Induced-charge electrokinetic flow in an asymmetric conducting nanochannel for a flexible control of ionic transport

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Abstract

In this study, we propose the implementation of the induced-charge electrokinetic (ICEK) flow in nanofluidics for the first time. Specifically, we analyse the ICEK phenomena in tapered conducting nanochannels, and further identify it to be a brand-new method for flexible modulation of surface charge which governs ionic species transport inside nanochannels. The detailed field information of ICEK phenomena in tapered conducting nanochannels was obtained by numerically solving the coupled Poisson, Nernst-Planck and Navier-Stokes equations. The results reveal interesting characteristics for the fluid flow and the ionic transport induced by the ICEK phenomena in tapered conducting nanochannels: (i) For the liquid flow, the tapered conducting nanochannel demonstrates a full-wave flow rectification that the fluid always flows from the narrow end of the nanochannel to the wide end regardless the polarity of applied electric biases. It is also found that the flow rate increases monotonically and nonlinearly with increasing the magnitude of electric bias. (ii) For the ionic transport, although the total ionic current does not show any rectification, the corresponding cationic and anionic currents do exhibit rectifying characteristics, which makes the nanochannel cation-selective when it is forward biased and anion-selective when it is reversely biased. Moreover, ionic selectivity increases monotonically with increasing the magnitudes of electric bias. Lastly, it is identified that concentration polarization leads to the saturation of ionic selectivity at large electric bias for tapered conducting nanochannels, which is similar to the ion transport through ion-selective nanochannels or membranes by utilizing conventional electrokinetic phenomena with insulating surfaces.

1 Introduction

Nanofluidics is of growing scientific and practical interests with various newly-induced phenomena and a broad range of potential applications, such as transport, separation and detection of ions and biomolecules, and energy conversion etc. [1-2]. Typically, in nanofluidics at least one dimension of the fluidic channel (h) becomes comparable to or even smaller than the Debye length (κ^{-1}) which measures the thickness of electric double layer (EDL) and usually ranges from 1 to 100 nm. Because of the overlap of EDLs ($\kappa h \ll 1$), counterions predominate inside the channel to neutralize the surface charge on channel walls [3]. The change of surface charge on channel wall breaks up the electric neutrality, and hence the quantity of ions and/or the charge density inside the channel must change accordingly to regain the neutrality of the system. Consequently, modulation of the surface charge has been shown an effective way for manipulating the ionic transport inside nanochannels [4, 5]. Generally, there are two established ways to control the surface charge [6. For an insulating surface, its surface charge is determined by the physicochemical properties of the solid surface and liquid

solution, such as the density/composition of chemical groups on the solid surface and the pH/ionic concentration of the bulk solution. Therefore, the surface charge of insulating nanochannel walls can be passively controlled by altering these physicochemical properties, and thus is usually fixed and is not affected by external electric field [7]. On the other hand, for an electrically conducting surface, its surface charge can be actively controlled by directly imposing electrical potential differences between the surface and the bulk electrolyte solution in conducting nanochannels [8].

This study reports the use of so-called induced-charge electrokinetic (ICEK) phenomena as a new means for modulating the surface charge on nanofluidic channels. The mechanism of surface change modulation with ICEK is resulted from the electric polarization which can be actively tuned by external electric field [9, 10]. Hence, the charge modulation mechanism in ICEK phenomena is not only different from that due to physiochemical properties of the solid–liquid interface in the conventional electrokinetics dealing with insulating surfaces, but also different from that by directly imposing the electric potential voltages on the conducting channel walls.

2 The nanochannel system and governing equations of ICEK phenomena

We consider a two dimensional tapered nanochannel with a length being L, a height of right opening being $2h_2$ and a height of left opening being $2h_1$, as shown in figure 1(a). The conducting nanochannel can be fabricated with multiple standard techniques developed in micro/nano fabrication, with firstly the nanochannel formed in an insulating or low-conductivity substrate (e.g., silicon) using an etching process and then the nanochannel wall coated with good conducting materials (e.g., diamond-like carbon or Au) using a sputtering process. The right driving electrode is grounded, and the potential on the left driving electrode is adjustable by a DC power source. The conducting nanochannel walls floating in the external driving electric field are polarised to acquire surface charge which can play the roles of physicochemical surface charge in the traditional electrokinetics [6]. At each opening, the nanochannel is connected to a reservoir containing an electrolyte (e.g., KCl solution) with a bulk concentration, c_0. For simplicity, the bulk concentrations in both reservoirs are assumed to the same.

At first, we nondimensionalise the governing equations that describe the ICEK phenomena in the system by introducing the following reference quantities for electric potential, velocity, pressure, electric current density, electric current and surface

charge density, respectively as

$$\varphi_{ref} = \frac{RT}{F} \quad u_{ref} = \frac{\varepsilon_0 \varepsilon_r \varphi_{ref}^2}{\mu L_{ref}} \quad p_{ref} = \mu \frac{u_{ref}}{L_{ref}} \quad i_{ref} = F u_{ref} c_{ref}$$

$$I_{ref} = F u_{ref} c_{ref} L_{ref} \qquad q_{ref} = \varepsilon_0 \varepsilon_r \frac{\varphi_{ref}}{L_{ref}} \qquad (1)$$

as well as Reynolds number for the liquid flow and Peclet number for the ionic species transport

$$Re = \frac{\rho u_{ref} L_{ref}}{\mu} \qquad Pe = \frac{u_{ref} L_{ref}}{D_{ref}} \qquad (2)$$

where L_{ref}, c_{ref} and D_{ref} denote the reference length scale, the reference ionic concentration and the reference ionic diffusion coefficient, respectively, and all of them are to be specified in the next section. φ_{ref} is the so-called thermal voltage with a value of 25.7mV at room temperature. In equations (1) and (2), F is the Faraday constant, R is the universal gas constant, T is the absolute temperature, ε_0 represents the permittivity of vacuum, ε_r, ρ and μ are the dielectric constant, density and dynamic viscosity of the electrolyte solution, respectively.
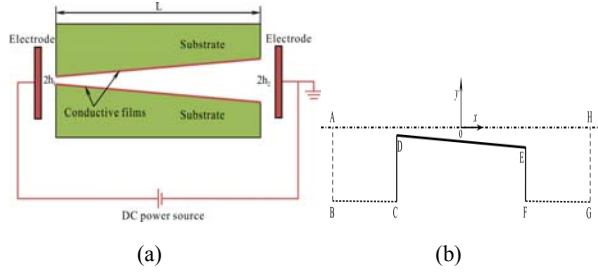

(a)   (b)

Figure 1. (a) Schematic of the nanofluidic system with a conducting tapered nanochannel. A DC power source is used to set up an external driving electric field for driving fluid flow inside the nanochannel. The conducting nanochannel walls are polarised upon turning on the external driving electric field. (b) The sketch of the simulated domain.

The local electric potential and net charge density are related by the Poisson equation in nondimensional form as

$$\nabla^2 \varphi = -\frac{1}{2} \left(\kappa L_{ref} \right)^2 \sum_{i=1,2} z_i c_i \qquad (3)$$

where φ is the dimensionless electric potential, c_i is the dimensionless concentration of ions in the electrolyte solution, z_i is the valence of ions, with subscript i=1 (2) corresponding to cations (anions), and κ is the inverse of Debye length given by, $\kappa = \sqrt{(2 c_{ref} F^2)/(\varepsilon_0 \varepsilon_r RT)}$.

At the steady state, the local concentration of ionic species is governed by the dimensionless Nernst-Plank equation

$$Pe\left(\mathbf{u} \cdot \nabla c_i \right) = D_i \nabla^2 c_i + D_i z_i \nabla \cdot \left(c_i \nabla \varphi \right) \qquad (4)$$

where $\mathbf{u}$ is the velocity vector, and it has two components (u, v) in x direction and y direction, respectively, D_i denotes the normalised diffusion coefficient for ionic species.

The motion of electrolyte solution is governed by the continuity and Navier–Stokes equations

$$\nabla \cdot \mathbf{u} = 0 \qquad (5a)$$

$$Re\left(\mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla^2 \mathbf{u} - \frac{1}{2} \left(\kappa L_{ref} \right)^2 \nabla \varphi \sum_{i=1,2} z_i c_i \qquad (5b)$$

where p is the dimensionless pressure and the third term on the right hand side of equation (5b) represents the electrostatic body force due to the non-electroneutrality. Although the liquid flow in nanofluidics is dominated by viscous effects because of very small Reynolds numbers, the convective transport of momentum in equation (5b) is still retained for completeness.

The electric current for species i can be obtained by integrating the current density over the cross section of the nanochannel

$$I_i = \int_{s_1} i_{i,x} \, d s_1 \qquad (6)$$

where s_1 is the surface element of cross-section of the channel, $i_{i,x}$ denotes the x component of the current density vector for the ion specie i, $\mathbf{i}_i$, which can be expressed as

$$\mathbf{i}_i = \mathbf{u} z_i c_i - \frac{1}{Pe} z_i D_i \nabla c_i - \frac{\nabla \varphi}{Pe} z_i^2 D_i c_i \qquad (7)$$

The ionic selectivity of tapered conducting nanochannels is defined in the same as that in insulating nanochannels [11]

$$S = \frac{|I_1| - |I_2|}{|I_1| + |I_2|} \qquad (8)$$

which ranges from -1 to 1. The selectivity defines a preference for particular ions to be transported. When S is in the range of (-1, 0), the channel shows anion selective function, while when S is in the range of (0, 1), the channel shows cation selective function. Ideally, S would be 1 (-1) for a nanochannel that is perfectly cation (anion) selective and S=0 for a nonselective nanochannel.

3 Description of the simulated domain and boundary conditions

Due to the symmetry to the channel axis, only the lower half of the system including the reservoirs and the nanochannel is simulated as sketched in figure 1(b). The solution is symmetric electrolyte KCl with z_1=-z_2=1. The reference ionic diffusion coefficient D_{ref} is chosen as 10^{-9} m²/s and then at room temperature (T=298K) the normalised ionic diffusion coefficients for two ionic species are D_1= 1.957 and D_2= 2.032 [12]. We can calculate that Pe=5.10×10^{-1} and Re=5.66×10^{-4}. Furthermore, c_{ref} is set to be the bulk ionic concentration inside the reservoirs, c_0, and L_{ref} is chosen as the half height of the right opening h_2. In all the simulations, we set L/h_2=200 and the electrokinetic parameter $\kappa L_{ref} = \kappa h_2$=1, which ensures that the channel dimension is comparable to the thickness of EDL and is in nanometre scale. These nondimensional values of L/h_2 and κh_2 together with h_1/h_2=0.2 typically represent a nanochannel system with geometric dimensions of $2h_1$=6nm, $2h_2$=30nm and L=3 μm, and a bulk ionic concentration of c_0= 4.1×10^{-4} M in two reservoirs.

To complete the formulation, the relevant boundary conditions must be specified on the boundaries sketched in Figure 1(b) for the Poisson, Nernst-Planck and Navier-Stokes equations. Symmetric boundary conditions for three governing equations are applied along the symmetric boundary AH. Along the boundary

AB, the electric potential is set to be φ_0 which is adjustable by the DC power source in figure 1. The boundary GH is taken as the potential reference (i.e., grounded as shown in Figure 1(a)). All walls of the reservoirs are assumed to be uncharged. DE is the conducting wall of the nanochannel that is floating in the electric field set up by the two driving electrodes inside two reservoirs. As a consequence, the electric field polarises the conducting walls and causes redistribution of the surface charge on them. There is no charge exchange between conducting walls and their surroundings since conducting walls are ideally polarisable. Then the floating boundary condition [13] which constrains the total charge on the conducting surface is used along boundary DE.
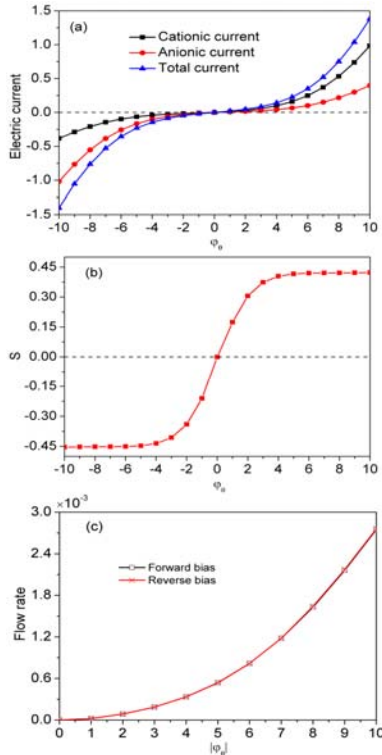

Figure 2. Dependence of the ionic transport and flow rate on electric bias for a tapered nanochannel with h_1/h_2=0.2. (a) Variation of cationic, anionic and total currents. (b) Variation of the ionic selectivity, S. (c) Variation of the flow rate with electric bias.

Boundaries AB and GH are the bulk reservoir and the concentrations of the positive and negative ions are the same as that of the bulk electrolyte in the reservoirs. Electrolyte ions cannot penetrate through the solid surfaces, so the net ionic fluxes normal to the walls of the reservoirs and the nanochannel (boundaries CD, DE, EF, BC and FG) vanish.

Finally, in order to solve the hydrodynamic problem governed by equations (5a) and (5b), nonslip boundary conditions are specified on the solid walls of nanochannel and reservoirs (boundaries CD, DE, and EF). Normal pressure p =0 is used on the boundaries AB and GH due to no applied pressure difference between two reservoirs. Finally, slip boundary conditions are applied on boundaries BC and FG which are away from the entrance and exit of the nanochannel.

The governing equations including the Poisson equation (3), the Nernst-Planck equation (4) and the Navier-Stokes equation (5b) are strongly coupled. In the present work, commercial finite element software package COMSOL Multiphysics 4.3 was adopted to solve the governing equations. In addition, the numerical model was verified using bench-mark tests.

4 Results and discussion

4.1 Characteristics of ionic transport and liquid flow in tapered conducting nanochannels

Figure 2 presents the effect of electric bias on the ionic transport characteristics and the fluid flow rate. It is seen from Figure 2(a) that, although the total ionic current shows no rectification, the corresponding cationic and anionic currents do exhibit rectifying behaviours. To be more specific, the magnitude of cationic current for the forward bias is larger than that for the reserve bias; while the magnitude of anionic current for the forward bias is smaller than that for the reverse bias. It should be noted that such ion transport is different from the literature studies because they only showed the total current rectification [11]. In particular, these studies reported the ion transport in conical (tapered) nanopores with asymmetric charge distributions, and they are based on the conventional electrokinetics for insulating surfaces with fixed surface charge which is not affected by external electric field. What is also identified from figure 2(a) is that the cationic current is larger than the anionic current under the forwardly biased condition, which indicates a cation-selective behaviour; while the situation is completely opposite under the reversely biased condition where an anion-selective behaviour is observed. At last, to gain an in-depth quantitative understanding of ionic selective characteristics of the tapered nanochannel with conducting walls, the characteristics of ionic selectivity defined in equation (10) is depicted in figure 2(b). Generally, the tapered conducting nanochannel is nonselective when the bias is zero, cation-selective when it is forwardly biased, and anion-selective when it is reversely biased. At relatively low voltages, magnitudes of both anionic and cationic selectivity increase significantly with increasing the magnitude of applied electric bias. At high voltages (e.g., larger than 4), the magnitude of selectivity however increases very slowly and tends to saturation. This behaviour at large magnitudes of electric bias is reminiscent of the similar phenomena in the electrodialysis across membranes [14] where bulk concentration gradients (concentration polarization) were identified as the cause for such saturation behaviour. The details of concentration polarization inside two reservoirs are to be discussed in the next section. Figure 2(c) is the plot for the variation of scaled fluid flow rate through the nanochannel with the magnitude of the electric bias. As discussed earlier in this work, for the same magnitude of electric biases, the reversion of electric field direction does not affect the flow field, so reverse and forward biases with the same magnitude produce a same flow rate. It is also shown that the flow rate increases nonlinearly with an increase of the magnitude of electric biases. This intrinsic nonlinearity differentiates ICEK phenomena from conventional electrokinetic phenomena in which the flow rate is linearly proportional to the applied biases.

4.2 Concentration polarization inside the reservoirs

Another fundamental aspect of an ion-selective nanochannel is the generation of bulk electrolyte gradients, usually known as

concentration polarization. Figure 3 shows the details of concentration polarization inside two reservoirs for various values of forward electric bias. It should be noted that only the electroneutral regions (with equal concentration of K^+ and Cl^+) are the bulk concentration polarization zones [15], and the charged regions near the channel inlet and outlet are so-called space charge zones. The formation of these two zones inside the reservoirs is universal for ion-selective nanochannels or membranes. Thus it would be expected that the ion-selective process in a conducting tapered nanochannel due to ICEK phenomena also induces two zones inside the reservoirs. For three cation-selective processes shown in figure 3, the bulk electrolyte concentration decreases along the channel axis inside both left and right bulk reservoirs. These characteristics of concentration polarization are similar to those for cation-selective nanochannels with physicochemical bond surface charge shown in [2, 15] (see figure 18 in [2] and figure 1 in [15]). Also Figure 3 shows that the intensity of the concentration polarization increases with increasing the magnitude of electric bias, and also the space charge zone tends to occupy a much larger portion of the reservoir as the magnitude of electric bias increases. With a larger forward electric bias applied, preferential transfer of cations through the nanochannel would significantly deplete cations near the inlet of nanochannel in the left reservoir, so that a concentration gradient must form inside the bulk reservoir to maintain an appreciably lower concentration of electrolyte near the nanochannel inlet. Such change in the ionic concentration is equivalent to the reduction of the effective bulk concentration of electrolyte which manifests as a tendency for ionic selectivity saturation [14]. When the magnitude of electric bias is large enough to completely deplete both cations and anions near nanochannel inlet, the electric current reaches its high limiting value (so-called limiting current) [2], and thus the selectivity approaches its limit of saturation. In the present technique, ion-selective function is achieved by the ICEK technique in a conducting nanochannel. A higher DC electric bias however would engender more negative effects in some applications, such as disruption of conducting films due to Faradaic reactions, which are beyond the scope of the present work. Therefore, limiting behaviours of concentration polarization and ionic selectivity at high voltages are not discussed here.
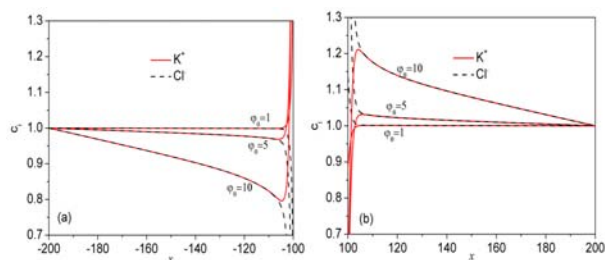

Figure 3. Concentration polarization inside the two reservoirs for three different values of forward electric bias when $h_1/h_2=0.2$. (a) Ionic concentration profiles along the nanochannel axis (y=0) inside the left (inlet) reservoir. (b) Ionic concentration profiles along the nanochannel axis (y=0) inside the right (outlet) reservoir.

Finally it is also relevant to discuss the effect of induced flow on the concentration polarization. Understandably, a stronger flow resulted from a stronger electric field (see Figure 2(c)) would convect more cations from the narrow end to the wide end of channel. Such effect certainly assists the depletion (enrichment) of cations inside the left (right) reservoir, and thus intensifies the concentration polarization and concentration gradient.

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