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Asymmetric properties of ion transport in a charged conical nanopore

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Recently, the experimentally observed asymmetric properties of ion transport in charged conical nanopores (CCNs) that resemble those in biological ion channels have attracted a lot of attention in theoretical studies in nanotechnology research. In this paper, we report several tactics to study this effect by directly solving the Poisson-Nernst-Planck (PNP) equations. The result shows that PNP equations can indeed quantitatively describe the properties of these nanopores. Based on our numerical solutions, we contribute the rectification effect to ion-enrichment and ion-depletion. A detailed study of length dependence of current indicates that a relatively long length is indispensable for the CCNs to have rectification effect. We suggest that PNP equations and the calculation method could be further used to study other shapes of nanopores.

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I. INTRODUCTION

For the reasons that a synthetic charged conical nanopore [1–3] in a polyethylene terephthalate (PET) membrane exhibits asymmetric properties of ion transport that resemble those in biological ion channels [4], such as current rectification [1,2,5–7] and ionic selectivity [8,9], and its potential applications for the detection of biomolecules, such as protein [10] and DNA [11,12], there is extensive research on exploring the basic physical properties of CCNs both in experiment [1–3,5,6,8,9] and theory [5,8,9,13–17]. A full understanding of these asymmetric phenomena can not only benefit the future studies on biological ion channels, but also promote nanotechnological applications. Several models have been proposed to explain this effect [14–17] but most of them aimed at a qualitative explanation rather than a quantitative fit with experimental data, and some of them are based on several unclear assumptions. Thus, the unsubstantiated assumptions in these models may overshadow the true understanding of the mechanism of the asymmetric character (see Siwy's recent review [18] for an overview of these models). In this work, we aim at providing a quantitative model to explain the current rectification effect in CCNs, and give more insight into ion transport properties in pores with nanometer size.

Our model is based on Poisson-Nernst-Planck (PNP) theory of electrodiffusion, in which the mobile ions are represented as a continuous charge density. This theory has been applied to study membrane electrochemistry [19], ion transport in nanofluidic channels [20–22] and the Gramicidin A channel [23,24]. Corry *et al.* [25] showed that this continuum theory still works well when the dimension of the nanopore is more than about 1 nm. Therefore, solving PNP equations directly should be a prospective way to understand all the ion transport properties of conical nanopores. While PNP equations had been directly solved under different conditions [20–24], we found that in the case of CCNs in PET membrane, the equations become numerically pathological and are hard to converge. Cervera *et al.* [16,17], in fact, had systematically studied the rectification effect of conical nanopore with PNP equations and get good results. However, in order to solve these equations, they neglected the influence of both reservoirs connected to the nanopore and used several assumptions to simplify the three dimension equations to one dimension. In comparison, we developed some tactics to solve PNP equations directly in the case of three dimensions, and also the reservoirs are taken into consideration. Based on our results, we get some definite results about the asymmetric properties of conical nanopore in addition to explaining the rectification effect.

Our model does not include any free parameters; all are taken from experimental data, including surface charge density (σ), the size of the nanopore, ion concentration of KCl (n_0), and diffusion coefficients. The diffusion coefficients taken from a bulk solution of infinite dilution may induce some errors to our calculated result. Although they only slightly decrease with the increase of concentration, they are probably affected by the restricted geometries [18]. Nevertheless, how they decrease with restricted size has not been fully understood, so we assume that in a dimension of several nanometers the diffusion coefficients approximately keep constant as in bulk solution. Our calculated result of current versus voltage bias shows a good agreement with experimental data, indicating that such an approximation might be valid to nanopores with such a dimension. The analysis of the model shows that the rectification effect is mainly due to ion enrichment and depletion, and that a relatively long length is indispensable for the conical pore to have rectification effect. This study indicates that PNP equations are essentially applicable in nanopores with such a dimension, and can quantitatively explain the mechanism of asymmetric properties of those kinds of charged conical nanopores.

II. THEORY AND MODEL

We suppose ion transport in nanofluidic channel is governed by Poisson-Nernst-Planck (PNP) equations, which

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combines Poisson equation that electrostatic potential (ϕ) should obey, and Nernst-Planck equation that governs the ion flux $(J_{\pm})$:

$$\nabla^2 \phi = -\frac{e}{\epsilon\epsilon_0}(n_+ - n_-), \tag{1}$$

$$J_i = -D_i\left(\nabla n_i + \frac{ien_i}{kT}\nabla\phi\right), \quad i = +,-, \tag{2}$$

where e is the electron charge, ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant of water, n_i is the concentration of ion species i (K^+ or Cl^-), k is Boltzmann constant, and T is the temperature of the solution. Together with the steady state continuity constraint $\nabla \cdot J_i = 0$, Eq. (2) becomes

$$\nabla \cdot \left(\nabla n_+ + \frac{en_+}{kT}\nabla\phi\right) = 0, \tag{3}$$

$$\nabla \cdot \left(\nabla n_- - \frac{en_-}{kT}\nabla\phi\right) = 0. \tag{4}$$

As K^+ and Cl^- are the only ions in our model, we use, respectively, "+" and "−" to represent the K^+ and Cl^- ions in the whole paper.

A more accurate model should include both electrophoresis and electroosmosis into consideration. However, the current due to electroosmosis (I_{EOF}) is often much less than that due to electrophoresis (I_{EFF}). Only when the diameter of the pore is about the same size of Debye length does the electroosmosis come into important. Daiguji *et al.* showed that $I_{\mathrm{EOF}}/I_{\mathrm{EFF}}$ is less than 10% in the cylinder nanochannel that they considered [20]. For the conical nanopore, since only a short length at the tip end has the size comparable to Debye length, the electroosmosis is much less important than electrophoresis. Our 2D numerical calculation also shows that the calculated current that takes electroosmosis into consideration is only several percent larger than that without electroosmosis. Therefore, neglecting electroosmosis would be a reasonable approximation.

Directly solving the full three-dimensional PNP equations is a formidable task in our system. Because the nanopore is axial symmetric, cylinder coordinate system is optimal for our calculating. Thus, the three-dimensional domain is simplified to a two-dimensional domain. Figure 1 shows the domain and cylinder coordinates for the calculation, where the conical nanopore is in contact with two reservoirs. It is necessary to take the reservoirs into consideration to avoid the uncertainty of the boundary conditions at the pore mouths [20,24]. We find when the sizes of the reservoirs (w and h) are large enough (typically more than 200 nm), the calculated result is almost independent of their size. So we can arbitrarily set the value of w and h as long as they are larger than 200 nm and r_b. The boundary conditions at the nanopore wall are $\nabla_\perp \phi = -\sigma/\epsilon_0\epsilon$, $J_{i\perp} = 0$; the ends of reservoirs: $\phi = \phi_b$ (b=left or right), representing the applied voltage on the electrodes $n_i = n_0$, where n_0 represents the concentration of KCl bulk solution; at the axis and other walls: $\nabla_\perp \phi = 0$, $J_{i\perp} = 0$. In the above statement, $\perp$ denotes the wall-normal component. After solving the coupled Eqs. (1), (3), and (4), the current of each ion can be calculated by integrating flux in any cross section of the nanopore

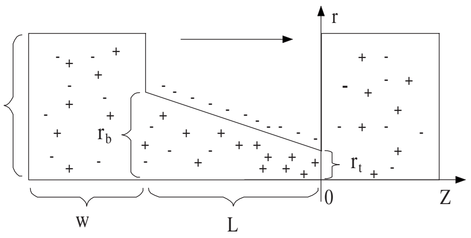

FIG. 1. Schematic view of a conical nanopore that connects two reservoirs (not to scale) and the cylinder coordinates for solving the PNP equations. "+" stands for the K^+ ion and "−" stands for the Cl^- ion. The arrow indicates the positive direction that we define in the whole paper.

$$I_i = 2\pi e \int rJ_i dr, \quad i = +,-. \tag{5}$$

The dielectric constant of KCl solution ϵ is 80 [20,21,23]. The diffusion coefficient of K^+ and Cl^-, D_+ and D_- are 1.96×10^{-9} and 2.03×10^{-9} m^2/s, respectively [20,21]. The surface charge density is approximately -0.24 C/m^2 (~ 1.5 e/nm^2) [7,26].

III. COMPUTATIONAL METHOD

We use finite element method to solve above PNP equations. These coupled partial differential equations are notoriously difficult in numerical calculation; it is almost impossible to converge when solving it directly with the parameters that taken in experiments. For one thing, the length of the nanopore (~ 1 μm) is thousands of times larger than the diameter of the pore tip (~ 5 nm). For another, the high surface charge density leads to sharp potential gradient near the surface. Only with lower surface charge density [20,21] and a small range of voltage bias does the direct finite element method converge and get the right answer. In order to solve this problem, we need to develop some new tactics. One tactic is to provide good initial values for ϕ, n_+, and n_-, and decompose the equations to two parts. To fulfill this goal, we first solve the equations without the applied voltage, and take the solution as ϕ^0, n_+^0, n_-^0. Under such static circumstance, since current equals zero, the solution for Eqs. (3) and (4) becomes $n_+^0 = n_0 \exp(-e\phi^0/kT)$, and $n_-^0 = n_0 \exp(e\phi^0/kT)$, which in fact stand for the Boltzmann distribution. Substitute them into Eq. (1), it becomes

$$\nabla\phi^0 = 2\frac{n_0 e}{\epsilon\epsilon_0}\sinh\left(\frac{e\phi^0}{kT}\right). \tag{6}$$

In this case, the coupled three equations become one. Although it is still nonlinear, it nevertheless is many times easier to solve. When applying voltage bias, we decompose ϕ, n_+, and n_-, with $\phi = \phi^0 + \phi^1$, $n_+ = n_+^0 + n_+^1$, and $n_- = n_-^0 + n_-^1$, together with the decomposition of the boundary conditions.

It is easy to deduce that ϕ^1, n_+^1, and n_-^1 obey the following equations:

$$\nabla^2\phi^1 = -\frac{e}{\epsilon\epsilon_0}(n_+^1 - n_-^1), \tag{7}$$

$$\nabla\cdot\left(\nabla n_+^1 + \frac{e}{kT}[n_+^1(\nabla\phi^0 + \nabla\phi^1) + n_+^0\,\nabla\,\phi^1]\right) = 0, \tag{8}$$

$$\nabla\cdot\left(\nabla n_-^1 - \frac{e}{kT}[n_-^1(\nabla\phi^0 + \nabla\phi^1) + n_-^0\,\nabla\,\phi^1]\right) = 0. \tag{9}$$

The corresponding boundary conditions at the end of the reservoirs are $\phi^1=\phi_b^1$ (b=left or right), $n_i^1=0$; at all other walls $\nabla_\perp\phi^1=0$, $J_{i\perp}=0$. Thus, the difficulty for convergence brought by the surface charge in the conical nanopore only influences the boundary condition of Eq. (6), which is much easier to solve. By doing so, we find that the remaining Eqs. (7)–(9) are relatively easier to converge. Furthermore, using the solution under small voltage bias as the initial value of larger voltage bias will speed up the calculation and bring convergence.

In some situations, such as high surface charge density with lower solution concentration, the problem becomes extremely pathologic, causing divergence of the numerical solver. Under such circumstances, more tactics to lead the program convergence are applied. We notice in Eqs. (8) and (9) that the nonlinearity comes from the term $n_\pm^1\nabla\phi^1$. If we get rid of this term, the equations become linear, which can quickly converge to the solution. This term, however, is not necessarily small. A new tactic for solving this problem is to multiply a coefficient in the nonlinear term, then gradually increase its value from zero to one. In this process, we always use the former solution as the later initial value. For example, solve the equations with $\delta=0$, and use its solutions as the initial value with $\delta=0.2$, and so forth until $\delta=1$.

With all these tactics, the complete PNP equations are numerically solvable. We also calibrate the calculation system with existing results, following the same steps as reported by Daigui *et al.* [20]. First, when the radii of r_t and r_b are much larger than the Debye length, the surface of the pore can be regarded as an isolated surface with charge density σ. Based on the Grahame equation [27], the theoretical values of surface potentials under three different concentrated solutions $n_0=1,0.1,0.01$ M are -57.3, -111.6, -170.5 mV. In comparison, the results from our numerical calculations are -57.4, -111, -170 mV, with a good agreement with the theoretical values. Secondly, for a cylinder channel ($r_t=r_b$) without surface charge, the current density can be calculated by Eq. (7) in Ref. [20]. For the concentration solution $n_0=0.01$ M, $L=1.01$ μm, and potential bias $\Delta\phi=1$ V, the above equation gives $j_{\mathrm{K}^+}=7.22\times10^4$ A/m^2 and $j_{\mathrm{Cl}^-}=7.48\times10^4$ A/m^2, while our calculated results with the PNP equations give $j_{\mathrm{K}^+}=7.13\times10^4$ A/m^2 and $j_{\mathrm{Cl}^-}=7.38\times10^4$ A/m^2, indicating the validity of our calculation method.

In computer simulation with finite element method, the mesh cells are split dynamically until the estimated uncertainty in the solution is less than a certain error tolerance which guarantees convergence of the solution. In our simulation, error tolerance is 1×10^{-3}. (We find that if we set error tolerance to a smaller value 1×10^{-4}, the numerical result is almost the same as before, while the time for computing increase substantially. Therefore, we think that an error tolerance of 1×10^{-3} is a good trade off between precision and the time for computing.) Typically, the number of mesh cells is about 100 000, and CPU time is about one hour with a 2.8 GHz CPU.

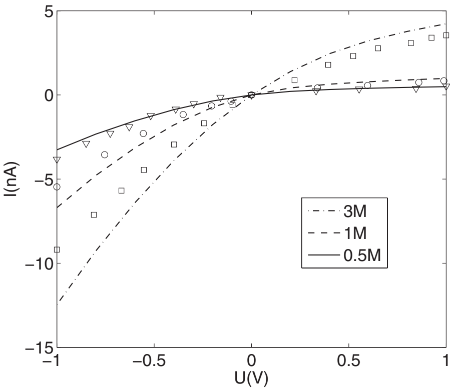

FIG. 2. The calculated current vs voltage bias under different concentrations $n_0=3,1,0.5$ M. Boxes (□), circles (○), and triangles (△) are the corresponding experimental data for $n_0=3,1,0.5$ M, respectively, which are obtained from Fig. 1(a) in Ref. [11]. Parameters: $r_t=3$ nm, $r_b=220$ nm, $L=12$ μm.

IV. CURRENT RECTIFICATION EFFECT

Figure 2 shows the current rectification effect; the calculated results are in a good agreement with experimental data. Slightly adjusting parameters would further improve the agreement, but this might be meaningless because of the uncertainties in taking parameters. For example, the exact shape of the pore may not be ideal conical, the estimated radius of the tip(r_t) which is based on $r_t=LI/\pi\kappa r_b U$ [9] may introduce a slight error, the diffusion coefficients might decrease slightly because of the restricted size, and they can also decrease with high concentration. Nevertheless, the good agreement between experiment and theory clearly demonstrates that PNP equations can essentially be used to study the ion transport properties in a nanopore with such a dimension. The powerful PNP equations and our calculating method could be further used in studying other nanopores with different geometries and parameters. It also might be helpful in further devising nanofluidic channels.

To clarify the influence of surface charge on the rectification effect, we set surface charge density $\sigma=0$, and the simulation result shows a linear *I*-*V* relationship. That is to say, the cone shape alone cannot result in such an asymmetric effect; the surface charge is essential to induce the rectification effect [1,5,9].

We contribute the rectification effect to ion-enrichment and ion-depletion effects, which are observed in charged cylinder nanochannels both in experiment [28] and theory [20]. Pu *et al.* reported that ions (both negative and positive) are

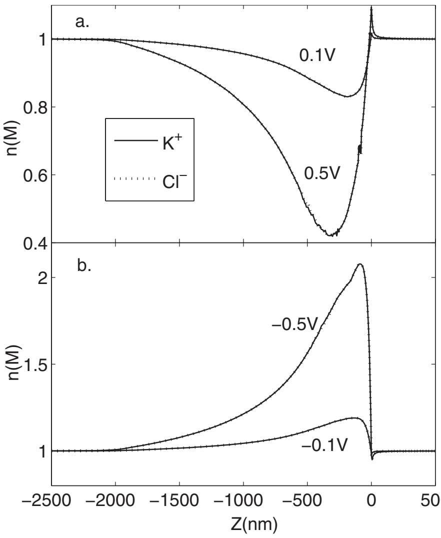

FIG. 3. (a) Ion distribution along the axis ($r=0$) of the nanopore under positive voltage bias ($U>0$). Notice that the concentration for both ions are almost identical along the axis that we can not differentiate the two lines for each ion [because of the screen effect, see Fig. 5(b)]. Both cation and anion deplete in the mid of the pore, and enrich slightly at the tip. (b) Ion distribution along the axis of the nanopore under negative voltage bias. Both cation and anion enrich in the middle of the pore, and deplete slightly at the tip. The parameters are $r_t=5$ nm, $r_b=500$ nm, $n_0=1$ M. In order to see clearly what happens in the tip of the pore, we just truncate the tip end with a length $L'=2$ μm. This means that we fix r_t and the angle θ [$\tan\theta=(r_b-r_t)/L$].

enriched at the cathode end region and depleted at the anode end region in a charged nanochannel [28]. Daiguji *et al.* studied nanofluidic channels and also demonstrated this effect [20]. Herein, these enrichment and depletion effects are deformed due to the specific shape of the conical pore. Figure 3 shows the distribution of K^+ and Cl^- along the pore axis when the applied voltage is positive [Fig. 3(a)] and negative [Fig. 3(b)]. While the anode is placed at the base end of the pore ($U>0$), ions deplete almost in the whole nanopore, and enrich slightly only at the tip end within a short length, as shown in Fig. 3(a). Thus the conductivity of the pore substantially decreases because of the decrease of the ion density in the pore. The more the voltage bias, the greater the depletion effect, contributing to lower conductivity. In contrast, while the anode is placed at the tip end ($U<0$), ions greatly enrich at most part of the nanopore, and deplete only at the tip end within a short length, as shown in Fig. 3(b). Thus the conductivity increases as the increase of the voltage bias. Compared with the results of a cylinder channel [20,28], we continually decrease the cone angle of the nanopore. As a result, the ion-enrichment and ion-depletion region shifts from the mid of the pore toward its base end. When the nanopore becomes cylindrical shape, this region reaches the "base end," which is consistent with the calculation of Ref. [20] and the experiment result [28]. As an illustration, Fig. 4 shows the case under negative voltage bias. The difference between Daiguji's result and ours in the case of cylindrical shape is that the enrichment and depletion effect in our case are much stronger because of high surface charge. We therefore conclude that the specific shape of the conical pore induces strong ion enrichment and ion depletion in the middle of the pore, resulting in the diodelike *I*-*V* curve of CCNs.

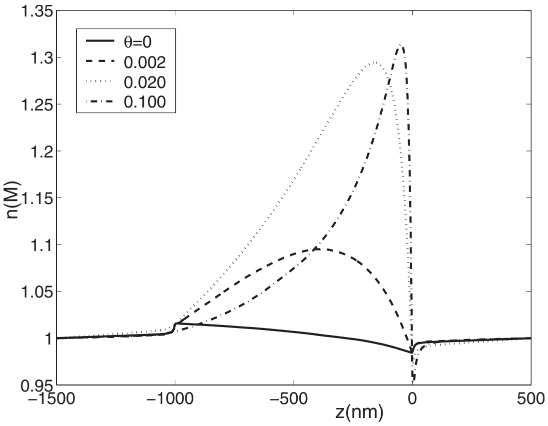

FIG. 4. The influence of the cone angle on ion enrichment and depletion effect. We only show the concentration of K^+ ion since the concentration of Cl^- is almost the same as that of K^+ ion in our case. The applied voltage is −0.2 V; parameters: $n_0=1$ M, $r_t=5$ nm, and $L'=1$ μm.

The ion enrichment and ion depletion effect can be understood in a more intuitive way [15]. Its mechanism can be compared with nanofluidic diode [21]. In that case, the surface charge densities at the right and left halves have the same absolute value but of different signs. Thus the concentration of K^+ is high at the negative charged end and low at the positive charged end; the distribution of Cl^- is opposite. The conductivity of the channel is high when the applied voltage forces both ions flux from higher concentration to lower concentration, while the opposite voltage bias causes the depletion of both ions in the mid region of nanochannel (see Fig. 1 in Ref. [21]). Realizing this fact, we find that the conical nanopore may be regarded as a deformation of the nanofluidic diode. Although it only has one kind of charge on its inner surface, the particular shape of cone helps the formation of asymmetric ion distribution along the axis, which produces the same effect as in nanofluidic diode. In this case, K^+ is high on the tip region and low at the base, while Cl^- is low at the tip region and relatively high at the base (see Fig. 1). Comparing with nanofluidic diode, therefore, the voltage bias in the base-to-tip direction causes the depletion of both ions in the nanopore, which corresponds to the low conductivity. Likewise, the voltage bias in the direction of tip-to-base will induce ion enrichment and high conductivity. In contrast, a conical nanopore without surface charge does not have an initial ion distribution as nanofluidic diode, so it has no ion-depletion and ion-enrichment effect. As a consequence, current is linearly depended on voltage bias as we mentioned before.

We also find that the profile of electric potential along the axis under zero voltage bias is similar to a rachet [Fig. 5(a)] [1], which might be evidence that the rachet model gives a qualitative explanation of rectification effect in a charged conical nanopore [1,9,18]. The depth of the potential well, however, is much less than the one that is calculated from the

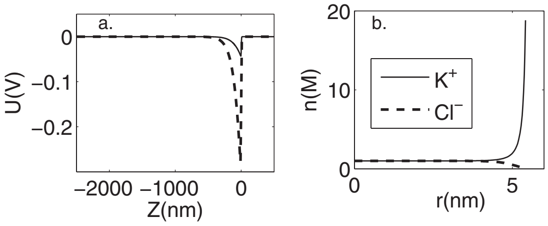

FIG. 5. (a) Profile of the electric potential along the axis ($r=0$) calculated from our model (full line) and from the Debye potential [dashed line, Eq. (7) in Ref. [10]]. (b) The radial ion distribution near the tip end shows the existence of electric double layer with thickness of Debye length 0.31 nm. In these two figures, the applied voltage is zero; parameters: $n_0=0.01$ M, $r_t=5$ nm, $r_b=1$ μm, and $L'=2$ μm.

screened electrostatic (Debye) potential [3,8,9]. We remind the reader that only when $e\phi/kT \ll 1$ does Eq. (6) become linear and give the Debye potential. In the case of a typical conical nanopore, however, $\phi(\sim 100$ mV) near the surface is often larger than $kT/e(\sim 26$ mV). Therefore, substituting $\sinh(e\phi/kT)$ with $e\phi/kT$ will underestimate the screening of ions in solution.

Figure 5(b) shows the radial ion distribution of K$^+$ and Cl$^-$ near the tip of the nanopore. It clearly shows a large increase of positive ion concentration near the negative charged surface, which stands for the formation of electric double layer. The calculated Debye length is 0.31 nm, approximately equal to the thickness of the electric double layer.

V. DISCUSSION AND CONCLUSION

Based on the explanation of the rectification effect in a nanopore, we argue that a relatively long length of the pore is indispensable for the CCNs to have notable asymmetric properties of ion transport. It is the cooperation of the small diameter of the tip, which is comparable to the thickness of the double electric layer, and the relatively long cone-shape body of the charged nanopore that contribute to the ion enrichment and ion depletion, resulting in current rectification. If the length of the conical nanopore is too short, the current rectification will be very weak since the mechanism for ion enrichment and depletion is weakened. A detailed study of length dependence verifies this argument. As shown in Fig. 6, the asymmetry in the I-V curve decreases as the length of the conical pore decreases; it becomes almost linear when $L'=100$ nm. Therefore we predict that a conical pore with the length comparable to its tip diameter cannot have an appreciable rectification effect. Furthermore, the exact shape of the tip end within several nanometers may have no apparent influence on current rectification. In experimental reality, the shape at the tip mouth may not be conical because of mutual interaction of stopping medium and etchant at the last several minutes of the etching process [2]. Yet the good agreement between experiment and theory in this paper might be the evidence for our argument.

As the length L' that we take into account increases, the current under a certain voltage bias gradually becomes independent of it. Figure 6 indicates that a length $L' \sim 1$ μm at the tip end is representative of the whole nanopore. This can be understood by the fact that the electric resistance mainly comes from the tip region, and the pore diameter is comparable to Debye length only in this region. Therefore, in order to reduce the amount of calculation, it is reasonable to just take a relatively shorter length of nanopore near the tip end, for example, $L' \geqslant 1$ μm, into consideration. Notice that this length is still much larger than the pore diameter.

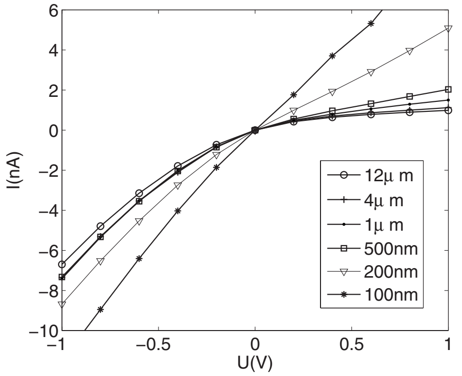

FIG. 6. The calculated current vs voltage bias under different length, $L'=100$, 200, 500 nm, 1, 4, 12 μm with parameters $r_b=220$ nm, $r_t=3$ nm, and $n_0=1$ M.

The observation of ion enrichment and ion depletion may be instructive for future devising complex nanofluidic devices. It gives us a direct view of the ion distribution in the charged nanochannel under a voltage bias. In a double conical pore, for instance, ions will be enriched in one half and depleted in the other. Furthermore, the cone shape is not necessary for a nanopore to have such asymmetric transport properties. Based on the ion-enrichment and ion-depletion effects discussed above, we think that a nanopore with the same sign charge on its surface is possible to exhibit rectification effect if one end of the pore is larger than the other, and the diameter of the small end is comparable to Debye length. For example, the pore in Fig. 7(a) can also exhibit such rectification effect [Fig. 7(b)]. This phenomenon has been observed in the experiment with a similar pore on the material of Si$_3$N$_4$/Si, when the surface of the nanopore is charged [29]. Since this kind of nanopore has been extensively studied in serving as single-molecule sensing devices [29–33], detailed information of ion transport properties by directly solving PNP equations can offer useful information for such studies.

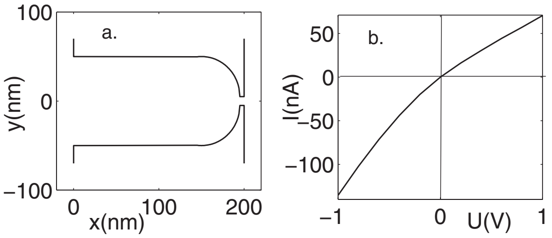

FIG. 7. (a) A kind of nanopore that has rectification effect other than a cone-shaped one. The diameter of the pore tip is 10 nm; surface charge density is taken as -0.24 C/nm^2. (b) The calculated I-V curve by solving PNP equations.

In conclusion, we developed some tactics to solve PNP equations directly in a system of CCNs. Based on the results of numerical calculation, we have a clear understanding of the asymmetric properties of ion transport in a nanopore or nanochannel. The particular shape of the conical pore deforms the ion-enrichment and ion-depletion effect that were founded in cylinder channels, causing the ion to be greatly enriched or depleted in the middle of the pore. Consequently, the conductivity of the pore is adjusted by the applied voltage. The good agreement between theory and experiment demonstrates that PNP equations are a good model to study ion transport in nanopores with a dimension of nm. Our calculation method could be further used in other shape pores with other parameters, and to devise new nanofluidic channels.

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