Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Ion size effect on electrostatic and electroosmotic properties in soft nanochannels with pH-dependent charge density – Supplementary Information

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## 1. Derivation of Eq.(24) from Eq.(4) in the main paper.

We can write Lagrangian for the present physical system as follows:

In the region of $-h \le y \le -h+d$ ,

$$L = \int \left( -\frac{\varepsilon_0 \varepsilon_r}{2} |\nabla \psi|^2 + e_0 \psi (n_+ - n_-) + e_0 \psi \left( n_{H^+} - n_{OH^-} \right) - e_0 \varphi(y) n_{A^-} \psi - Ts - \mu_+ n_+ - \mu_- n_- - \mu_{H^+} n_{H^+} - \mu_{OH^-} n_{OH^-} \right) dr$$
$$+ \alpha \left[ N_p - \frac{\sigma}{a^3} \int_{-h}^{-h+d} \varphi(y) dy \right]$$

(1-1)

In the region of $-h+d \le y \le 0$ ,

$$L = \int \left( -\frac{\varepsilon_0 \varepsilon_r}{2} |\nabla \psi|^2 + e_0 \psi (n_+ - n_-) + e_0 \psi \left( n_{H^+} - n_{OH^-} \right) - e_0 \varphi(y) n_{A^-} \psi - Ts - \mu_+ n_+ - \mu_- n_- - \mu_{H^+} n_{H^+} - \mu_{OH^-} n_{OH^-} \right) dr$$

(1-2)

Here $\alpha$ is the Lagrangian undetermined multiplier.

As we proved in the main paper, the entropy density are given by the following equation.

$$s = k_B \left( N \ln N - n_+ \ln n_+ - n_- \ln n_- - n_{H^+} \ln n_{H^+} - n_{OH^-} \ln n_{OH^-} \right) - k_B \left( N - n_+ - n_- - n_{H^+} - n_{OH^-} \right) \ln \left( N - n_+ - n_- - n_{H^+} - n_{OH^-} \right)$$

(1-3)

Considering the fact that $n_{A^-}$ isn't relevant to $n_+$, we can get

$$\frac{\partial n_{A^-}}{\partial n_+} = 0\,. \tag{1-4}$$

On the other hand,

$$\frac{\partial \varphi}{\partial n_+} = \frac{\partial n_{H^+}}{\partial n_+} = \frac{\partial n_{OH^-}}{\partial n_+} = \frac{\partial n_-}{\partial n_+} = \frac{\partial \psi}{\partial n_+} = \frac{\partial (\nabla \psi)}{\partial n_+} = 0\,. \tag{1-5}$$

Using Eq. (1-3, 1-4 and 1-5), we can get the variation of the Lagrangian with respect to $n_+$.

$$\frac{\delta L}{\delta n_+} = e_0\psi - \mu_+ - T\frac{\partial s}{\partial n_+} = e_0\psi - \mu_+ - k_B T\left(-\ln n_+ - 1 + \ln\left(N - n_+ - n_- - n_{H^+} - n_{OH^-}\right) + 1\right) = 0 \tag{1-6}$$

## 2. Derivation of Eq. (47) in the main paper

$$\frac{\delta L}{\delta n_+} = e_0\psi - \mu_+ - k_B T\left(-\ln n_+ - 1 + \ln\left(N - n_+ - n_- - n_{H^+} - n_{OH^-}\right) + 1\right) = 0 \tag{2-1}$$

Considering $\psi(x \to \infty) = 0$ and $n_+(x \to \infty) = n_{+,\infty}$, we derive the chemical potential of the positive ions in the present system:

$$\mu_+ = k_B T \ln \frac{n_{+\infty}}{N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}}\,. \tag{2-2}$$

Substituting Eq.(2-2) into Eq. (2-1) yields the following equation:

$$e\psi + k_B T \ln \frac{n_+\left(N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}\right)}{n_{+\infty}\left(N - n_+ - n_- - n_{H^+} - n_{OH^-}\right)} = 0\,. \tag{2-3}$$

Rearranging Eq. (2-3) yields the following equation:

$$n_+ = n_{+,\infty}\frac{N - n_+ - n_- - n_{H^+} - n_{OH^-}}{N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}}\exp\left(-\frac{e_0\psi}{k_B T}\right)\,. \tag{2-4}$$

In the same way as in the case of $n_+$, corresponding equations for $n_-$, $n_{OH^-}$ and $n_{H^+}$ are obtained

$$n_- = n_{-,\infty}\frac{N - n_+ - n_- - n_{H^+} - n_{OH^-}}{N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}}\exp\left(\frac{e_0\psi}{k_B T}\right), \tag{2-5}$$

$$n_{OH^-} = n_{OH^-,\infty}\frac{N - n_+ - n_- - n_{H^+} - n_{OH^-}}{N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}}\exp\left(\frac{e_0\psi}{k_B T}\right), \tag{2-6}$$

$$n_{H^+} = n_{H^+,\infty} \frac{N - n_+ - n_- - n_{H^+} - n_{OH^-}}{N - n_{+\infty} - n_{-\infty} - n_{H^+\infty} - n_{OH^-\infty}} \exp\left(-\frac{e_0\psi}{k_B T}\right). \tag{2-7}$$

Dividing Eq. (2-4) , Eq. (2-6) and Eq. (2-7) by Eq. (2-5) results in the following equations:

$$\frac{n_+}{n_-} = \frac{n_{+,\infty}}{n_{-,\infty}} \exp\left(-\frac{2e_0\psi}{k_B T}\right), \tag{2-8}$$

$$\frac{n_{OH^-}}{n_-} = \frac{n_{OH^-\infty}}{n_{-,\infty}} , \tag{2-9}$$

$$\frac{n_{H^+}}{n_-} = \frac{n_{H^+\infty}}{n_{-,\infty}} \exp\left(-\frac{2e_0\psi}{k_B T}\right), \tag{2-10}$$

Substituting Eqs. (2-8), (2-9) and (2-10) into Eq. (2-5), we can get the following equation:

$$n_- = n_{-,\infty} \frac{1 - n_- v_0 \left(\frac{n_{+\infty}}{n_{-\infty}} \exp\left(-\frac{2e_0\psi}{k_B T}\right) + 1 + \frac{n_{OH^-\infty}}{n_{-\infty}} + \frac{n_{H^+\infty}}{n_{-\infty}} \exp\left(-\frac{2e_0\psi}{k_B T}\right)\right)}{1 - \left(n_{+\infty} + n_{-\infty} + n_{H^+} + n_{OH^-}\right) v_0} \exp\left(\frac{e_0\psi}{k_B T}\right). \tag{2-11}$$

Rearrangement of Eq. (2-11) provides the following equation:

$$n_- = \frac{n_{-\infty} \exp\left(\frac{e_0\psi}{k_B T}\right)}{D_0}, \tag{2-12}$$

$$n_+ = \frac{n_{+\infty} \exp\left(-\frac{e_0\psi}{k_B T}\right)}{D_0}, \tag{2-13}$$

$$n_{OH^-} = \frac{n_{OH^-\infty} \exp\left(\frac{e_0\psi}{k_B T}\right)}{D_0}, \tag{2-14}$$

$$n_{H^+} = \frac{n_{H^+\infty} \exp\left(-\frac{e_0\psi}{k_B T}\right)}{D_0}, \tag{2-15}$$

where

$$D_0 = \left(1 - n_{+\infty} v_0 - n_{-\infty} v_0 - n_{H^+\infty} v_0 - n_{OH^-\infty} v_0\right) + n_{+\infty} v_0 \exp\left(-\frac{e_0\psi}{k_B T}\right) + n_{-\infty} v_0 \exp\left(\frac{e_0\psi}{k_B T}\right) + n_{OH^-\infty} v_0 \exp\left(\frac{e_0\psi}{k_B T}\right) + n_{H^+\infty} v_0 \exp\left(-\frac{e_0\psi}{k_B T}\right). \tag{2-16}$$