



## Short communication

## Solute transport and separation in nanochannel chromatography

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## Abstract

An analytical model is developed to study the solute transport and separation in pressure-driven liquid flow through cylindrical nanochannels. The flow-induced streaming potential is found to significantly affect the solute speed, retention and dispersion in nanochannel chromatography. These effects are sensitive to the solute charge, and found to be mainly dependent on an electrokinetic “figure of merit”.

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## 1. Introduction

Traditional chromatography utilizes a stationary phase, which may be packed or coated onto a micro-column (e.g., tube or planar substrates), to separate solutes dissolved in a mobile phase [1]. Recently, a new concept of chromatography was proposed in nanoscale channels without using a stationary phase [2,3], named here as nanochannel chromatography. In nanochannels where the hydraulic diameter is on the order of electric double layer thickness, solutes can be separated based on charge [2,3]. This separation mechanism is attributed to the solute–wall interactions via the electric field inherent to the electric double layer [4–6], which also applies to nanochannel electrophoresis [2,3,7,8].

The solute transport [2–8], separation [2–4,7,8] and dispersion [2,9] in both nanochannel chromatography and nanochannel electrophoresis have been studied. For the former case, however, the effects of streaming potential [10,11] are often neglected. The flow-induced streaming potential has been long known to generate a strong electroosmotic backflow against the pressure-driven flow in nanoscale channels, giving rise to the so-called electroviscous effects [12–14]. These two opposing flows exhibit coupled dispersion effects [15–17], the result of which is a decreased hydrodynamic dispersion while an increased dispersion coefficient of solutes (charged or neutral) in slit nanochannels [18,19]. However, the effects of stream-

ing potential on solute transport and separation in nanochannel chromatography still remain unclear. This communication aims to clarify this issue using the analytical model developed by the author [19].

## 2. Theoretical formulation

## 2.1. Solute transport in nanochannel chromatography

The local solute speed  $u_i$  in nanochannel chromatography is expressed as

$$u_i = u_p + u_e + v_i z_i F E \quad (1)$$

where  $u_p$  and  $u_e$  are the pressure-driven and electroosmotic fluid velocities,  $v_i$  the solute mobility,  $z_i$  the solute charge,  $F$  the Faraday's constant, and  $E$  the flow-induced streaming potential field. The two fluid velocities in a cylindrical nanochannel are given by [13,20]

$$u_p = \frac{a^2}{4\mu} \left( 1 - \frac{r^2}{a^2} \right) P \quad \text{and} \quad u_e = -\frac{\varepsilon \zeta}{\mu} \left( 1 - \frac{\Psi}{\zeta^*} \right) E \quad (2)$$

where  $a$  is the channel radius,  $\mu$  the fluid viscosity,  $r$  the radial coordinate,  $P$  the pressure drop per unit channel length,  $\varepsilon$  the fluid permittivity, and  $\zeta^* = F\zeta/RT$  the non-dimensional zeta potential  $\zeta$  with  $R$  the universal gas constant and  $T$  the fluid temperature. The non-dimensional double layer potential  $\Psi$  is solved from Poisson–Boltzmann equation, whose solution under

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the Debye–Huckel approximation is [10]

$$\Psi = \zeta^* \frac{I_0(\kappa r)}{I_0(\kappa a)} \quad (3)$$

where  $I_0$  denotes the zero order modified Bessel function of the first kind,  $\kappa = \sqrt{2F^2 c_b / \varepsilon RT}$  is the inverse of Debye length with  $c_b$  the ionic concentration of a symmetric, unit-charge electrolyte (e.g., KCl), and  $\kappa a$  is the normalized channel radius.

The pressure-driven flow-induced streaming potential field  $E$  is determined from the zero current condition. The electric current density  $j$  is written as [13,20]

$$j = -\frac{1}{r} \frac{d}{dr} \left( r \frac{d\Psi}{dr} \right) \frac{\varepsilon RT}{F} (u_p + u_e) + c_b \lambda_b \cosh(\Psi) E \quad (4)$$

where  $\lambda_b$  is the molar conductivity of the bulk electrolyte. Substituting  $u_p$  and  $u_e$  with Eq. (2) into Eq. (4) and then area-averaging the new Eq. (4) yield

$$E = \frac{g_1 / \zeta^*}{2c_b F (g_2 + \beta g_3 / \zeta^{*2})} P \quad (5)$$

where  $g_1 = 1 - (2I_1(\kappa a)) / (\kappa a I_0(\kappa a))$ ,  $g_2 = (I_1^2(\kappa a) / I_0^2(\kappa a)) + (2I_1(\kappa a) / \kappa a I_0(\kappa a)) - 1$ ,  $g_3 = \int_0^a \cosh(\Psi) (r/a) d(r/a)$ , and  $\beta = \lambda_b \mu / \varepsilon RT$  (previously termed Levine number [21]) is a non-dimensional combination of fluid properties spanning only the range  $2 < \beta < 10$  for normal aqueous solutions [21,22]. Thus, area-averaging  $u_p$  and  $u_e$  in Eq. (2) after replacing  $E$  with Eq. (5) leads to

$$\frac{\langle u_e \rangle}{\langle u_p \rangle} = -Z \quad (6)$$

where  $Z$  is termed electrokinetic “figure of merit” as it gauges the performance of electrokinetic energy conversion devices [23,24], and is defined as

$$Z = \frac{8g_1^2}{(\kappa a)^2 (g_2 + \beta g_3 / \zeta^{*2})} \quad (7)$$

It is noted that  $Z$  is unconditionally positive and less than 1 [24], providing a measure of the so-called electroviscous effects [25].

The solute mean speed  $\bar{u}_i$  in nanochannel chromatography is given by [2–8,26]

$$\bar{u}_i = \bar{u}_{ip} + \bar{u}_{ie} + v_i z_i F E \quad (8)$$

$$\bar{u}_{ip} = \frac{\langle u_p B_i \rangle}{\langle B_i \rangle} \quad \text{and} \quad \bar{u}_{ie} = \frac{\langle u_e B_i \rangle}{\langle B_i \rangle} \quad (9)$$

where  $\bar{u}_{ip}$  and  $\bar{u}_{ie}$  denote, respectively, the solute speed due to a pure pressure-driven flow ( $E=0$ ) and a pure electroosmotic flow ( $P=0$ ), and  $\langle \cdots \rangle = 2 \int_0^a \cdots (r/a) d(r/a)$  indicates the area-average over the channel cross-section.  $B_i = \exp(-z_i \Psi)$  characterizes the Boltzmann distribution of spherical solutes across the channel that is dependent on the solute charge  $z_i$ . The general form of  $B_i$  for charged solutes should, however, be  $B_i = \exp(-v_i z_i RT \Psi / D_i)$  where  $D_i$  is the solute diffusivity [2,4–6,26]. Combining Eqs. (8) and (9) provides a measure of the streaming potential effects on solute speed in nanochannel

chromatography,

$$\frac{\bar{u}_i}{\bar{u}_{ip}} = 1 + \frac{\langle u_e B_i \rangle + v_i z_i F \langle B_i \rangle E}{\langle u_p B_i \rangle} \quad (10)$$

## 2.2. Solute separation in nanochannel chromatography

Solute separation in chromatography is typically characterized by retention, plate height, and resolution [27]. Retention  $R_i$  in this case is defined as the ratio of the mean speed of charged solutes to that of neutral solutes,

$$R_i = \frac{\bar{u}_{ip} + \bar{u}_{ie} + v_i z_i F E}{\langle u_p \rangle + \langle u_e \rangle} \quad (11)$$

which is reduced to  $R_{ip} = \bar{u}_{ip} / \langle u_p \rangle$  for a pure pressure-driven flow. Therefore, the effects of streaming potential on solute retention are characterized by

$$\frac{R_i}{R_{ip}} = \frac{\bar{u}_i / \bar{u}_{ip}}{1 - Z} \quad (12)$$

Note that  $R_i / R_{ip}$  is reduced to 1 for neutral solutes ( $z_i = 0$ ) as alluded to above.

The plate height is the spatial variance of the solute peak distribution divided by the solute travel distance, of which the former depends on the effective diffusion due to a combination of hydrodynamic dispersion and molecular diffusion while the latter depends on the solute mean speed. Here, we examine only the effects of streaming potential on solute dispersion,  $K_i$ , which is expressed as [2,19,26,27]

$$K_i = \frac{a^2}{D_i} (F_{ip} \langle u_p \rangle^2 + F_{ipe} \langle u_p \rangle \langle u_e \rangle + F_{ie} \langle u_e \rangle^2) \quad (13)$$

$$\begin{aligned} F_{ip} &= \left\langle B_i^{-1} \left[ r^{*-1} \int_0^r (u_p^* - \bar{u}_{ip}^*) B_i r^* dr^* \right]^2 \right\rangle \langle B_i \rangle^{-1}, \\ F_{ie} &= \left\langle B_i^{-1} \left[ r^{*-1} \int_0^r (u_e^* - \bar{u}_{ie}^*) B_i r^* dr^* \right]^2 \right\rangle \langle B_i \rangle^{-1}, \quad \text{and} \\ F_{ipe} &= 2 \left\langle B_i^{-1} \left[ r^{*-1} \int_0^r (u_p^* - \bar{u}_{ip}^*) B_i r^* dr^* \right] \right. \\ &\quad \times \left. \left[ r^{-1} \int_0^r (u_e^* - \bar{u}_{ie}^*) B_i r^* dr^* \right] \right\rangle \langle B_i \rangle^{-1} \end{aligned} \quad (14)$$

where  $u_m^* = u_m / \langle u_m \rangle$ ,  $\bar{u}_{im}^* = \bar{u}_{im} / \langle u_m \rangle$  ( $m = p$  and  $e$ ), and  $r^* = r/a$ . For the cases of a pure pressure-driven flow, Eq. (13) is reduced to  $K_{ip} = F_{ip} a^2 \langle u_p \rangle^2 / D_i$ . Therefore, the effects of streaming potential on solute dispersion in nanochannel chromatography are given by

$$\frac{K_i}{K_{ip}} = 1 - \delta_2 Z + \delta_3 Z^2 \quad (15)$$

where  $\delta_2 = F_{ipe} / F_{ip}$  and  $\delta_3 = F_{ie} / F_{ip}$ . Unlike the above defined  $\bar{u}_i / \bar{u}_{ip}$  and  $R_i / R_{ip}$ , the dispersion ratio  $K_i / K_{ip}$  is independent of solute diffusivity.

Hydrodynamic dispersion  $K_i$  is often expressed in terms of a dispersion coefficient  $\chi_i$  as  $K_i = \chi_i Pe_i^2 D_i$  [2,9,18,19,26,28–31],

where the Peclet number is based on the mean fluid velocity,  $Pe_1 = (\langle u_p \rangle + \langle u_e \rangle) a / D_i$ , in keeping with the dispersion studies of neutral solutes [15–19,28–31]. As such, the dispersion coefficient is derived as

$$\chi_i = F_{ip} \frac{1 - \delta_2 Z + \delta_3 Z^2}{(1 - Z)^2} \quad (16)$$

If streaming potential effects are ignored, i.e.,  $Z=0$ ,  $\chi_i$  reduces to  $\chi_{ip} = F_{ip}$ , yielding

$$\frac{\chi_i}{\chi_{ip}} = \frac{1 - \delta_2 Z + \delta_3 Z^2}{(1 - Z)^2}. \quad (17)$$

Therefore,  $\chi_i/\chi_{ip}$  differs from  $K_i/K_{ip}$  by only the square of the apparent viscosity ratio in electroviscous effects, i.e.,  $\gamma = 1/(1 - Z)$  [25]. As  $\gamma$  is independent of the solute charge  $z_i$ , it is expected that the variation of  $\chi_i/\chi_{ip}$  with respect to  $z_i$  will be identical to that of  $K_i/K_{ip}$ .

### 3. Results and discussion

A MATLAB program was written to examine the streaming potential effects on solute speed, retention and dispersion in nanochannel chromatography. The zeta potential was fixed to  $\zeta = -25$  mV (or  $\zeta^* = -0.973$ ) in compliance with the Debye–Hückel approximation [10,13]. The solute diffusivity was selected as  $D_i = 10^{-10}$  m<sup>2</sup>/s, and the Levine number was  $\beta = 4$  [21,22].

Fig. 1 shows the ratio of solute mean speed,  $\bar{u}_i/\bar{u}_{ip}$ , as a function of the normalized channel radius  $\kappa a$ . As expected, streaming potential effects reduce the solute speed due to the induced electroosmotic backflow. This reduction varies with solute charge  $z_i$  and attains a minimum at about  $\kappa a = 3$ , where the figure of merit  $Z$  (dashed line, refer to the right ordinate) reaches its maximum indicating the largest streaming potential effects. In both the high and low limits of  $\kappa a$ , streaming potential effects become negligible, i.e.,  $Z \rightarrow 0$ . Accordingly,  $\bar{u}_i/\bar{u}_{ip}$  reduces to 1 for all solutes at large  $\kappa a$  while varying with  $z_i$  at small  $\kappa a$  because of the finite solute mobility.

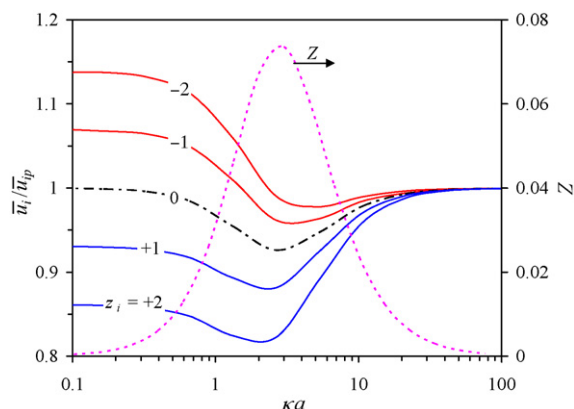


Fig. 1. Solute speed ratio  $\bar{u}_i/\bar{u}_{ip}$  (refer to the left ordinate) and electrokinetic “figure of merit”  $Z$  (dashed line, refer to the right ordinate) as a function of the normalized channel radius  $\kappa a$ .

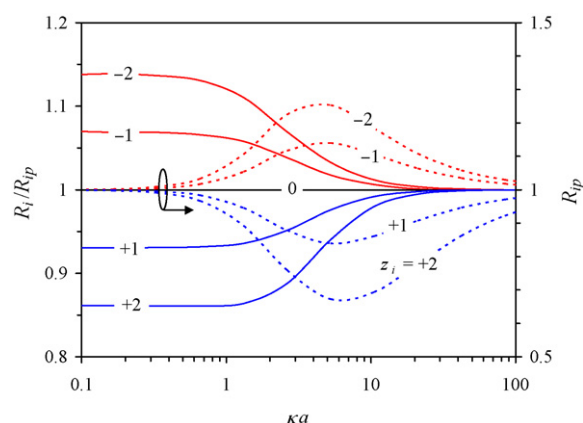


Fig. 2. Solute retention ratio  $R_i/R_{ip}$  (refer to the left ordinate) and solute retention  $R_{ip}$  in a pure pressure-driven flow (dashed lines, refer to the right ordinate) as a function of the normalized channel radius  $\kappa a$ .

Fig. 2 shows the ratio of solute retention,  $R_i/R_{ip}$ , as a function of  $\kappa a$ . Over the range of  $\kappa a$ , streaming potential effects reduce the retention of positive solutes (i.e.,  $R_i/R_{ip} < 1$ ) while enhancing that of negative solutes (i.e.,  $R_i/R_{ip} > 1$ ). These effects get weak when  $\kappa a > 1$ . As  $R_{ip} < 1$  for positive solutes (or more generally,  $z_i \zeta^* < 0$ ) and  $R_{ip} > 1$  for negative solutes (or  $z_i \zeta^* > 0$ ) in a pure pressure-driven flow (dashed lines, refer to the right ordinate), streaming potential effects favorably improve the solute separation in nanochannel chromatography.

The ratios of solute dispersion,  $K_i/K_{ip}$ , and dispersion coefficient,  $\chi_i/\chi_{ip}$ , are both displayed in Fig. 3 for a better comparison. In all cases,  $K_i/K_{ip}$  is less than 1 indicating that streaming potential effects result in a decrease in hydrodynamic dispersion. This reduction, as a consequence of the induced electroosmotic backflow, gets larger (i.e.,  $K_i/K_{ip}$  deviates further away from 1) when the solute charge  $z_i$  increases. The optimum  $\kappa a$  at which  $K_i/K_{ip}$  achieves its extreme increases slightly with  $z_i$  but remains smaller than that at which the figure of merit  $Z$  or the apparent viscosity ratio  $\gamma$  (dashed line, refer to the right ordinate) is maximized.

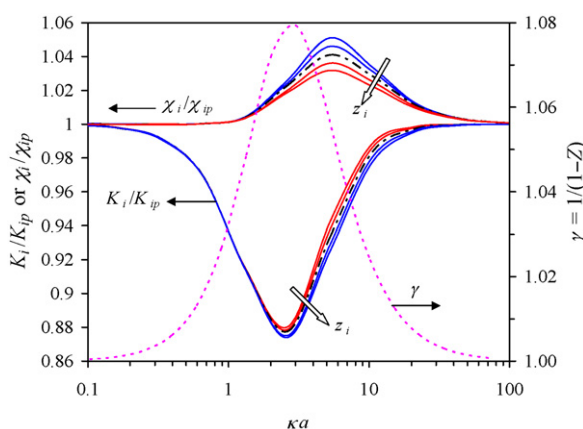


Fig. 3. Solute dispersion ratio  $K_i/K_{ip}$  and dispersion coefficient ratio  $\chi_i/\chi_{ip}$  (both refer to the left ordinate) as a function of the normalized channel radius  $\kappa a$ . Also illustrated is the apparent viscosity ratio,  $\gamma = 1/(1 - Z)$  (dashed line, refer to the right ordinate). The block arrows indicate the direction along which the solute charge number  $z_i$  increases from  $-2$  to  $+2$ .

In contrast to the decrease in solute dispersion, Fig. 3 indicates that the dispersion coefficient is increased by the effects of streaming potential, i.e.,  $\chi_i/\chi_{ip} > 1$ . These dissimilar trends stem from the dependence of  $\gamma$  on  $\kappa a$ . As streaming potential effects increase (i.e., an increase in  $Z$ ), electroosmotic backflow increases causing a decrease in  $K_i/K_{ip}$  (and  $K_i/K_{ip} < 1$ ) while an increase in  $\gamma$  (and  $\gamma > 1$ ). The net result is the observed variation of  $\chi_i/\chi_{ip}$  with  $\kappa a$ . The increase in dispersion coefficient is more sensitive to  $z_i$  than the decrease in dispersion. However, the trend that  $\chi_i/\chi_{ip}$  varies with respect to  $z_i$  is consistent with  $K_i/K_{ip}$  as pointed out earlier. In addition,  $\chi_i/\chi_{ip}$  attains a maximum at a larger value of  $\kappa a$  than that at which  $K_i/K_{ip}$  is minimized. The former optimum  $\kappa a$  is also larger than that at which  $Z$  or  $\gamma$  is maximized.

We have also calculated the solute dispersion at lower zeta potentials (i.e.,  $\zeta < -25$  mV, data not shown for brevity), where the effects of streaming potential on  $K_i/K_{ip}$  and  $\chi_i/\chi_{ip}$  are both diminished due to the smaller  $Z$  value. The variations of both ratios with respect to the solute charge  $z_i$  also get smaller. In addition, it is important to note that the solute dispersion in nanochannels is generally much smaller than the diffusion, i.e.,  $K_i/D_i = \chi_i Pe_i^2 \ll 1$ , unless  $Pe_i = O(1)$  because the dispersion coefficient  $\chi_i = O(0.1)$  [2,9,18,19]. This Peclet number requires the mean fluid velocity be on the order of 2 mm/s in a 100 nm diameter nanochannels (corresponding to  $\kappa a \approx 5$ ), which may be generated readily in nanofluidics [32].

#### 4. Conclusion

We have developed an analytical model to examine the effects of streaming potential on solute transport and separation in nanochannel chromatography. It is found that the streaming potential-induced electroosmotic backflow reduces the solute speed. The solute separation is, however, enhanced by the streaming potential effects because the resulting solute retention deviates further away from 1 for both positive and negative solutes. It is also found that streaming potential effects decrease the solute dispersion while increasing the dispersion coefficient as traditionally defined. All these influences are sensitive to the solute charge, and can be correlated with an electrokinetic “figure of merit”.

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