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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,

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

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

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

Therefore, the induced streaming potential field is determined as

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

Employing the integration by parts rewrites eq S3 as

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

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

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

Thus, eq S4 can be simplified to eq 12 after mathematical manipulations, wherein the expression $\kappa^{*2}=2a^2F^2c_b/\varepsilon RT$ 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 $\kappa^{*2}=2a^2F^2c_b/\varepsilon RT$ again receive

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