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Streaming potential effects on solute dispersion in nanochannels

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This Supporting Information includes the derivation of the pressure-driven flow induced streaming potential field, eq 12, and the derivation of the electrokinetic “figure of merit”, eq 15.

Combining equations 2 and 11 yields the electric current density \( j \) in electrokinetic flow along a slit channel,

\[
 j = -\frac{eRT}{2\mu F} \frac{d^2\Psi}{dy^2} (1 - y^2) + \frac{\varepsilon^2 \zeta RT}{a^2 \mu F} \frac{d^2\Psi}{dy^2} \left( 1 - \frac{\Psi}{\zeta} \right) E + c_b \lambda_b \cosh(\Psi)E. \tag{S1}
\]

The zero electric current in a steady-state pressure-driven flow forces

\[
 0 = -\frac{eRT}{2\mu F} \int_0^1 \frac{d^2\Psi}{dy^2} (1 - y^2)dyP + \frac{\varepsilon^2 \zeta RT}{a^2 \mu F} \int_0^1 \frac{d^2\Psi}{dy^2} \left( 1 - \frac{\Psi}{\zeta} \right) dyE_{st} + c_b \lambda_b \int_0^1 \cosh(\Psi)dyE_{st}. \tag{S2}
\]

Therefore, the induced streaming potential field is determined as
Employing the integration by parts rewrites eq S3 as

\[
E_{st} = \frac{\varepsilon RT}{2 \mu F} \int_0^1 \frac{d^2 \Psi}{dy^2} \left(1 - y^2 \right) dy - \frac{\varepsilon^2 \zeta RT}{a^2 \mu F} \int_0^1 \frac{d^2 \Psi}{dy^2} \left(1 - \frac{\Psi}{\zeta^2} \right) dy + c_b \lambda_b \int_0^1 \cosh(\Psi) dy \cdot P. \tag{S3}
\]

Employing the integration by parts rewrites eq S3 as

\[
E_{st} = \frac{\varepsilon RT \zeta^*}{\mu F} g_1 - \frac{\varepsilon^2 R^2 T^2}{a^2 \mu F^2} \int_0^1 \left( \frac{d\Psi}{dy} \right)^2 dy + c_b \lambda_b g_3 \cdot P \tag{S4}
\]

where the functions \( g_1 \) and \( g_3 \) are as defined in the main text. Multiplying the two sides of the Poisson-Boltzmann equation by \( 2d\Psi/dy \) and then integrating the new eq 3 leads to

\[
\left( \frac{d\Psi}{dy} \right)^2 = 2\kappa^{*2} \left[ g_3 - \cosh(\Psi_0) \right]. \tag{S5}
\]

Thus, eq S4 can be simplified to eq 12 after mathematical manipulations, wherein the expression \( \kappa^{*2} = 2a^2 F^2 c_b / \varepsilon RT \) has been invoked.

As for the definition of electrokinetic “figure of merit”, we first get the following relationship by area-averaging the two fluid velocity components in eq 2

\[
\frac{\langle u_e \rangle}{\langle u_p \rangle} = \frac{3\varepsilon \zeta}{a^2 g_1} \frac{E_{st}}{P}. \tag{S6}
\]

Then, replacing \( E_{st} \) with eq 12 and invoking \( \kappa^{*2} = 2a^2 F^2 c_b / \varepsilon RT \) again receive

\[
\frac{\langle u_e \rangle}{\langle u_p \rangle} = - \frac{3\zeta^{*2} g_1^2}{2\phi^2 \left[ (1 + \beta / 4) g_3 - \cosh(\Psi_0) \right]} = -Z. \tag{S7}
\]