Streaming Potential in Narrow Fluidic Confinements - A Theoretical Perspective

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Abstract

Streaming potential is one of the four major electrokinetic phenomena where the flow of aqueous electrolytes due to an applied axial pressure gradient causes the generation of an induced axial electric field. The field may be evaluated by considerations of a net zero current due to the absence of an applied axial electric field. We elaborate on the theoretical aspects of streaming potential from fundamental considerations of electrostatics and fluid mechanics. Later, we focus on an exciting and futuristic application of streaming potential, where the induced electric field is tapped to drive a current through an external resistor thereby allowing one to convert mechanical energy into electrical energy.

1. INTRODUCTION

Miniaturization of many devices having functionalities such as flow actuation, mixing, energy generation, particle separation etc. have been made possible in recent times due to several novel fabrication techniques [1-12]. Shrinking the pertinent length scales down to several tens of nanometers unveils a large number of phenomena which affect the transport processes that are otherwise negligible or absent at larger scales. A prominent example of one such phenomenon is the spontaneous charging of the walls of the substrate (channel) in the presence of an aqueous electrolyte. The presence of a charged substrate leads to Coulombic forces of attraction and repulsion on oppositely and like-charged species (counterions and coions respectively); the result of this being the formation of a charged interfacial layer near the wall. This makes flow manipulation by electric fields a very viable option due to advantages such as ease of on-chip integration (electrode sputtering), low solutal dispersion and so on [13-16]. The transport processes where such a charged mobile layer interacts or induces electric fields due to relative motion between the substrate and solution are collectively termed as electrokinetics [13-16]. Broadly speaking, this encompasses electroosmosis (generation of flow in aqueous solutions by the application of an applied electric field), electrophoresis (electric field induced transport of particles), streaming potential (generation of electric field due to a pressure driven transport of aqueous solution) and sedimentation potential (generation of electric field due to gravity driven sedimentation of charged particles) [13-16]. In this article, we focus on the fundamental aspects of streaming potential and attempt to quantify the same beginning from basic considerations of distribution of charges in the aqueous solution and the concomitant fluid flow.

From the above discussion, it is clear that the presence of a charged layer close to the wall is pivotal to all the electrokinetic phenomena. The charged interfacial layer, known as the electrical double layer (EDL), will therefore be the first topic of study in this article. The region near the walls is charged while the bulk region remains neutral. When this aqueous solution is driven by an axially applied pressure gradient, there is a net flux of ions downstream which is also known as streaming current or the advection current [15-16]. For example, as depicted in Fig. 1, the negatively charged walls lead to a net positively charged mobile layer which leads to a net positive advection current. However, in the absence of any externally applied electric field (as opposed to an external applied electric field in the case of electroosmosis), we cannot have a net positive advection current alone. In such a case, the bulk
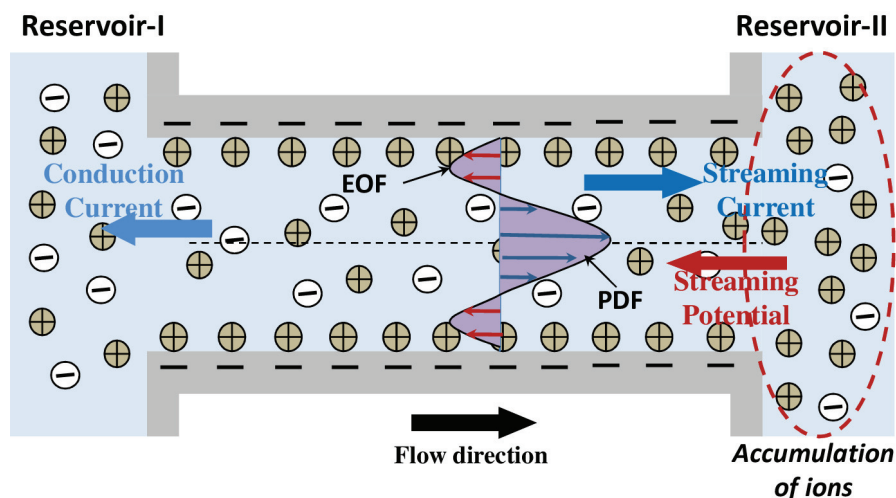
Figure 1. Schematic of the flow of an aqueous electrolyte in a channel with negatively charged walls. Near the wall, the EDL tends to contain excessive positive ions. The pressure driven flow causes a fluid flow from the left to the right. The current due to downstream advection is the streaming current while the current due to the conduction in the bulk is the conduction current which is caused due to an electric field acting from right to left in this case. Owing to the excess positive ions near the wall, the effect of the electric field is to push them towards the left, as obvious by the back flow close to the wall.

conductivity of the aqueous solution offers a path for an induced back-current known as the conduction current, which is nothing but the induced electric field times the conductivity of the aqueous electrolyte solution. As a matter of fact, the sum total of both these currents must be identically zero owing to the fact that there is no external electric field present to drive any currents - this constraint is often referred to as electroneutrality of current; violation of the current electroneutrality would imply presence of electric currents without any applied electric field, and thus, is physically implausible [15-16]. We note that the magnitude of the conduction current is *not* independent of the streaming current; rather, it is generated in a feedback-like system based on the 'input' streaming current. If there is a large pressure gradient driving the flow, the larger advection of ions lead to a high advective or streaming current. Now, the electroneutrality of current constraint dictates that the conduction current must balance this streaming current, i.e. the conduction current is equal in magnitude but opposite in direction to the streaming current. Thus, for a fixed bulk conductivity, we would expect a higher induced electric field for a larger streaming current, implying that the conduction current varies with the nature of the streaming current. Notably, at equilibrium when there is no flow, there is no streaming current and hence no conduction current.

Apart from the streaming current, there exists an electromigration (or a conduction) current through the bulk of the fluid. This current explicitly depends on the magnitude of the induced electric field through an Ohm's law-like description of the current [15-16]. The downstream advection of the net positive solution leads to a net positive charge accumulation downstream leading to an electric field pointing downstream to upstream. This induced field tends to push the net positive solution in the direction opposite to that of the pressure driven flow resulting in lower observed flow rate, equivalently described by means of an enhanced viscosity. The quantification of the induced electric field by appropriate balances of the steady state zero net current is the second part of the analysis described in this paper.

It is clear that the induced electric field occurs in pressure driven aqueous solutions over a charged substrate. The flow is retarded due to the aforementioned consequences and one must, eventually, apply

a larger pressure gradient to obtain the same volumetric flow rate. Regardless, it is an indicator of geophysical pressure changes (typical porous rocks have surface charges) [17], thought to be one of the mechanisms of mechanotransduction in bones [18], an implicit method of evaluating the surface potential (from flow measurements) [19-22] and lastly it provides a mechanism for converting the mechanical energy (utilized for pumping) into electrical energy [23-24]. Such a mechanism is known as electrokinetic energy conversion (EKEC) and has been a topic of much research in recent times from both a theoretical and experimental perspective. In this paper, the last discussion pertains to the various aspects of the maximization of the EKEC efficiency (which is typically low ~ 2-8%).

The paper is organised as follows - the structure of the EDL is first discussed from a free energy consideration; the modified Cauchy's momentum equation is then solved to obtain the velocity field in terms of the unknown electric field; the unknown electric field is then obtained by means of current electroneutrality for a closure of the problem. Lastly, strategies for improving electrokinetic conversion efficiencies are discussed.

2. MATHEMATICAL FORMULATION
2.1. Electrical Double Layer
The most central aspect to all electrokinetic phenomena is the presence of a mobile electrically charged phase between the substrate and the aqueous solution. From a surface chemistry perspective, the chemical state of an ionizable solid surface in contact with an electrolyte solution may get altered due to various mechanisms; common mechanisms being ion adsorption or surface group ionization [15,16]. Such a pH dependent process therefore leads to the generation of a surface charge. For e.g. common glass (Si-OH) in contact with water (H_2O) acquires a negative charge due to formation of SiO^- at the surface at the cost of releasing a proton into the solution [15,16]. Quite intuitively, the ions from the aqueous solutions are either repelled (coions) from the surface or the ions are attracted towards the surface (counterions). The primitive description of ions at the charged interface predicts that the counterions are molecularly 'stacked' at the wall which leads to a perfect sheilding of the charged substrate. However, it is now well known that the equilibrium description of the coions and counterions is only possible by duly accounting for the thermal agitation of the ions (random thermal motion of the ions). Such an interaction of the Couloumbic attraction and thermal motion predicts, instead of a perfect shielding, a distribution of coions and counterions in the vicinity of the charged substrate as seen from Fig. 2 [16].
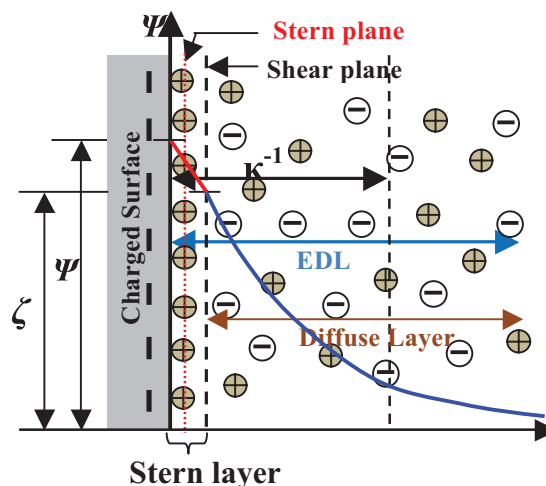

Figure 2: Charge distribution and potential distribution within the EDL. The characteristic length over which the potential decays to $\zeta/\exp(1)$ is denoted by κ^{-1}. The potential decays linearly from the bare charged surface to the value at the shear plane within the Stern layer. Beyond this, the potential decays with an exponential trend to the value in the bulk.

The excess counterions form an immobile layer adjacent to the surface known as the Stern layer or the Helmholtz layer. The thickness of the Stern layer is in the order of the ionic diameter (few Angstroms). The electric potential at this plane is termed as Stern potential. The charge and the potential distributions within this layer are strong functions of the geometrical characteristics of the ions and the short range interaction forces between the ions, wall and the adjacent dipoles. From the Helmholtz layer to the electrically neutral bulk solution, the net charge density gradually decreases to zero. Beyond the Stern layer, the mobile layer consisting of both the coions and counterions is known as diffuse layer or Gouy-Chapman layer. The plane separating the Stern layer and diffuse layer is known as the shear plane and the potential at this plane is known as the zeta potential (ζ). The Stern layer and the diffuse layer together form the electric double layer (EDL), which act as a screening layer over the surface in such a way that the wall charge effect is not felt beyond it.

We focus on two main parameters involved in the charge distribution are Debye length and the zeta potential. We briefly remark over other parameters affecting the distribution of the EDL. The characteristic thickness of the EDL is known as Debye length, which is the length from the shear plane over which the EDL potential value becomes (1/e) of the value of zeta potential. The Debye length is in the order of a few nanometers, sometimes even a micron depending on the ionic concentration of the solution.

2.2. Poisson equation for charge density within the EDL

The total charge density ($\rho_{e,total}$) within the EDL consists of bound charges ($\rho_{e,bound}$) and free charges ($\rho_{e,free}$). The corresponding electric field (**E**) within the EDL is given by the Gauss' law (net electric flux = total enclosed charge) as,

$$\varepsilon_0 \int_S \mathbf{E} \bullet d\mathbf{S} = \int_V \rho_{e,total} \, dV \qquad (1)$$

where ε_0 is the permittivity of free space, **S** is the surface area vector of the control volume having a volume V. Applying the divergence theorem to convert surface integral to volume integral and using $\rho_{e,total} = \rho_{e,bound} + \rho_{e,free}$ [25], one may rewrite the equation as:

$$\varepsilon_0 \int_V (\nabla \bullet \mathbf{E}) dV = \int_V \left(\rho_{e,bound} + \rho_{e,free} \right) dV \qquad (2)$$

Since the elementary control volume is arbitrary, considering the notation $\rho_{e,free} \equiv \rho_e$, equating the integrand of both sides, the equation gives

$$\varepsilon_0 (\nabla \bullet \mathbf{E}) = \rho_{e,bound} + \rho_e \qquad (3)$$

In terms of polarization density vector, the bound charge density can be written as[25]

$$\rho_{e,bound} = -\nabla \bullet \mathbf{P} \qquad (4)$$

where **P** denotes the polarization density vector, which is the dipole moment per unit volume that originates due to gradients in local dipole densities of the medium. Under the approximation that it varies linearly with the electric field, **P** can be written as [25]

$$\mathbf{P} = \varepsilon_0 \chi_S \mathbf{E} \qquad (5)$$

where $\chi_S = \bar{\varepsilon}_r - 1$ is the susceptibility of the medium and $\bar{\varepsilon}_r$ is the dielectric constant of the medium.

Then the equation (3) can be written in the form

$$\nabla \bullet (\varepsilon_0 \bar{\varepsilon}_r \mathbf{E}) = \rho_e \tag{6}$$

Expressing the electric field $\mathbf{E}$ in terms of a EDL potential ψ as $\mathbf{E} = -\nabla \psi$ and substituting in equation (6), one can gets

$$\nabla \bullet (\varepsilon \nabla \psi) = -\rho_e \tag{7}$$

where $\varepsilon = \varepsilon_0 \bar{\varepsilon}_r$. Equation (7) is known as the Poisson Equation for potential distribution within the electric double layer.

2.3. Boltzmann equation for ionic distribution within the EDL
We consider a single plate or surface in an infinite liquid phase. For the system to be in equilibrium, the electrochemical potential ($\bar{\mu}_i$) of the ions need to be constant everywhere, which implies

$$\frac{\partial \bar{\mu}_i}{\partial y} = 0 \tag{8}$$

where the subscript 'i' indicates type i ions. $\bar{\mu}_i$ can be expressed as the sum of chemical potential (μ_i) and the electric potential ($z_i e \psi$), which gives

$$\bar{\mu}_i = \mu_i + z_i e \psi \tag{9}$$

where z_i is the valence of type $-i$ ion and e is the electronic charge. The chemical potential can be expressed (from thermodynamic considerations) by considering an ideal solution of ions, as

$$\mu_i = \mu_i^0 + k_B T \ln(n_i) \tag{10}$$

where μ_i^0 is a constant for type-i ion, k_B is the Boltzmann constant, T is the absolute temperature of the solution and n_i is the number concentration of the type-i ion. From equation (8) to (10), one may get

$$\frac{dn_i}{n_i} = -\frac{z_i e}{k_B T} d\psi \tag{11}$$

Integrating equation (11) with pertinent boundary conditions, the ionic number density distribution can be obtained. Considering that as $y \to \infty$, $\psi = 0$ and $n_i = n_0$ (the number density tends to a bulk number density n_0 at infinity), equation (11) gives

$$n_i = n_0 \exp\left(-\frac{z_i e \psi}{k_B T}\right) \tag{12}$$

Equation (12) is known as Boltzmann distribution of ionic species near a charged surface. The important assumptions made for the derivation of this distribution are: (i) ions are uncorrelated point charges, (ii)

the system is in equilibrium, with no macroscopic advection or diffusion of ions, (iii) the solid surface is microscopically homogeneous, (iv) the charged surface is in contact with an infinitely large liquid medium, (v) the strength (intensity) of the EDL field significantly overweighs the strength of any imposed electric field, close to the interface, and (vi) far stream boundary condition is applicable. In practice the validity of some of these assumptions may indeed be questionable, in a strict sense. For instance one may consider the case of ionic charge distribution in presence of fluid flows, for which the system is not in thermodynamic equilibrium. However, for low flow velocities ($Re \sim O(1)$), the Boltzmann distribution give a reasonably good approximation of ionic charge distribution [26].

2.4. THE POISSON-BOLTZMANN EQUATION AND ITS LIMITATIONS

For a binary electrolyte of valence $z_{\pm}$ and ionic number densities $n_{\pm}$, the total charge density within the EDL is given by

$$\rho_e = e\left(z_+ n_+ + z_- n_-\right) \tag{13}$$

By the help of equations (12) and (13), and considering a symmetric electrolyte, equation (7) may be simplified as

$$\nabla^2 \psi = \frac{2 n_0 e z}{\varepsilon} \sinh\left(\frac{e z \psi}{k_B T}\right) \tag{14}$$

Equation (14) is known as Poisson-Boltzmann equation for potential distribution inside the EDL. This equation has its own set of limitations, especially when the surfaces under consideration constitute too narrow a fluid passage (<50 nm) within which distinctive intermolecular and surface interactions take place [26-27]. In the diffused EDL, the mobile counterions form a highly polarizable layer at each interface. For small distances (typically <4 nm) between these two interfaces, an attractive van der Waals force or an ion correlation force is experienced by these two opposing 'conducting' layers. This force may have significant contribution in describing Poisson-Boltzmann equation. The osmotic pressure of a van der Waals gas increases due to the finite size of the gas molecules. In a similar fashion, the finite size of coions and counterions (steric effect) tends to enhance the repulsive force between the two surfaces. If the coions are adsorbed into the surface, this repulsion is nothing but the steric repulsion between the overlapping Stern layers. Moreover, the interaction between ionic charge and the surface occurs due to the reflected field of that polarized surface. This reflected field is the same as if there were an image charge on the other side of the surface at the same distance. If the permittivity of the aqueous medium is less than the permittivity of the surface, an additional repulsive force will occur due to this image charge interaction. If the distance between two surfaces comes closer than a few nanometers, some short-range forces (oscillatory solvation force, monotonic solvation force) become important in describing the EDL theory. The short-range oscillatory solvation force of geometric origin arises if the liquid molecules are induced to order into highly restricted spaces or in quasi-discrete layers between two surfaces. The monotonic solvation force arises in surface-solvent interactions which induces an orientational reordering in the adjacent liquid. This force usually decays exponentially with the surface separation. These forces depend on the physical and geometrical properties of the surface and are not considered in the description of continuum-level EDL theories. Also implicit in the calculations is that the permittivity remains spatially constant. However, for polar solvents like water, the preferential orientation leads to significant dipolar orientation near the wall and thus a sharp drop in the permittivity near the wall. Recent works have attempted to quantify such effects on electrokinetic transport.

   To describe the most fundamental limitation of the Poisson-Boltzmann equation in a more precise way, one may consider the finite sized effect of the ions in the EDL potential distribution [28-31]. In

such cases, the Boltzmann distribution for ionic species is modified by a factor which quantifies the amount of steric repulsion. Within the mean field approximation, the total free energy of the system can be written as, $\Sigma = U - TS$, where U is the electrostatic energy and TS is the entropic contribution to the free energy. In terms of the electrostatic potential the free energy, Σ, may be expressed as [28-31]

$$\Sigma = \int \left[-\frac{\varepsilon}{2}\left|\nabla\psi\right|^2 + e\psi\left(z_+ n_+ - z_- n_-\right) - \left(\mu_+ n_+ + \mu_- n_-\right) \right] dV$$
$$+ \frac{k_B T}{b^3} \int \left[n_+ b^3 \ln\left(n_+ b^3\right) + n_- b^3 \ln\left(n_- b^3\right) + \left(1 - n_+ b^3 - n_- b^3\right) \ln\left(1 - n_+ b^3 - n_- b^3\right) \right] dV \tag{15}$$

where b is an ion specific length scale. In case of a symmetric $z{:}z$ electrolyte, the ionic concentration distributions may be obtained by minimizing the free energy with respect to ψ and $n_\pm$. The variation of (15) with respect to ψ, i.e., $\dfrac{\delta\Sigma}{\delta\psi} = 0$ leads to the Poisson equation

$$\nabla^2\psi = -\frac{e\left(z_+ n_+ + z_- n_-\right)}{\varepsilon} \tag{16}$$

Whereas, the minimization with respect to $n_\pm$, i.e., $\dfrac{\delta\Sigma}{\delta n_\pm} = 0$ (please note that the δ operator is the variational derivative), assuming that the electrochemical potential of each type of ions is constant in the system [28], gives the modified Boltzmann distributions for ionic species which are given by

$$n_\pm = \frac{n_0 \exp\left(\mp \dfrac{ze\psi}{k_B T}\right)}{1 + 2\upsilon\sinh^2\left(\dfrac{ze\psi}{2k_B T}\right)} \tag{17}$$

where $\upsilon = 2n_0 b^3$, is the steric or size factor and b signifies the size of the solute ions or the solvation radius(taken to be same for all types of ions for simplicity). One must note here that, the hydraulic radius of the particle (ionic length scale) is different from the solvation radius[60]. Equations (16) and (17) together give

$$\nabla^2\psi = \frac{zen_0}{\varepsilon} \frac{2\sinh\left(\dfrac{ze\psi}{k_B T}\right)}{1 + 2\upsilon\sinh^2\left(\dfrac{ze\psi}{2k_B T}\right)} \tag{18}$$

Equation (18) is essentially the modified form of the Poisson-Boltzmann equation considering finite size effects of ions, under the mean-field approximation that neglects any correlation between them.

2.5. Fluid flow equations
We reiterate that electric fields can drive flows owing to the electrical body force which is the product of the applied electric field and the charge density. In a similar fashion, the induced electric field also has a net contribution towards the body force which needs to be accounted while describing the fluid

flow. It is clear that the velocity field is needed in order to estimate the advective current flux. At the same time, the complete description of the velocity field necessitates knowledge of the magnitude of the induced electric field which, as we had discussed earlier, can be found out by enforcing current neutrality. The description of the fluid flow is achieved through the continuity equation and momentum equation with an additional electrical body force which are given by

$$\frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \mathbf{u}) = 0 \tag{19}$$

$$\rho_f \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla \cdot \bar{\bar{\tau}} + \mathbf{F}_{EK} \tag{20}$$

$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + (\mathbf{u} \cdot \nabla)$ is the material derivative, $\mathbf{u}$ is the velocity vector, ρ_f is the fluid density, p is hydrostatic pressure, $\bar{\bar{\tau}}\left(= \frac{\eta}{2}\left(\nabla\mathbf{u} + \nabla\mathbf{u}^T\right)\right)$ is the deviatoric stress tensor, η is the dynamic viscosity, $\mathbf{F}_{EK}$ is the electrokinetic body force and is given by [16]

$$\mathbf{F}_{EK} = \rho_e \mathbf{E} - \frac{1}{2}\mathbf{E}\cdot\mathbf{E}\nabla\varepsilon + \frac{1}{2}\nabla\left(\rho_f \frac{\partial\varepsilon}{\partial\rho_f}\mathbf{E}\cdot\mathbf{E}\right) \tag{21}$$

where ρ_e is the total electric charge density, $\mathbf{E}$ is the electric field. The consideration of incompressibility and constant permittivity of the medium reduces the above body force to $\mathbf{F}_{EK} = \rho_e\mathbf{E}$. For steady state, low Reynolds number flow of Newtonian fluids with constant fluid properties, the above equations (19) and (20) can be written in a more simplistic manner as

$$\nabla \cdot \mathbf{u} = 0 \tag{22}$$

$$0 = -\nabla p + \eta\nabla^2\mathbf{u} + \rho_e\mathbf{E} \tag{23}$$

These equations may be solved with proper boundary conditions to obtain the velocity profile. In equation (23) the electric field $\mathbf{E}$ refers to an externally applied electric field or an induced streaming field. Here we will mainly focus on the latter case. After obtaining the velocity field, one may calculate the ionic current (i_{ion}), for a binary electrolyte, as [32]

$$i_{ion} = e\left(z_+ n_+ u_+ + z_- n_- u_-\right), \tag{24}$$

where z_+ (z_-), u_+ (u_-) and n_+ (n_-) refers to the valence, axial velocity and ionic concentration (number densities) of the cations (anions) respectively. The axial velocities $u_\pm$ can be expressed as $u_\pm = u + \frac{ez_\pm E_S}{f_\pm}$ (here u is the contribution from the fluidic transport and remaining part is the electromigration of the ionic species), $f_\pm$ is the ionic friction coefficient and E_S is the induced electric field. For a symmetric electrolyte ($z_+ = -z_- = z$) and equal cationic and anionic friction coefficients ($f_+ = f_- = f$), the ionic concentration equals to [32]

$$i_{ion} = \underbrace{ze(n_+ - n_-)u}_{\text{streaming current}} + \underbrace{\frac{z^2 e^2 E_S}{f}(n_+ + n_-)}_{\text{conduction/electromigration current}} \qquad (25)$$

The ionic friction coefficient f can be related to the ionic mobility Λ, Faraday's constant F and Avogadro number N_A as $f = \frac{e^2 N_A}{F^2 \Lambda}$.

A primitive approach is to neglect the contribution of the body force towards evaluation of the velocity field - an approximation which holds true in the case of very weak electric fields[21-22,33-35]. Such an approximation implies that the electric field does not alter the flow. This assumption leads to a straight-forward calculation for the streaming potential which is outlined hereafter. If a pressure difference Δp is applied across a channel of length L and cross-sectional area A to drive the ionic liquid of bulk conductivity σ_b and permittivity ε ($= \varepsilon_0 \bar{\varepsilon}_r$), the total streaming current $I_{stream} = -\frac{\varepsilon \zeta}{\eta} \frac{\Delta p}{L} A$ and conduction current $I_{cond} = \sigma_b \frac{\Delta \phi}{L} A$, where $\Delta \phi$ is the potential difference between the two electrodes. So, the amount of streaming potential ($\Delta \phi$) generated across the channel is given by [35]

$$\frac{\Delta \phi}{L} = \frac{\varepsilon \zeta}{\eta \sigma_b} \frac{\Delta p}{L} \qquad (26)$$

where ζ is the zeta potential at the surface. The treatment made so far is well regarded as Helmholtz-Smoluchowski theory for electrokinetics [35]. However, a major fault in this assumption is that the flow rate does not get altered in the presence of the electric field. From experimental findings, it has been observed that there is distinct flow retardation in the channel due to the induced electric field [34-55]. This is manifested in experiments as a lower flow rate and can be thought of as an enhanced viscosity - this phenomenon is termed as electroviscous effect [49]. The theoretical framework considering complete electro-hydrodynamic equations are initially proposed by Burgreen and Nakache [41] for rectangular geometry and is later extended to cylindrical capillary by Rice and Whitehead [42]. On the basis of these works, other studies have made significant improvements towards exploring the underlying physics of electro-hydrodynamics which involves various effects such as, high surface potential, strong EDL interaction [43-55], surface conductivity [35,56-58], steric repulsion [28,59-60], viscoelectric effect, form of driving field [61-64], fluid rheology [65-66], channel geometry [67-70], surface properties [71-105] (includes electro-chemical properties as well as hydrodynamic properties such as hydrophobocity), etc. In the subsequent sections, we will address some of the issues through a simple mathematical formalism. Mainly, we have discussed the streaming potential phenomenon in slit like micro and nanochannels [32, 41, 106-110]. A similar methodology can be followed for other cross-sectional geometries like circular, elliptic, trapezoidal, etc [67-70].

For demonstration of the underlying calculations, let us consider a steady state pressure-driven flow of an ionic liquid, presumably a Newtonian fluid, in a slit micro or nano-channel of height $2H$, whose centre is located at the midplane. The fluidic velocity u can be obtained by simplifying equations (22), (23) for low Re and unidirectional flow and is given by

$$u = -\frac{H^2}{2\eta}\frac{dp}{dx}\left(1 - \frac{y^2}{H^2}\right) - \frac{\varepsilon \zeta E_S}{\eta}\left(1 - \frac{\psi}{\zeta}\right) \qquad (27)$$

where $-\frac{dp}{dx}$ is the applied pressure gradient and E_S represents the streaming potential yet to be known.

The velocity distribution is obtained from an emphasis that, although this is a pure pressure driven transport, the back electroosmotic flow due the induced streaming potential field has enough contribution on the overall flow field. The boundary conditions imposed here are no-slip condition ($u(\pm H) = 0$) at the channel wall and flow symmetry at the channel central line ($\left.\dfrac{du}{dy}\right|_{y=0} = 0$). It is also to be noted here that, in conjunction with the boundary condition for the velocity, the condition on the potential distribution is also required to complete the profile. Although the specified zeta potential (ζ) is considered in most cases, it often appears to be ill conditioned because of its variation with the salt and pH condition of the solution. Moreover, the zeta potential is merely a hypothetical entity. Alternatively, one may use the surface charge (σ) as a possible boundary condition. In this case the boundary condition reads $\sigma = -\varepsilon\left.\dfrac{d\psi}{dy}\right|_{wall}$. In addition, the surface charge can be relate with the zeta potential by the expression [13]

$$\zeta = \frac{4k_B T}{ez}\tanh^{-1}\left(-\frac{4n_0 ez}{\sigma} \pm \sqrt{\left(\frac{4n_0 ez}{\sigma}\right)^2 + 1}\right)$$

The total ionic current for a binary electrolyte is given by [32] (please also refer to equation 25)

$$I_{ion} = \int_{-H}^{H} i_{ion}\, dy = 2e\int_{0}^{H}(z_+ u_+ n_+ + z_- u_- n_-)\, dy \tag{28}$$

According to the electronuetrality constraint the total ionic current is zero ($I_{ion} = 0$). Under the consideration for the Poisson-Boltzmann equation (14) for EDL potential distribution, equation (28) with $I_{ion} = 0$ gives an estimation for E_S as,

$$E_S = \frac{zen_0 \displaystyle\int_0^H \left(-\frac{H^2}{2\eta}\frac{dp}{dx}\right)\left(1-\frac{y^2}{H^2}\right)\sinh\left(\frac{ez\psi}{k_B T}\right)dy}{\dfrac{n_0 z^2 e^2}{f}\displaystyle\int_0^H \cosh\left(\frac{ez\psi}{k_B T}\right)dy + \dfrac{zen_0\varepsilon\zeta}{\eta}\displaystyle\int_0^H\left(1-\frac{\psi}{\zeta}\right)\sinh\left(\frac{ez\psi}{k_B T}\right)dy} \tag{29}$$

Because of this streaming potential field, an electroosmotic flow will be created in the direction opposite to the imposed pressure driven flow. As a result the actual flow slows down, which may be understood grossly in terms of the fluid flowing with a higher viscosity which resemblance the electroviscous effect as mentioned earlier. If the reduced flow rate is compared with the flow rate predicted by conventional fluid dynamics (without considering the electrokinetic effects), it appears that the fluid would have an enhanced effective viscosity (η_{eff}). To quantify this effect, one may consider a pure pressure driven flow with the effective viscosity, which produces same net volumetric flow rate as that of the combined pressure-driven and back electroosmotic flow due to the streaming effect. Mathematically, this can be given as

$$\int_0^H \left\{-\frac{H^2}{2\eta_{eff}}\frac{dp}{dx}\left(1-\frac{y^2}{H^2}\right)\right\}dy = \int_0^H \left\{-\frac{H^2}{2\eta}\frac{dp}{dx}\left(1-\frac{y^2}{H^2}\right) - \frac{\varepsilon\zeta E_S}{\eta}\left(1-\frac{\psi}{\zeta}\right)\right\}dy$$

which implies

$$\frac{\eta_{eff}}{\eta} = \frac{\int_0^H \left\{ -\frac{H^2}{2}\frac{dp}{dx}\left(1-\frac{y^2}{H^2}\right) \right\} dy}{\int_0^H \left\{ -\frac{H^2}{2}\frac{dp}{dx}\left(1-\frac{y^2}{H^2}\right) - \varepsilon\zeta E_S\left(1-\frac{\psi}{\zeta}\right) \right\} dy} \tag{30}$$

We note that for $E_S = 0$, we have no enhanced electroviscous effects while for a non-zero E_S, we get a higher effective viscosity.

2.6. Effect of surface conductivity

The above methodology neglects the effect of surface conduction and the EDL polarization [35, 56-58]. Surface conduction refers to the additional mode of current conduction apart from the conduction through the aqueous solution. A modification has been made to equation (25) by considering the surface conduction which is quantified by the Dukhin number (Du), and is given in the weak field limit as[35]

$$\frac{\Delta\phi}{L} = \frac{\varepsilon\zeta}{\eta\sigma_b(1+\ell Du)}\frac{\Delta p}{L} \tag{31}$$

where, Du is the ratio between the surface conductivity (or the Stern layer conductivity) and the surface equivalent bulk ionic conductivity and ℓ is a factor depending upon the confinement geometry ($\ell = 2$, for cylindrical capillary). A more detailed description about the dependence of surface conduction can be found in the IUPAC report of Delgado et.al. [35].

In conjunction with the theoretical formalism as described in equation (28) and (29), on accounting the effect of Stern layer conductivity, σ_{stern}, the total ionic current (28) will be enhanced by the Stern layer conduction current $I_{stern} = \sigma_{stern}E_S$, and is given by

$$I_{ion} = \underbrace{2ze\int_0^H (n_+ - n_-)u\,dy}_{I_{stream}} + \underbrace{2\frac{z^2e^2E_S}{f}\int_0^H (n_+ + n_-)\,dy}_{I_{cond}} + \underbrace{2\sigma_{stern}E_S}_{I_{stern}} \tag{32}$$

Accordingly, the streaming potential can be modified as

$$E_S = \frac{zen_0\int_0^H \left(-\frac{H^2}{2\eta}\frac{dp}{dx}\right)\left(1-\frac{y^2}{H^2}\right)\sinh\left(\frac{ez\psi}{k_BT}\right)dy}{\sigma_{stern} + \frac{n_0z^2e^2}{f}\int_0^H \cosh\left(\frac{ez\psi}{k_BT}\right)dy + \frac{zen_0\varepsilon\zeta}{\eta}\int_0^H \left(1-\frac{\psi}{\zeta}\right)\sinh\left(\frac{ez\psi}{k_BT}\right)dy} \tag{33}$$

Representing in terms of the bulk ionic conductivity, $\sigma_b\left(=2n_0z^2e^2/f\right)$, and introducing the Dukhin number $Du\left(=\sigma_{stern}/H\sigma_b\right)$, the above expression can be simplified as

$$E_S = \frac{2zen_0 \int\limits_0^H \left(-\frac{H^2}{2\eta}\frac{dp}{dx}\right)\left(1-\frac{y^2}{H^2}\right)\sinh\left(\frac{ez\psi}{k_BT}\right)dy}{\sigma_b\left(2Du + \frac{1}{H}\int\limits_0^H \cosh\left(\frac{ez\psi}{k_BT}\right)dy\right) + \frac{2zen_0\varepsilon\zeta}{\eta}\int\limits_0^H \left(1-\frac{\psi}{\zeta}\right)\sinh\left(\frac{ez\psi}{k_BT}\right)dy} \tag{34}$$

2.6. Steric effects - finite size effects

The above calculations for streaming potential are free from the ionic size effects. To consider this effect, the streaming current and the conduction current is rewritten with the help of modified Boltzmann distribution (17), and is given by [59-60, 66]

$$I_{stream} = ze\int\limits_{-H}^H (n_+ - n_-)u\,dy = 2n_0ze\int\limits_{-H}^H \frac{\sinh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}u\,dy \tag{35}$$

$$I_{cond} = \frac{z^2e^2E_S}{f}\int\limits_{-H}^H (n_+ + n_-)\,dy = \frac{2n_0z^2e^2E_S}{f}\int\limits_{-H}^H \frac{\cosh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}dy \tag{36}$$

The total ionic current (I_{ion}) is given by

$$I_{ion} = 2n_0ze\int\limits_{-H}^H \frac{\sinh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}u\,dy + \frac{2n_0z^2e^2E_S}{f}\int\limits_{-H}^H \frac{\cosh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}dy \tag{37}$$

So, the streaming potential field can be evaluated from equation (37) by equating the total ionic current to be zero and is given by [32]

$$E_S = \frac{zen_0 \int\limits_0^H \left(-\frac{H^2}{2\eta}\frac{dp}{dx}\right)\left(1-\frac{y^2}{H^2}\right)\frac{\sinh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}dy}{\frac{n_0z^2e^2}{f}\int\limits_0^H \frac{\cosh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}dy + \frac{zen_0\varepsilon\zeta}{\eta}\int\limits_0^H \left(1-\frac{\psi}{\zeta}\right)\frac{\sinh\left(\frac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\frac{ez\psi}{k_BT}\right)}dy} \tag{38}$$

2.8. Electrokinetic energy conversion (EKEC)

The most important technological relevance of generating streaming potential is the development of energy conversion device in which a hydrostatic energy is converted into electric power [23-24, 111-130]. At the open circuit conditions described above, we have the streaming electric field given by E_S while the current in a short-circuit mode would be essentially the streaming current I_{stream}. However, when there is an external load applied to the circuit, we can only draw a fraction of the streaming current and streaming electric field. The consideration of a linear load line dictates the operation zone and the current and potential at that operation zone. In the case where the external load is equal to the resistance of the aqueous solution, we obtain the maximum power which is equal to half of the open circuit voltage times the half of the short circuit current. So if we consider the half voltage and half current line, the power generated will be proportional to $\frac{1}{4}\left|I_{stream}E_S\right|$. The concept of the operation zone dictates that in the presence of an externally connected resistor, the potential-current characteristics follow that of a straight line. When the external resistor is highly conducting, the current flowing through it is the short circuit current. On the other hand, when the external resistance is very high, the potential drop across it is the open circuit voltage. For any other values, the current and potential lie between a straight line joining the two extreme operating conditions (for an equivalent circuit representation, please refer to Fig. 2 of [111]).

Theoretically, efficiency is measured by the ratio of electric power (product of streaming current and the streaming potential, i.e., $\frac{1}{4}\left|I_{stream}E_S\right|$) to the hydrostatic energy (product of applied pressure gradient and volume flow rate, i.e., $\left|\frac{dp}{dx}Q\right|$)[127-130]. Therefore, the efficiency, γ, may be given as

$$\gamma = \frac{1}{4}\frac{\left|I_{stream}E_S\right|}{\left|\frac{dp}{dx}Q\right|} \tag{39}$$

Quite obviously, we can have a larger EKEC efficiency if we can somehow obtain a higher streaming current or a higher streaming electric field at the means of a lower pressure gradient. In the case of surface treated nano- and microchannels, the physical considerations may deviate from the classical paradigm of the no-slip boundary condition and the fluid may effectively slip at the wall. The common intuition would be that the pressure gradient to drive the same volume flow rate would reduce. However, we note that owing to the feedback-like evaluation of the streaming potential, we have a scenario where the flow rate would tend to increase in the presence of slip for a given pressure gradient. This increased flow rate would lead to an increased streaming current which would thus imply a stronger induced streaming field. This augmented streaming electric field would lead to a larger retardation on the flow rate, thereby essentially modulating the flow rate. It is observed that the flow rate retardation and consequently the streaming current retardation is overwhelmed by the increase in the induced electric field. Given the proximity of the effects of the EDL near the wall, any alteration of the velocity profile is expected to drastically influence the electrokinetics.

To quantify the effect of hydrodynamic slip, the usual no-slip boundary condition for obtaining velocity profile (27) is replaced with Navier-slip boundary condition which may be stated as $u\big|_{wall} = -l_{slip}\frac{du}{dy}\bigg|_{wall}$ [100, 131-132], where l_{slip} represents the slip length which is a hypothetical distance beyond the surface where the velocity extrapolates to zero. The inclusion of this slip condition reformulates the velocity profile (27) as

$$u = -\frac{H^2}{2\eta}\frac{dp}{dx}\left(1-\frac{y^2}{H^2}+2\frac{l_{slip}}{H}\right) - \frac{\varepsilon\zeta E_S}{\eta}\left(1-\frac{\psi}{\zeta}-\frac{l_{slip}}{\zeta}\frac{d\psi}{dy}\Big|_{y=H}\right) \tag{40}$$

This velocity profile changes the streaming potential field (38) to [133-135]

$$E_S = \frac{zen_0\int_0^H\left(-\frac{H^2}{2\mu}\frac{dp}{dx}\right)\left(1-\frac{y^2}{H^2}+2\frac{l_{slip}}{H}\right)\dfrac{\sinh\left(\dfrac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\dfrac{ez\psi}{k_BT}\right)}dy}{\dfrac{n_0z^2e^2}{f}\int_0^H\dfrac{\cosh\left(\dfrac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\dfrac{ez\psi}{k_BT}\right)}dy+\dfrac{zen_0\varepsilon\zeta}{\mu}\int_0^H\dfrac{\left(1-\dfrac{\psi}{\zeta}-\dfrac{l_{slip}}{\zeta}\dfrac{d\psi}{dy}\Big|_{y=H}\right)\sinh\left(\dfrac{ez\psi}{k_BT}\right)}{1-\upsilon+\upsilon\cosh\left(\dfrac{ez\psi}{k_BT}\right)}dy} \tag{41}$$

Accordingly, one can find the streaming current I_{stream} from equation (35) and consequently the conversion efficiency from equation (39). Not only the fluid slip but the steric effect, surface conduction, fluid rheology, may also have considerable effect [136-140] on determining EKEC, predicting enhanced efficiencies to the tune of 25-30%.

3. CONCLUSIONS

The detailed steps described in this paper on quantifying streaming potential are expected to be the basic building blocks towards addressing more complicated issues of streaming potential calculations in a variety of situations. Complications arising out of stick-slip motion, effects of the wettability of the substrate, utility of streaming potential for mixing of solutes and so on are various issues which still require substantial experimentation as well as theoretical probing. Theoretical understanding of the various issues involved in evaluating streaming potential, however, need to be significantly advanced for acting as a robust design tool for the development of more efficient energy harvesting devices.

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