refer to the left ordinate) and electrokinetic figure of merit Z (refer to the right ordinate) as a function of the normalized channel height κ^*. The block arrows indicate the direction along which the charge number z_i increases.
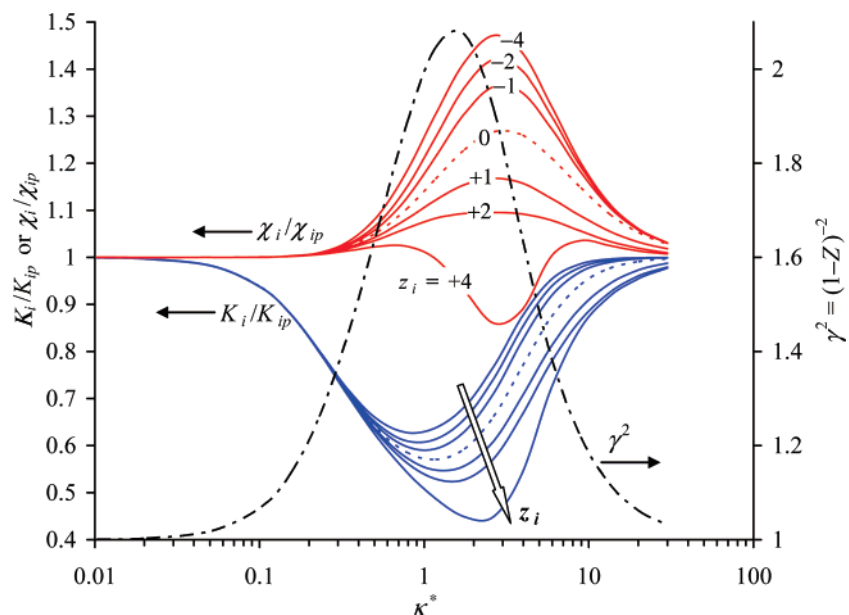

Figure 2. Solute dispersion coefficient ratio χ_i/χ_{ip} and dispersion ratio K_i/K_{ip} (refer to the left ordinate) as a function of the normalized channel height κ^* for $\zeta^* = -4$. Also shown is the square of the apparent viscosity ratio, $\gamma^2 = (1 - Z)^{-2}$ (dashed–dotted line, refer to the right ordinate). The block arrow indicates the direction along which the charge number z_i increases.

potential except for $z_i = +4$. These dissimilar trends stem from a dependence of the apparent viscosity ratio γ on κ^*, whose square, $\gamma^2 = (1 - Z)^{-2}$ as appearing in χ_i/χ_{ip} (see eq 20), is plotted as a dashed–dotted line in Figure 2 (refer to the right ordinate). When streaming potential effects increase, electroosmotic backflow increases causing a decrease in K_i/K_{ip} (and $K_i/K_{ip} < 1$) while an increase in γ^2 (and $\gamma^2 > 1$) occurs. The result is the observed variation of $\chi_i/\chi_{ip} = \gamma^2 K_i/K_{ip}$. When the solute charge z_i is increased from -4 to $+2$, χ_i/χ_{ip} decreases (and thus approaches 1), which is consistent with K_i/K_{ip} in trend because γ^2 is independent of z_i. It is, however, important to note that, for this case, a decrease in χ_i/χ_{ip} corresponds to smaller effects of streaming potential while a decrease in K_i/K_{ip} actually means greater effects of streaming potential. In addition, χ_i/χ_{ip} is more

sensitive to z_i than K_i/K_{ip} is. For example, still at $\kappa^* = 4$, streaming potential increases the dispersion coefficient for z_{-2} solutes by 40% while increasing that for z_{+2} solutes by only 9%. Moreover, χ_i/χ_{ip} attains a maximum at a relatively larger value of κ^* than that at which K_i/K_{ip} is minimized and that at which γ^2 (equivalent to Z) is maximized. The former optimum κ^* decreases when either z_i or ζ^* (not shown) is increased. Again, χ_i/χ_{ip} returns to 1 when κ^* is either very small or very large.

Another noteworthy aspect in Figure 2 is that $\chi_i/\chi_{ip} < 1$ happens for z_{+4} solutes at $1 < \kappa^* < 6$, indicating an actually reduced dispersion coefficient due to streaming potential effects. This is because the decrease in K_i/K_{ip} for z_{+4} solutes has overcome the increase in γ^2. The influence of z_i on K_i/K_{ip} and χ_i/χ_{ip} is illustrated in Figure 3 as a function of $z_i\zeta^*$ for $\zeta^* = -4$ and $\kappa^* =$
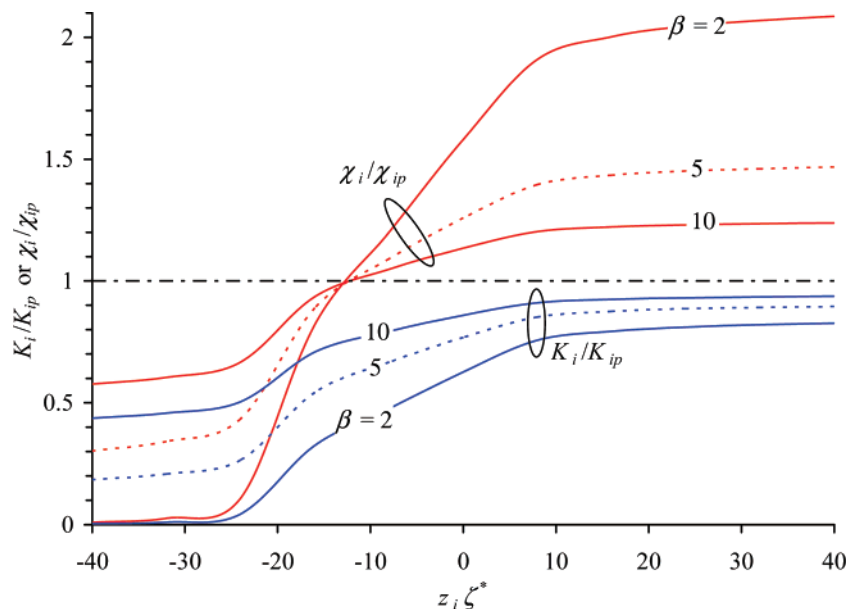
Figure 3. Solute dispersion ratio K_i/K_{ip} and dispersion coefficient ratio χ_i/χ_{ip} as a function of $z_i\zeta^*$ for $\zeta^* = -4$ and $\kappa^* = 4$.

4. Three different values of Levine number, that is, $\beta = 2$, 5, and 10, are considered. We see that streaming potential effects result in a decrease in solute dispersion ($K_i/K_{ip} < 1$) in all circumstances. This reduction is more significant at a smaller value of $z_i\zeta^*$, especially when $z_i\zeta^* < 0$ corresponding to solutes carrying a charge opposite to that of the channel wall. Such solutes are concentrated to the channel surface due to the intrinsic electric field within the electric double layer.[1–8] In contrast to the solute dispersion, streaming potential effects result in an increase in the dispersion coefficient ($\chi_i/\chi_{ip} > 1$) when $z_i\zeta^* > -12$ and a decrease ($\chi_i/\chi_{ip} < 1$) when $z_i\zeta^* < -12$. When $z_i\zeta^*$ is very large and very small, χ_i/χ_{ip} becomes nearly independent of this product. The turning point at which $\chi_i/\chi_{ip} = 1$ has unnoticeable dependence on the value of β. However, a higher β (and thus a higher Z in eq 15) does enhance the effects of streaming potential on both χ_i/χ_{ip} and K_i/K_{ip} in the whole range of $z_i\zeta^*$. We have also calculated χ_i/χ_{ip} at other values of ζ^* and κ^* and found that the turning point of $z_i\zeta^*$ slightly decreases (that is, shift to the direction of $-\infty$) when either ζ^* is increased or κ^* is decreased.

SUMMARY

We have studied the effects of streaming potential on the hydrodynamic dispersion of solutes (charged or neutral) in slit nanochannels. The pressure-driven flow and the induced electroosmotic backflow exhibit coupled dispersion effects. Analytical formulas are derived for the solute dispersion and dispersion coefficient, where the influence of streaming potential is found to be mainly dependent on the electrokinetic figure of merit. Results indicate that streaming potential effects decrease the solute dispersion in all circumstances. However, the dispersion coefficient, as traditionally defined, may be significantly increased or decreased depending on the product of $z_i\zeta^*$. These effects are strongly associated with the solute charge and should be accounted for in, for example, nanochannel chromatographic applications. The approach presented in this correspondence can also be extended to the analysis of solute dispersion in cylindrical nanochannels. However, a numerical simulation would then be required to compute the double layer potential from the Poisson–Boltzmann equation.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.