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Research Article

Direct simulation of electroosmosis around a spherical particle with inhomogeneously acquired surface charge

Uncovering electroosmosis around an inhomogeneously acquired charge spherical particle in a confined space could provide detailed insights into its broad applications from biology to geology. In the present study, we developed a direct simulation method with the effects of inhomogeneously acquired charges on the particle surface considered, which has been validated by the available analytical and experimental data. Modeling results reveal that the surface charge and zeta potential, which are acquired through chemical interactions, strongly depend on the local solution properties and the particle size. The surface charge and zeta potential of the particle would significantly vary with the tangential positions on the particle surface by increasing the particle radius. Moreover, regarding the streaming potential for a particle-fluid tube system, our results uncover that the streaming potential has a reverse relation with the particle size in a micro or nanotube. To explain this phenomenon, we present a simple relation that bridges the streaming potential with the particle size and tube radius, zeta potential, bulk and surface conductivity. This relation could predict good results specifically for higher ion concentrations and provide deeper understanding of the particle size effects on the streaming potential measurements of the particle fluid tube system.

Keywords:

Direct simulation / Electroosmosis / Inhomogeneously acquired surface charge / Lattice Boltzmann method / Spherical particle DOI 10.1002/elps.201600378



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1 Introduction

The electrophoresis and electroosmosis of charged and polarizable particles have found promising applications in various fields of science such as biology, environment, and geology. As a matter of fact, the particles could possess electric charges depending on their material properties and the medium in which they are immersed. Considering the particle material properties, one can categorize them into conducting and nonconducting types. The conducting one in the presence of an applied external electric field could be polarized and possesses inhomogeneous positive and negative charges [1–4]. For the nonconducting case, when a particle with chemically reactive surface immersed in an aqueous solution, due to the

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Abbreviations: EDL, electric double layer; ETL, electrical triple layer

chemical and physical adsorption or desorption of the ions on the solid–liquid interfaces, the surface would acquire a certain amount of negative or positive charges. This charge is strongly dependent on the local solution properties such as pH, ion concentration, and the particle surface material [5,6]. Based on the electrostatic theory, the acquired surface charge attracts the counterions and repels the co-ions. As a result, a polarized layer, which is so-called electric double layer (EDL), induces at the vicinity of the solid–liquid interface [7]. By applying an external electric field, the counterions at the EDL start to move along the electrical field. However, the ions within the aqueous medium experience the superposition of the applied external electric field and the internal electric field. The internal electric field is a result of the electrical field of ions themselves as charged particles.

Basically, the ionic transport within the EDL could be explained by such coupled convection, diffusion, and electromigration transport phenomena [8]. Although the

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aforementioned transport phenomena bring complexity to analyze the ionic transport through straight surfaces, for curved surfaces, one can expect great complexity since the tangential electric field varies with the tangential positions on the particle surface. Though a very large body of literature assumed the uniform zeta potential [9–16], in real world, the surface charge could not be uniform [17, 18]. To this aim, few attempts have been conducted to consider particles with a random distribution of zeta potential [19], arbitrary zeta potential [20–22], and arbitrary double layer thickness [23]. However, neither the prescribed uniform surface charge density or zeta potential could represent the realistic electroosmosis around the particle nor the random or other nonuniform considerations of the surface charge and zeta potential.

To our best knowledge, no work has performed the realistic electroosmosis around a spherical particle which the zeta potential and surface charge density are acquired based on the local solution properties i.e. pH and ion concentration. In this contribution, for the first time, we perform a direct simulation of the electroosmosis around a spherical particle in a confined space (i.e., tube) which is inhomogenously acquired surface charge. In this particle-fluid-tube configuration, three characteristic lengths as micro or nanotube radius, particle radius, and EDL thickness could significantly influence the electroosmosis around the particle. In order to fully take into account the mentioned determinative factors, the coupled Nernst-Planck, Navier-Stokes, and Poisson's equations are solved numerically in an iterative procedure by coupled lattice Boltzmann methods to find out the ion distribution, flow field, and internal electric potential field, respectively. However, determination of the local zeta potential as the boundary condition for Poisson's equation is a big challenge. To overcome this challenge, the electrical triple layer (ETL) model that involves the contribution from the salt-ion adsorption to the chemically reactive mineral surfaces has been adopted for numerous fields from geophysics and geochemistry [24,25] to electrokinetic transport in microfluidics or nanofluidics [26]. In this contribution, we modified the standard ETL model [5]

which the local surface charge density and zeta potential could obtain based on the local solution properties. It should be noted that the proposed modified ETL model could also be employed when the EDLs are overlapped. By using the presented numerical framework, we investigated the electroosmosis around the particle in confined medium for different solution pH and particle sizes.

2 Materials and methods

2.1 Problem definition

In this study, we consider a silica spherical particle in an aqueous solution within a tube that is coated by silica. The tube is initially filled with the aqueous solution. The solution was prepared by dissolving KCl with $C_{\rm KCl} = 3.6 \times 10^{-4} \, {\rm M}$ in deionized water at the room temperature. Considering the acidity of the solution, by adding the HCl and KOH, one can control the pH of the solution. In order to retain the initial electroneutrality, the molar concentration of the counterions (K^+) and co-ions (Cl^-) should be equal to $[K^+] = [KCl] +$ [KOH] and $[Cl^-] = [KCl] + [HCl]$, respectively. The bulk pH and pOH of the solution could also be obtained from the concentration of hydronium and hydroxyl as $[H^+] = [HCl]$ and $[OH^{-}] = [KOH]$, respectively. Since this work aims to study the electroosmosis around a spherical particle, it is assumed that the particle is fixed at the middle of the tube and let the aqueous solution flow around it by applying an external pressure gradient or electric field. In addition, because of the symmetrical boundary conditions around the ϕ direction (in spherical coordinate (r, θ, φ)), it allows people to solve this defined problem in a 2D fluid channel configuration as in the previous work [27-29]. Fig. 1 illustrates our particlefluid-tube configuration. The walls of the tube and the particle acquire surface charge due to the chemical interactions with the electrolyte. This surface charge might be inhomogeneous while the local properties of the solution (i.e., pH and



Figure 1. Schematic illustration of a particle fluid tube configuration in which the spherical particle placed at the middle of the tube. The tube contains multispecies ions as K⁺, Cl⁻, H⁺, and OH⁻. The solid–liquid interface of the tube and particle acquire surface charge due to the chemical interactions. $\zeta_p(\theta)$ denotes the acquired zeta potential on the particle surface that could be changed by tangential position (θ) and $\zeta_t(r, \theta)$ denotes the zeta potential on the tube–liquid interface.



Figure 2. The iteration procedure to solve the coupled lattice Boltzmann methods for Poisson, Nernst–Planck, and Navier–Stokes equations. The METL model solving in each iteration to figure out the updated zeta potential for the solid–liquid interfaces. In this contribution, the tolerance is equal to 10^{-8} .

counterion concentration) at the solid-liquid interfaces determine the surface charge. It is well realized that three main transport phenomena as diffusion, electrochemical migration, and convection govern the ion transport. In our system, the ions start to move by applying the external electric field or the pressure gradient. For the fluid flow, it would be generated by connecting pressurized chamber (pressure-driven flow) or nonzero voltage electrode (electroosmotic flow) to the inlet reservoir while the outlet reservoir would be left open to a nonpressurized chamber (atmosphere) or grounded. The dimensions of the tube are chosen as the diameter H = 2b =0.14 μ m, the length $L = 1 \mu$ m. It should be mentioned that the inlet of the tube is connected to a reservoir with a refilling solution to make sure that the reservoir could provide our system with bulk concentration. It is assumed that the diffusion coefficients of the ions, kinetic viscosity, and solution temperature would be constant everywhere in the solution and equal to: D_{K+} = 1.95 \times 10 $^{-9}$, $D_{Cl.}$ = 2.03 \times 10 $^{-9}$, $D_{\rm H+} = 9.31 \times 10^{-9}$, $D_{\rm OH}^- = 5.27 \times 10^{-9} \text{ m}^2/\text{s}$, $\nu = 8.89 \times 10^{-9} \text{ m}^2/\text{s}$

 10^{-7} m²/s, and T=293.15 K, respectively. The vacuum electrical permittivity and the ratio of the electrolyte solution permittivity to vacuum permittivity would be $\epsilon_0=8.854\times 10^{-12}$ C/V \cdot m and $\epsilon_r=78.54$, respectively. Since the pH of the solution plays a key role to determine the local surface charge on such mineral surfaces, we considered two pH 4 and 6 to investigate the influence of the pH on the electroosmosis around the particle.

Regarding the presence of a surface charge on the solid–liquid interfaces, based on the electrostatic theory, the counterions are attracted and co-ions repelled due to the electrostatic forces. Consequently, a polarized layer with a higher amount of counter-ions concentration formed near to the charged surface. The combination of these two layers is so-called the EDL. Based on the classical electrokinetic theories [8], the thickness of the formed layer near to the solid surface could be characterized by a characteristic length named Debye length and calculated as $\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_r K_B T}{2 Z^2 e^2 n_0}}$.

2.2 Mathematical models

As mentioned before, the ion and hydrodynamic transport phenomena in this problem are modeled by employing the Nernst-Planck and Navier-Stokes equations, respectively. For the Nernst-Planck equation, the three main ion transport mechanisms (convection, electrochemical migration, and diffusion) have been considered. In addition, to perform the direct simulation of the electroosmosis around the particle, the electric potential due to the ions themselves should be solved. Thus, the Poisson's equation that governs the internal electric potential field will be solved coupled with the NP and NS equations. For the applied external electric field, the Laplace's equation also should be solved by considering the silica surfaces as ideal dielectric. In this section, we present a general multi-ion mass transport model that is coupled with the incompressible Navier-Stokes equations and the Poisson's equation. To solve the system of Poisson + Nernst-Planck + Navier-Stokes equations, the coupled lattice Boltzmann methods are solved in an iterative procedure (Figure 2) (for details see the Supporting Information). The grid system in our simulation is based on the Cartesian coordinate (x,y). Thus, it would be essential to construct the spherical particle curve surface in this coordinate system and solve the equations in this system.

2.2.1 For hydrodynamics (Navier-Stokes equations)

For a multicomponent constant-property Newtonian fluid flow in a domain with no mass source, the governing equations for laminar flow are [30, 31]:

(a)
$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0,$$

(b) $\frac{\partial (\rho u)}{\partial t} + u \cdot \nabla (\rho u) = -\nabla p + \nabla \cdot (\nu \nabla (\rho u)) + F,$ (1)

where ρ (kg/m³) is the density of the electrolyte, u (m/s) the flow velocity vector, t (s) the time, p (Pa) the fluid pressure, ν (m²/s) the kinematic viscosity, and F (N/m³) the body force density that may include all the implemented body forces such as electrical field force or pressure gradient. Equation (1) is subjected to the nonslip boundary condition at the solid–liquid interfaces. For the inlet and outlet boundary conditions, if the fluid flow is generated by electrical force due to the free bulk charges (electroosmotic flow), the inlet and outlet of the channel will subject to atmospheric pressure. If the fluid flow would be a pressure-driven scenario, the inlet pressure is equal to the chamber pressure while the outlet is left to atmospheric pressure.

2.2.2 For ion transport (Nernst–Planck equations)

The mass conservation equation that governs the transport phenomena and includes the advection–diffusion with a source term could describe the ion transport in an aqueous solution. It is worth point out that the source term for the ion transport represents the electrochemical migration phenomenon. One can propose the mass conservation equation for the ith ion species in an electrolyte [32, 33]:

$$\frac{\partial C_{i}}{\partial t} + \nabla \cdot \boldsymbol{J}_{i} = \boldsymbol{0}, \qquad (2)$$

where C_i demonstrates the ith ion concentration and J_i denotes the species flux. J_i consists of advection, diffusion and dispersion terms. Neglecting the dispersion, one can denote the flux of ions in the form of [33]:

$$\boldsymbol{J}_{i} = -\left(\frac{e Z_{i} D_{i}}{KT}\right) C_{i} \nabla \psi - D_{i} \left(\nabla C_{i}\right) + C_{i} \boldsymbol{u}, \qquad (3)$$

where the first term on the right-hand side denotes the electrochemical migration, the second term to ions diffusion, and the last term to advective transport. This is the famous Nernst–Planck equation. At Eq. (3), *e*, Z_i , D_i , *K*, and *T* denote as the absolute charge of electron, valance number for ith ion, diffusion coefficient for ith ion, Boltzmann constant, and the absolute temperature, respectively. By introducing Eqs. (3) to (2) and considering is othermal electrolyte solution, the ions electrodynamic transport equation would be as [34]:

$$\frac{\partial C_i}{\partial t} + \boldsymbol{u} \cdot \nabla C_i = D_i \, \nabla^2 C_i + \frac{e \, Z_i \, D_i}{K \, T} \nabla \cdot (C_i \nabla \psi). \tag{4}$$

Since in this work the equilibrium state is still available, the Boltzmann ion distribution equation could be employed to find out the boundary conditions for ith ion species at the solid–liquid interfaces. However, the electric potential in the Boltzmann equation should be determined yet. In the next section, we will propose a model that could predict the local surface charge based on the solution properties. Eventually, the boundary conditions for Eq. (4) are as:

For solid-liquid interfaces :

$$C_{i,\sigma} = n_{i,0} \exp\left(-\frac{Z_i e \psi_{\sigma}}{K_{\rm B} T}\right)$$

for inlet and outlet:

$$x = 0 \rightarrow C_i = n_{i,0}$$

 $x = L \rightarrow \frac{\partial C_i}{\partial x} = 0,$ (5)

where $n_{i,0}$ denotes the ith ion bulk number density concentration and ψ_{σ} denotes the solid–liquid interface electric potential.

2.2.3 For electric fields (Poisson's and Laplace's equations)

Following the classical electrostatic theory [35], the electric potential at each point of space could be a linear superposition of the applied external electric field and the electric potential due to the ions themselves, which should satisfy the Poisson's equation as [27, 28] follows:

$$\nabla \cdot (\varepsilon_{\rm r} \varepsilon_0 \nabla \Psi) = -\rho_{\rm e}, \tag{6}$$

where Ψ denotes the total electric potential in space as $\Psi = \Phi + \psi$. It is noteworthy that Eq. (6) could be demonstrated as a linear superposition of the Laplace's and Poisson's equations to describe the applied external and internal electric field, respectively. Since in this contribution the electrolyte permittivity is assumed to be constant everywhere, as a result, Eq. (6) could be redefined for internal electric potential field as follows:

$$\nabla^2 \psi = -\frac{\rho_e}{\epsilon_0 \epsilon_r},\tag{7}$$

where ρ_{e} denotes the free bulk charge and is equal to $\sum_{i=1}^{n} e Z_i C_i$ Equation (7) is subjected to zeta potential on the particle surface $(\boldsymbol{\zeta}_p)$ and zeta potential on the tube surface (ζ_t). Determination of ζ_p and ζ_t are challenging since this contribution aims to study the realistic electroosmosis around a spherical particle that acquires charge from the solution around. One well-known model is so-called ETL model [5]. In this model, it is assumed that the solid-liquid interface acquires electric charge when it is isolated whereas for overlapped EDLs the isolated surface assumption would not be physically available anymore. Wang and Revil [26] presented a theoretical framework based on the ETL model in which the influence of the EDLs overlap studied in a narrow channel. However, as we know, in narrow channels, the concentration of counterions would be enriched due to the EDLs interaction. As a result, the standard ETL models could not fully consider the EDL interactions. To tackle this bottleneck for the present work, we introduced the enrichment model as modified bulk ion concentration [36] to the ETL model. Therefore, a modified ETL (METL) model has been presented that not only obtained the local surface charge acquirement at the solid-liquid interfaces but also takes into account the charge regulation due to the EDLs interaction (see the Supporting Information for the details of METL model).

Regarding the external electric field, the solid–liquid interfaces are assumed to have zero permittivity for the external electric field. As a result, based on the mentioned assumptions, the electric potential associated with the applied external electric field must satisfy the Laplace's equation [27]:

a)
$$\nabla^2 \Phi(r, \theta) = 0$$

b) $\frac{\partial \Phi}{\partial r} = 0.0$ at all solid surfaces,
 $\Phi_{\rm in} = \phi_0 , \Phi_{\rm out} = 0,$ (8)

where Φ denotes the applied external electric potential which is subjected to the boundary conditions of Eq. (8b) where Φ_{in} and Φ_{out} denote the inlet and outlet electric potential, respectively. In this work, we applied the inlet external electric potential as $\phi_0 = 5$ V.

3 Results and discussion

3.1 Benchmarks

 $\nabla \nabla^2 = (0)$

In order to examine our theoretical and numerical framework proposed in the last section, in this section, first we valid our METL model with the available experimental data for the measured streaming [37] and electrical conductance [38] in a straight microchannel. Second, a uniform charged particle in a noncharged tube with thin EDLs is considered. In this scenario, the fluid flow is driven by an applied external electric



field. For more simplicity, the particle charge considered to be small and homogeneous to meet the assumptions claimed by Smoluchowski for rigid electrically insulating particles of any shape [28]. Based on the mentioned assumptions, one can propose analytical solutions for internal electric potential field and ion distribution around a spherical particle in a tube.

Fig. 3A shows the streaming conductance, $S_{\rm str}$, predictions by the present work framework (PNP + NS) for the microchannel fabricated by Heyden et al. [37]. In this study, the streaming conductance is calculated as follows:

$$S_{\rm str} = \frac{1}{\Delta P} \int \rho_{\rm e} (\gamma) \, u(\gamma) \, d \, A. \tag{9}$$

It is shown that for a wide range of the background KCl concentration from 10^{-6} to 1.0 M, the results have good agreement with experimental measurements. Moreover, it is demonstrated that the present numerical framework could predict more accurate streaming conductance for nonoverlapped EDLs (C_{KCl} > 10^{-3} M) compared with the overlapped EDLs (C_{KCl} < 10^{-3} M). The solution pH is prescribed equal to 8.0. Fig. 3B proves that our framework could predict electrical conductance, *S*_{ek}, which is calculated as:

$$S_{\rm ek} = \frac{1}{\Delta V} \left(\sum_{i} Z_{i} e \int J_{i} dA \right)$$
(10)

in good agreement with the experimental measurements performed by Karnik et al. [38]. In accordance to what mentioned for Fig. 3A, the presented framework could predict more accurate results when the EDLs interaction would be weak which derived from higher ionic strength.

Figure 3. The benchmarks for streaming and electrical conductance. (A) Streaming conductance, $S_{\rm str}$ (pA/bar), for a silica microchannel with 140 nm height, 4.5 mm length, and 50 μ m width, applied pressure gradient $\Delta P = 4$ and background solution pH 8; (B) Electrical conductance, $S_{\rm ek}$ (nS), for a silica microchannel with 35 nm height, 120 μ m length, and 1 μ m width, applied external electric field E = 41667 V/m and the deionized background solution with pH 7; as a function of KCl concentration.

As the second benchmark, we assume a homogeneously charged particle with radius r = a in a tube with diameter H = 2b whereas a/b = 0.1. As mentioned above, the tube does not possess electrical charge in contact with aqueous solution. As a result, one can denote the boundary condition for internal electric potential as $\psi(a) = \zeta_p$, $\psi(b) = 0$. In order to make sure that the EDLs would not interact, we choose the molar concentration for KCl equal to 3.6 mM that makes the tube diameter to EDL thickness as $\kappa b = 40$. Considering the facts that for this benchmark the EDLs thickness is thin and the thermodynamic equilibrium state is available, one can denote that the concentration of ions could be determined by the Boltzmann distribution equation:

$$C_{i}(r) = n_{0} \exp\left(-\frac{e Z_{i} \psi(r)}{K_{b} T}\right).$$
(11)

However, the internal electric potential is still unknown and it should be determined. Based on the above assumptions and boundary conditions, one can simply obtain an analytical solution for Eq. (7) as [27]:

$$\psi(r) = \frac{a\zeta_{p}}{r} \cosh(\kappa(r-a)) + \frac{b(-\lambda\zeta_{p}\cosh(\kappa(b-a)))}{r\sinh(\kappa(b-a))} \sinh(\kappa(r-a)), \quad (12)$$

where $\lambda = a/b$ and *r* is the radius from the center of the particle. Fig. 4 demonstrates the predicted results by the present work framework compared with the analytical solutions mentioned above. As it is shown, our proposed numerical framework could predict well agreement results with the analytical solution for internal electric potential, counterion, and co-ion concentration.

To examine the hydrodynamic part of our numerical framework, Zydney [27] proposed an analytical solution for a stationary spherical particle in which the fluid around it will start to move due to the electrokinetic phenomena induced by the presence of the charged sphere while the tube does not gain any surface charge. It is assumed that the sphere has zeta potential, ζ_p , and the strength of the external electric field is E_z . So, the fluid flow velocity far from the sphere could be obtained as follows:

$$U_{\rm E} = \left(\frac{1 - 2.5\lambda^3 + 1.5\lambda^5}{(1 - \lambda^3)(1 - \lambda^5)}\right) \ U_{\rm HS},\tag{13}$$

where $U_{\rm HS}$ denotes the Helmholtz–Smoluchowski velocity $U_{\rm HS} = \frac{-\epsilon_0 \epsilon_r E_z \zeta_p}{\mu}$. Equation (13) demonstrates that when $\lambda \rightarrow 0$, $U_{\rm E} = U_{\rm HS}$. Fig. 5 shows the present work prediction versus the analytical solution which proposed by Eq. (13) as a function of the ratio of the sphere to the tube radius. As it is shown, for $\lambda \leq 0.1$, the present work framework could predict the non-dimensional velocity in good agreement with the analytical solution.

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3.2 Effects of solution pH and particle radius

According to what mentioned in Section 2.2.2, it is well understood that the inhomogeneously acquired surface charge of a solid-liquid interface is strongly depend on the local solution properties specifically the solution pH. The higher solution pH does not only increase the zeta potential on the edge of the diffuse layer (ψ_d) but also increase the surface charge of the solid-liquid interface due to the higher concentration of the hydroxyl ions (OH⁻) [26]. This acquired surface charge has a key role for ion transport in micro and nanoscale. Physically, a higher amount of surface charges will attract more counterions to the EDL in order to retain the electroneutrality of the double layer. However, sometimes due to the very low ionic strength and small channel height, the EDLs may overlap and as a result the whole electroneutrality of the system does not retain. In order to study the effects of the particle and tube EDL interactions on the surface charge and zeta potential of the particle, we considered two particle sizes where the ratio of the particle radius to the tube radius would be $\lambda = 0.2$ and 0.48. The concentration of the KCl in the background solution is assumed to be 3.6 \times 10 $^{-4}$ M with two solution acidity as pH 4 and 6. It is worth mentioning that the tube radius to the EDL thickness would be $\kappa b = 4.97$. By applying an external electric field, the nonzero net charges in the vicinity of the particle and tube walls make a fluid flow which is so-called electroosmotic flow.

Fig. 6 demonstrates the contours for the internal electric potential field, net charge density, and the fluid flow velocity along the tube when all the solid-liquid interfaces acquired surface charge locally based on the local solution properties. It is shown that for the internal electric potential field (Fig. 6A and B), qualitatively, one can denote symmetry even near to the particle surface. Considering the net electric charge density (ρ_e) (Fig. 6C and D), as we expected, the presence of the particle with negative surface charge induces a nonzero net electric charge on a region near to the particle. The net electric charge is obtained as $\rho_e = \sum_{i=1}^4 Z_i e C_i$, where the concentration of hydronium and hydroxyl ions also take into account. Fig. 6E and F show the nondimensional velocity of the electroosmotic flow in the x-direction. Comparing the small and the big particles, it is revealed that the big particle influenced wider region around itself and decreases the electroosmosis velocity compared with the small particle.

Despite the general symmetry that was observed based on the results of Fig. 6, a careful insight into the EDL around the particle reveals the general asymmetrical distribution of the zeta potential, ions concentration, and the surface charge density. This asymmetrical behavior could be explained physically by considering the exerted forces on the ions due to two different electrical field. These two forces are demonstrated by the red and blue arrows in Fig. 7, which represent the electrical forces due to the applied external electric field and the negative acquired charge on the particle surface, respectively. It is worth noting that the electrical forces originated from the negative charge on the particle could be dependent on θ since the ζ is determined based on the solution properties



Figure 4. The nondimensional (A) internal electric potential, (B) counterion concentration, and (C) the co-ion concentration predicted by analytical solution (solid line) compared with the present work predictions (symbols).



Figure 5. The nondimensional velocity of the fluid far from a charged sphere at the noncharged nanotube. The fluid flow is generated due to the applied external electric field. λ denotes the ration of sphere to nanotube radius and U_{HS} denotes the HS velocity by definition.

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Figure 6. The contours of the internal electric potential field, net charge density, and the flow velocity in the *x*-direction for two particles when reservoir bulk solution properties are pH 4 and $C_{KCI} = 3.6 \times 10^{-4}$ M. The particles are illustrated by a filled gray circle. ζ_0 in (A) and (B) represents the reference electrical potential which is obtained by solving the METL model based on the reservoir bulk solution properties.

near to the solid–liquid interface. Considering the ions in front of the particle, Fig. 7 shows that both aforementioned forces are exerted to the positive ions in the *x*-direction since they are in (-x)-direction for the negative ions. As a result, the concentration of the counterions should be increased. Based on our proposed METL model (see the Supporting Information), we know that by increasing the concentration of the counterions, the thickness of the EDL decreases and consequently the zeta potential would be decreased. Besides, we expect that the solution acidity, pH, should be decreased in front of the particle since the H⁺ concentration increased by

the same reason we have mentioned for the counterions increment. Thus, the zeta potential also should be decreased due to the decrease in pH [26]. On the other hand, the exerted forces in the rear of the particle (right-hand side) for both positive and negative ions would have different directions depending on the ion charge. As shown in Fig. 7, the positive ions experience an electrical force from the applied external electric fields in the *x*-direction since the electrical force exerted from the negative charge of the particle would be in the (–*x*)-direction. The exerted forces on the negative ions from the external electric field and negative charges on the particle



Figure 7. Schematic illustration of the electrical forces which are exerted on the ions with positive and negative charges in front (left-hand side) and in rear (right-hand side) of the particle. The red and blue arrows represent the electrical forces due to the external electric field and the negative charge on the particle surface, respectively.

should be in opposite directions of what for positive ions. Considering the bidirectional forces configuration, one can state that the concentration of the co- and counterions, as well as the solution pH, could be determined as a result of these forces competition.

Fig. 8 demonstrates the nondimensional zeta potential and surface charge density on the particle surface for two solution acidity pH 4, 6 and for two particle sizes. As we expected and described in the physics of the ion distribution at the presence of a negatively charged particle (Fig. 7), Fig. 8A shows that the minimum nondimensional zeta potential would be attributed to the front of the particle when $\theta = 180^{\circ}$. The changes of the nondimensional zeta potential as a function of θ shows the fact that the maximum amount of it would be in the rear of the particle ($\theta = 0^{\circ}$ or 360°). The modeling results indicate that by increasing the θ , the nondimensional zeta potential decreases up to $\theta = 180^{\circ}$. By further increasing of θ , the zeta potential again increases. Consequently, one can denote that the acquired charge particle in a solution induces asymmetrical distribution of zeta potential around the tube length.

Studying the effects of the solution pH on the surface charge density and zeta potential, Fig. 8A and B shows that for both a/b = 0.2 and 0.48, the more basic solution induces higher nondimensional zeta potential. It is revealed that the higher pH solution would make the zeta potential of the particle to be more sensitive to the variation of θ (Fig. 8A). However, Fig. 8B shows that the surface charge density does not change significantly by θ when pH 6. The interesting point is that the results uncover the nondimensional zeta potential and surface charge density would not change significantly for different particle sizes when pH 6. In other word, one can express that for a more basic solution, the particle size would not have a significant impact on the acquired surface zeta potential and charge density. However, it should be noted that the surface charge density and zeta potential still depend on θ . On the other hand, for a solution with pH 4, it is shown that the predicted zeta potential and surface charge density are not only dependent on the θ but also the particle size influences them significantly (Fig. 8).

As mentioned above, around the particle an EDL formed in response to the acquired charge because of chemically reactive surface of the particle. This double layer has two parts. The first which form in the vicinity of the particle surface contains mobile cations and so-called as the stern layer. The second part is called diffuse layer that contains both cations and anions. It is worth pointing out that the surface charge on the solid–liquid interface could generate surface current density that is defined as [39]:

$$J^{\sigma} = K^{\sigma} E, \tag{14}$$

where J^{σ} denotes the surface current density (in A/m) and E is the applied tangential electric field which is equal to $E = (-E \sin \theta) e_{\theta}$ where E represents the strength of the applied external electric field. Here, we should note that the J^{σ} is the surface current density through e_{θ} which illustrated at Fig. 7. K^{σ} is the conductivity of the surface and in this contribution we defined it as

$$K^{\sigma} = \mathcal{M} \sigma,$$
 (15)

where σ and \mathcal{M} denote the surface charge density (in C/m²) and the ionic mobility which is defined as $\mathcal{M} = U_{HS}/E$ (in m²/sV), respectively. Considering the pH solutions and particle sizes mentioned in Fig. 8, by employing Eqs. (14) and (15), one can calculate the surface current density (Fig. 9). Fig. 9 demonstrates that the surface current density significantly depends on θ when the solution has the acidity of pH 6. However, it is shown that the particle size does not have considerable influence on the J^{σ} for a prescribed solution pH. In addition, Fig. 9 reveals the fact that for lower solution pH, solution with pH 4, the surface current density could be roughly considered as θ independent parameter.

In order to provide a detailed insight into the effects of the presence of the inhomogeneously charged particle in micro or nanotube, Fig. 10 shows the nondimensional averaged results for K⁺ concentration (Fig. 10A), Cl⁻ concentration (Fig. 10B), H⁺ concentration (Fig. 10C), and the velocity of the fluid flow (Fig. 10D) in the *x*-direction for both particle sizes in two prescribed solution pH. It is worth noting that the applied external electric field is $E_p = 10^4$ V/m. Several interesting results have been found from the averaged properties of the aqueous solution. Regarding the K⁺ concentration, it is shown that the higher solution pH induces higher K⁺ concentration. The main reason in favor of this fact could simply due to the higher surface charge density on the solid–liquid



Figure 8. The nondimensional surface electric potential (A) and charge density (B) for particles with $\lambda = 0.2$ and 0.48 when the background solution has two acidity pH 4 and 6 as a function of θ (the degree of surface points on the particle as shown in (A)). The ζ_0 denotes the reference zeta potential that is obtained based on the reservoir solution properties. So, for pH 4, $\zeta_0 = -1.6 \times$ 10^{-2} V and pH 6, $\zeta_0=$ -7 \times 10^{-2} V. In addition, σ_0 denotes the reference surface charge density similar to reference zeta potential obtained based on the reservoir solution properties. The reference zeta potential for pH 4 and 6 are $\sigma_0=$ -8 \times 10^{-4} C/m^2 and $\sigma_0=$ -4 \times 10⁻³ C/m², respectively. All mentioned scenarios are solved when $E_p = 10^4$ V/m.

interfaces, which attract more counterions to retain the electroneutrality. The presence of the particle and its radius has significant impact on the increment of the K⁺ concentration at the particle region specifically for higher solution pH (Fig. 10A). On the other hand, the concentration distribution of the co-ions (Fig. 10B) would be in contrast to what mentioned for counterion (Fig. 10A). Modeling results showed that by increasing the solution pH and for higher a/b, the

averaged concentration of Cl^- around the particle could be decreased up to 0.2 times of the bulk concentration.

Since the aim of this work is to study the electroosmosis around a particle that is charged due to the chemically reactive surface, the concentration of the H^+ has a key role. The nondimensional average of the H^+ concentration along the tube shows (Fig. 10C) that the presence of a negatively charged particle in a tube induces lower pH solution at the



Figure 9. The surface current density for four different scenarios of particle size and solution pH on the particle surface.

particle region. However, this decrease of pH strongly depends on the bulk solution pH and the particle size. For instance, as Fig. 10C shows, for higher bulk pH solution, the concentration of H⁺ at the particle region increases up to seven times of the bulk H⁺ concentration. In addition, by increasing the particle size for a prescribed bulk solution pH, the averaged concentration of the H⁺ also increased. An interesting phenomenon revealed that for bulk solution with pH 4, when we increase the particle size, two depleted regions of H⁺ in front and rear of the particle are formed. In other word, the particle induces two regions of the higher pH solution in front and rear of it. To explain this phenomenon, we have to address again the surface charge distribution on the particle surface (Fig. 8B). It is indicated that for θ = 0° and 180° the particle has the minimum surface charge density. As we know, the less surface charge density will attract fewer counterions to the EDL. Moreover, as it is shown, the pH decreases in same applied external electric field and particle size just happened for when the solution has pH 4, which has the lowest surface charge compared with higher solution pH.

Considering the electroosmotic velocity along the tube, Fig. 10D indicates nearly constant averaged *x*-direction velocity along the tube in front of the particle. However, it is shown that the presence of the particle speeds up the velocity when the fluid flow reaches the up and down part of the particle. By increasing the particle size, this velocity increment would be enhanced as predicted for a/b = 0.48. Furthermore, for the same bulk solution pH, the electroosmotic velocity outside of the particle region has smaller amounts for a particle with bigger radius. However, in the particle region, as Fig. 10D shows, the velocity for big particle accelerates enough to reach the velocity predicted for the small particle.

In order to study the effects of the particle on the pH distribution around itself, we need to look insight into it with more quantitative data. To this aim, the nondimensional H⁺ concentration distribution for a cross-section of tube from a x/H near to the particle to x/H = 2.5 is presented by Fig. 11. The data showed that by getting closer to the particle in the *x*-direction, a negative pH gradient ($\nabla pH_x < 0$) along the tube induces due to the presence of the particle. It should be pointed out that far from the particle, there would not be any pH gradient. On the other hand, for the *y*-direction, the particle induces negative pH gradient ($\nabla pH_y < 0$) for the region near to it. This pH gradient behavior implies the fact that the particle resembles as a sink for solution pH.

3.3 Streaming current and potential for particle-fluid-tube configuration

3.3.1 Streaming current for simple nanotube capillary

In the last section, we presented the surface current density on the particle that is a result of the surface charge density obtained by our direct simulation. In 1998, Lyklema and Minor [39] showed that the anomalous behavior of the zeta



Figure 10. The nondimensional averaged amounts of K⁺, C1⁻, H⁺, and U on the microchannel cross-section.

potential obtained by the conventional definition for streaming potential

$$E_{\rm str} = \frac{\varepsilon_{\rm r} \varepsilon_0 \zeta \Delta P}{\mu K^{\rm L}} , \qquad (16)$$

which sometimes radius-dependent and sometimes not, could be explained by defining a new dimensionless parameter, so-called Dukhin number, as

$$Du \equiv \frac{K^{\sigma}}{a K^{\perp}},\tag{17}$$

where K^{σ} was defined previously by Eq. (15) and K^{L} , the bulk conductivity, could be obtained as $K^{L} = e n_{0} \mathcal{M}$ in C/Vms. Based on this definition, they proposed a relation for

streaming potential in a cylindrical capillary tube of radius *a* as [8]

$$E_{\rm str} = \frac{\varepsilon_{\rm r} \varepsilon_0 \zeta \Delta P}{\mu K^{\rm L} \left(1 + 2Du\right)} \,. \tag{18}$$

By employing the streaming potential (Eq. (18)), one can obtain the streaming current as follows:

$$I_{\rm str} = \frac{E_{\rm str} A K^{\rm L}}{L} , \qquad (19)$$

where *A* and *L* denote the cross-section area and length of the capillary tube, respectively.

To compare our direct simulation prediction for streaming current with what proposed by Eq. (19), we solved the streaming current by employing present work framework for different capillary tube radius. The pressure gradient for



Figure 11. The H⁺ concentration distribution along the microchannel cross-section from a region near to the particle to the half of the channel length. The last concentration distribution illustrates the hydronium concentration when x/H = 0.5. The decreasing solution pH has been shown by $\nabla pH < 0$ in the *x* and *y* direction.

all scenarios kept unchanged and the solid–liquid interfaces were acquired charge based on the local solution properties. Fig. 12 demonstrates that our direct simulation results and what predicted by Eq. (19) have good agreement. It is found that for a nanotube capillary, by increasing the nanotube radius, the streaming current would be increased even if the surface and bulk conductivities are remained nonchanged.

3.3.2 Streaming current for particle-fluid-tube system

In this section, we consider the same scenarios mentioned at Section 3.1 in which the fluid flow generated by applied external pressure gradient instead of the external electric field. As a result, the ion transport could be generally due to the convection, diffusion, and electromigration. However, the EDLs still formed in the vicinity of the particle and tube walls since the surfaces are chemically reactive and may possess negative charges. By solving the governing equations mentioned before, Fig. 13 shows the overall zeta potential and surface charge density predicted by the METL model coupled with the PNP + NS. One interesting point, it is found that both the zeta potential and surface charge density are not changed when the particle size changes. However, by increasing the KCl concentration, the overall absolute zeta potential decreases while the absolute surface charge density increases. This behavior of zeta potential and surface charge density is expected based on the previous experimental and theoretical studies [26].

In experimental measurements, the main important measurable parameter to identify the intrinsic solid-liquid interface electric potential is streaming potential. Therefore, making a meticulous relation between measured streaming potential and surface electric potential would be of great importance. In the last section, we presented a relation that reveals the dependence of streaming potential not only to the bulk electric conductance but also the Dukhin number. Based on this relation (Eq. (18)), by increasing the nanotube capillary radius, the streaming or current potential should be increased and decreased for smaller nanotube radius. However, for the particle fluid tube system, this behavior of the streaming potential could not be available when the particle size is changed instead of the tube radius. Fig. 14 shows the fact that the streaming current predicted by our direct simulation would have higher amounts by decreasing the particle radius. To explain this particle fluid tube behavior, we revisit the assumption that the conductivity of the system should be considered as [8]

$$\frac{I_{\rm str}}{E_{\rm str}} = AK^{\rm L} + SK^{\sigma}, \tag{20}$$



Figure 12. The streaming current predicted by our direct simulation compared with what predicted by Eq. (19) as a function of nanotube height.



Figure 13. The overall zeta potential, ζ (V), and surface charge density, σ (C/m²) the microchannel particle system as a function of bulk solution ion concentration in which the fluid flow generated by the applied external pressure gradient. The solution has pH 4 and $E_p = 10^4$ V/m.

Figure 14. The streaming current as a function of bulk solution ion concentration. The results for streaming current from the direct simulation have been compared with what predicted by proposed equation for streaming current (Eq. (26)). The solution has pH 4 and $E_p = 10^4$ V/m.

where *A* and *S* denote the tube cross-section and circumference, respectively. By using the definition of streaming potential (Eq. (9)) one can propose the streaming current as

$$I_{\rm str} = \int \rho_e(\mathbf{y}) \, u(\mathbf{y}) \, dA \,. \tag{21}$$

If the simple pressure-driven velocity in a tube introduced to Eq. (21) and employing the Poisson equation for internal electric potential field, based on the particle-tube symmetry, one can find out the streaming current as

$$I_{\rm str} = \frac{\varepsilon_0 \varepsilon_r \, A\zeta \Delta \, P}{\mu L} \,. \tag{22}$$

By introducing Eqs. (20) to (22), the $I_{\rm str}$ would be eliminated and, eventually, we have a general relation for streaming potential, zeta potential, bulk conductivity, and surface conductivity as

$$E_{\rm str} = \frac{\varepsilon_0 \varepsilon_{\rm r} \zeta \Delta P}{\mu \left(K^{\rm L} + \frac{S}{4} K^{\sigma} \right)} . \tag{23}$$

For the particle fluid tube system, we present the effective cross-section and circumference as

$$A_{\rm eff} = \pi b^2 - \pi a^2$$

$$S_{\rm eff} = 2\pi b + 2\pi a. \tag{24}$$

Introducing the effective cross-section area and circumference to Eq. (23), we have the relation for streaming potential for particle-tube configuration as

$$E_{\rm str} = \frac{\varepsilon_0 \varepsilon_r \zeta \Delta P}{\mu \left(K^{\rm L} + \frac{2}{b-a} K^{\sigma} \right)}$$
(25)

whereas the streaming current would be

$$I_{\rm str} = \frac{\varepsilon_0 \varepsilon_r \zeta \Delta P}{\mu \left(K^{\rm L} + \frac{2}{b-a} K^{\sigma} \right)} \left(\frac{\left(\pi b^2 - \pi a^2 \right) K^{\rm L}}{L - 2a} \right).$$
(26)

Fig. 14 demonstrates the predicted streaming current by our direct simulation and Eq. (26). It is shown that for higher KCl concentrations, the presented streaming current relation (Eq. (26)) could predict more accurate results. However, still, for lower KCl concentration that the EDLs may interact strongly, the streaming current equation could predict streaming current with acceptable deviation compared with direct simulation results. It is worth mentioning that in Eqs. (23) and (26), the ζ and K^{σ} are substituted with the overall amounts presented in Fig. 13.

4 Concluding remarks

The electroosmosis around a spherical particle immersed into a micro or nanotube that is filled with aqueous solution is investigated. The tube and spherical particle surfaces are considered to be chemically reactive and acquire electric charges due to the chemical interaction with the electrolyte solution. The following interesting points would be the results of the particlefluid tube configuration:

- (i) The surface charge density and zeta potential depend on the tangential positions on the particle surface. This dependency became more significant for solutions with a higher pH. On other hand, the particle size had significant effects when the solution pH decreased.
- (ii) As an excess quantity, the surface current density on the particle surface had a sinusoidal behavior and for higher solution pH, it would be significantly depend on the tangential position.
- (iii) Considering the pH distribution around the spherical particle, by moving through *y*-direction to the middle of the microchannel, the pH decreased. Further approaching to the particle in the *x*-direction imposed lower pH amounts. This pH distribution resembled a pH sink at the middle of the tube due to the presence of a negatively charged particle.
- (iv) By utilizing the proposed numerical framework for pressure-driven flow case, the streaming potential for a system of particle fluid tube had reverse relation with the particle size. This finding is in contrast to what proposed for the direct relation of streaming potential with the tube radius. This implies that the streaming potential in a micro or nanochannel could be changed by the particle size even if the surface charge and zeta potential on the solid–liquid surfaces would not be changed.

To elucidate the main reason in favor of this fact, we presented a new simple relation between streaming potential, zeta potential, bulk, and surface conductivity. In this relation, the streaming potential decreases with the increasing particle size.

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