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Short communication

# Analytical expressions for the electroosmotic flow in a charge-regulated circular channel

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ABSTRACT

Analytical expressions are derived for the flow velocity and ionic current for the electroosmotic flow (EOF) in a charge-regulated circular channel, focusing on the effect of types of ions and their concentrations. We show that the mean flow velocity for those two cases can be different both quantitatively and qualitatively, implying that the true charged conditions can be inferred by appropriately designed experiments. The types of ionic species and their concentrations are also found to play a significant role. Both the EOF velocity and the current density increase with increasing ionic concentration, in general. However, the reverse trend is also observed at a sufficiently high ionic concentration.

## 1. Introduction

Due to recent applications of microfluidics and nanofluidics in versatile areas such as characterization/sensing of single bio-entities [1], energy conversion [2–4], and ionic diodes [5–7], there is a need for a detailed understanding of the fields associated with micro- or nano-scaled devices. In addition to fluid velocity, these fields can also be characterized by ionic current/conductance [8–10]. Therefore, the transport of ionic species inside that device and the mechanisms of the corresponding electrokinetic phenomena need be known.

The electrically driven flow of a salt solution in a channel originates from its charged surface. Often, the charge density on the channel surface is assumed to be independent of the solution properties [11–15]. This is usually unrealistic for many kinds of surfaces including organic and metal oxide, where their charged conditions and the associated fields depend highly on solution properties such as pH [16–22]. Tseng et al. modeled the electroosmotic flow (EOF) in a pH-regulated, cylindrical nanochannel containing multiple ionic species, focusing on the flow field [23] and ionic current [24]. To simulate the buffer effect on the ionic conductance in a pH-regulated nanochannel, Mei et al. [25] proposed using a four layer model. These studies all reveal that the influence of the charged conditions on a channel on the electrokinetic behavior inside it is significant.

Here, the EOF in a charge-regulated circular channel is solved analytically for the flow velocity and ionic current, focusing on the effect of the types of ions and their concentrations. The main difference in the flow behaviors arising from assuming a constant surface potential and a constant surface charge is also discussed.

## 2. Theory

We consider the electroosmotic flow (EOF) of an aqueous, incompressible, Newtonian salt solution containing ionic species $i$ of valence $z_i$ and molar concentration $C_i$ in a long, charged cylindrical channel subject to an applied uniform electric field $\mathbf{E}_\infty$ of strength $E_\infty$. The cylindrical coordinates $(r,\theta,z)$ are adopted with the origin on the channel axis; $r$, $\theta$, and $z$ are the radial, the angular, and the axial coordinates, respectively, and $\mathbf{E}_\infty$ is in the $z$ direction. The electrical potential arising from the channel wall, $\psi_{\mathrm{DL}}(r,\theta)$, is $z$ independent, that is, $\psi_{\mathrm{DL}} = \psi_{\mathrm{DL}}(r,\theta)$. The electrical potential, $\psi_{\mathrm{tot}}$, comprises $\psi_{\mathrm{DL}}$ and that from $\mathbf{E}_\infty$,

$$\psi_{\mathrm{tot}}(r,\theta,z) = \psi_{\mathrm{DL}}(r,\theta) + \psi_\infty(z), \tag{1}$$

where $\mathbf{E}_\infty = -\nabla\psi_\infty$. Suppose that the channel surface has amphoteric functional groups AB with associated dissociation reactions

$$\mathrm{AB}_2^+ \leftrightarrow \mathrm{AB} + \mathrm{B}^{Z+} \tag{2}$$

$$\mathrm{AB} \leftrightarrow \mathrm{A}^{Z-} + \mathrm{B}^{Z+} \tag{2a}$$

$\mathrm{B}^{Z+}$ is the dissociated ion of valence $Z$. Let $K_+$ and $K_-$ be the equilibrium constants for the reactions expressed in Eqs. (2) and (2a),

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respectively. Because the surface charge, $AB_2^+$ and $A^{Z-}$, depends on the concentration of $B^{Z+}$ in the bulk solution, it is called the potential determining ion (PDI). For organic surfaces, $B^{Z+}$ is usually $H^+$, and for the inorganic ones, $B^{Z+}$ can be the ion dissociated from ionic solids (e.g., $Ag^+$ from AgI). Note that ions different from PDI might also present, but they do not affect the chemical equilibria on the channel surface and, therefore, called indifferent ions (IDI). If the surface potential $\psi_s$ is low, the net surface charge density $\sigma$ is [26,27]

$$\sigma = \Xi - \Gamma\psi_s, \tag{3}$$

where

$$\Xi = \sigma_0 \frac{\delta \sinh(\psi_N)}{1+\delta\cosh(\psi_N)} \tag{4}$$

$$\Gamma = \frac{\sigma_0}{\psi_0}\frac{\delta\cosh(\psi_N)+\delta^2}{[1+\delta\cosh(\psi_N)]^2} \tag{4a}$$

$\sigma_0 = FZN_s$, $\psi_0 = RT/F$, $\psi_N = 2.303(\mathrm{pK_0} - \mathrm{pB})$, $\mathrm{pK_0} = (\mathrm{pK_+} + \mathrm{pK_-})/2$, and $\delta = 2 \times 10^{-\Delta \mathrm{pK}/2}$, where $N_s$, $F$, $R$, and $T$ are the molar density of AB, Faraday constant, gas constant, and the absolute temperature, respectively. The sign of $\psi_N$ depends upon that of the surface charge. $\Delta\mathrm{pK} = \mathrm{pK_-} - \mathrm{pK_+}$; the larger the $\Delta$pK the lower the surface charge density. For two same surfaces having a small $\Delta$pK, their surface potential maintains about constant as their separation distance varies, but their surface charge remains about constant if $\Delta$pK is large [28]. However, the influence of $\Delta$pK on EOF has not been discussed previously.

If the electrical potential coming from the charged channel is low, it can be shown that

$$\psi_{\mathrm{DL}} = \frac{\Xi}{\varepsilon\kappa\frac{I_1(\kappa a)}{I_0(\kappa a)}+\Gamma}\frac{I_0(\kappa r)}{I_0(\kappa a)} \tag{5}$$

$I_0$ is the modified Bessel function of the first kind of order zero, $\varepsilon$ the permittivity of the liquid phase, and $\kappa = \left(F^2\sum_i Z_i{}^2 C_{i\infty}/\varepsilon RT\right)^{1/2}$. Because the potential on the channel axis might not vanish, $C_{i\infty}$ is regarded as a reference concentration, the value of $C_i$ corresponding to $\psi \to 0$ [29].

The fluid velocity in the $z$ direction, $v_z$, is $z$ independent, and if no pressure drop is applied, then at steady state

$$\rho v_z \cdot \nabla v_z = \mu\nabla^2 v_z + \rho_E E_\infty \tag{6}$$

$\nabla^2$ is the Laplace operator, $\mu$ the fluid viscosity, and $\rho$ the fluid density. Since $v_z$ is supposed to be independent of $z$, $v_z \cdot \nabla v_z = 0$. The space charge density in the liquid phase $\rho_E$ is

$$\rho_E = -\varepsilon\nabla^2\psi_{\mathrm{DL}} \tag{7}$$

Substituting Eqs. (7) into (6) yields

$$\nabla^2\left(v_z - \frac{\varepsilon E_\infty}{\mu}\psi_{\mathrm{DL}}\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\phi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\phi}{\partial\theta^2} = 0, \tag{8}$$

where $\phi = v_z - \frac{\varepsilon E_\infty}{\mu}\psi_{\mathrm{DL}}$. We assume the following boundary conditions:

$$\frac{d\phi}{dr} = 0 \text{ at } r{=}0 \tag{9}$$

$$\phi = \phi_s = -\frac{\varepsilon E_\infty}{\mu}\psi_s \text{ at } r{=}a \tag{10}$$

$\psi_s = \Xi/\left[\varepsilon\kappa\frac{I_1(\kappa a)}{I_0(\kappa a)} + \Gamma\right]$ is the electrical potential on the channel wall obtained from Eq. (5). Because $\phi_s \neq \phi_s(\theta)$, Eqs. (9)–(10) suggest that $\phi$ is constant. It can be shown that

$$v_z = \frac{\varepsilon E_\infty}{\mu}\left\{\psi_{\mathrm{DL}} - \frac{\Xi}{\varepsilon\kappa\frac{I_1(\kappa a)}{I_0(\kappa a)}+\Gamma}\right\} \tag{11}$$

This is similar to the Smoluchoski's result for a planar surface. The averaged EOF velocity $\langle v_z\rangle$ is

$$\langle v_z\rangle = \frac{\iint_{A_p} v_z dA}{A_p} = \frac{\varepsilon E_\infty}{\mu}\frac{\Xi}{\varepsilon\kappa\frac{I_1(\kappa a)}{I_0(\kappa a)}+\Gamma}\left(\frac{2}{\kappa a}\frac{I_1(\kappa a)}{I_0(\kappa a)} - 1\right) \tag{12}$$

$A_p$ is the cross section area of the channel. The following limiting cases apply:

$$\langle v_z\rangle = \frac{\varepsilon E_\infty}{\mu}\frac{\Xi}{\varepsilon\kappa+\Gamma}\left(\frac{2}{\kappa a} - 1\right), \text{ as } \kappa a \to \infty \tag{12a}$$

$$\langle v_z\rangle = -\frac{\varepsilon E_\infty}{\mu}\frac{\Xi}{\Gamma}, \text{ as } \kappa a \to 0 \tag{12b}$$

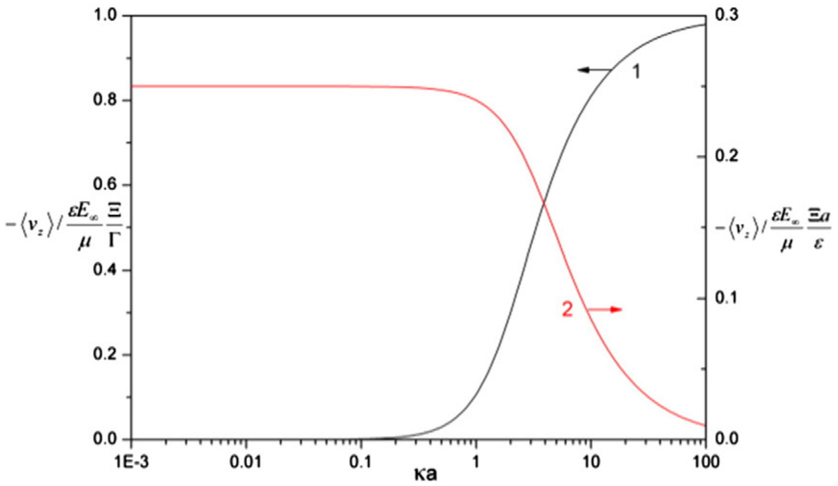

**Fig. 1.** Variation of the scaled averaged EOF velocity with $\kappa a$. Curve 1: constant surface potential; 2: constant surface charge density.