

Electroosmosis of the Second Kind on Flat Charged Surfaces - a Direct Numerical Simulation Study

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Abstract

While the electroosmosis of the first kind (equilibrium) is accepted widely, the electroosmosis of the second kind (nonequilibrium) is still controversial. In this work, the theory of electroosmosis slip, of either the first kind or of the second kind at electrolyte membrane system is revisited via our direct numerical simulation. The obtained results show that above a certain voltage threshold, the basic conduction state becomes electroconvectively unstable. This instability provides a mechanism for explaining the over-limiting conductance in concentration polarization at a permselective membrane. The most important work in our study is to examine the famous electroosmosis of the second kind formula suggested by Rubinstein and Zaltzman in 1999. Although their formula has been presented for a long time, there has been no work to validate its accuracy experimentally or numerically due to the difficulty in pinpointing exactly the extended space charge layer in their formula. By using direct numerical simulation, we could solve this problem and inspect the application range of their formula. This also helps to strongly confirm the relationship between the electroosmosis of the second kind and the instability in concentration polarization at electro dialysis membranes.

Keywords: Electroosmosis, concentration polarization, permselective membrane.

1. Introduction

Concentration polarization (CP) is generated from complicated effects which relate to the formation of electrolyte concentration gradients resulting from the passage of an electric current through a solution adjacent to a permselective membrane. This phenomenon transfers counterion from electrolyte solutions to ion-exchange membranes. The specific aspect of concentration polarization we address here concerns the stationary voltage-current (I-V curves) of highly permselective membranes employed in electro dialysis which are generally depicted in Fig. 1. There are three distinguishable regions in such a typical curve [1], [2]. The first low electric region is called as Ohmic region (region I). The nearly flat region beside the Ohmic region is named as the limiting one (region II). The end of the plateau is followed by the over-limiting region III. Transition to region III is accompanied by a threshold appearance of a low-frequency excess electric noise, whose amplitude increases with the distance from the threshold and may reach up to a few percent of the respective mean value.

While the Ohmic and limiting conductance were widely gained the explanation, the mechanisms of the over-limiting conductance remained unclear for a long time. To clarify the mechanisms of transporting additional charge carriers to a permselective membrane which cause the over-limiting current at

high voltage, various mechanisms have been suggested as a source of this region, including electroconvection [1] and bulk electroconvection [2], [3], chemical effects [4], and electrostatic effects in micro-scale system [5].

Finally, with the accumulation of evidence, the electroconvection was suggested to cause the over-limiting behavior in the depleted diffusion layer at the CP of the permselective membranes [6]. The electroconvection mechanism also has been confirmed indirectly by an experimental finding: If the surface of the permselective membrane facing the dilute is coated by a gel, a plateau is reached at saturation, and the excess electric noise disappears [7].

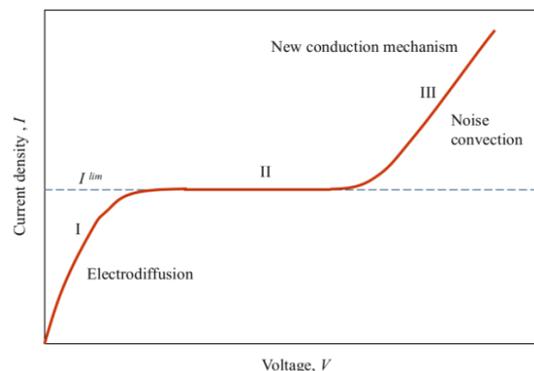


Fig. 1. Sketch of a typical voltage-current of a permselective membrane.

There are two types of electroconvection in strong electrolytes. The first is regularly described as the bulk electroconvection, due to the volume electric forces acting on a macroscopic scale in a locally electroneutral electrolyte. The second is commonly known as electroosmosis, either of the first kind or the second kind [8]. The term electroosmosis of the first kind (EO1) relates to the electrolyte slip resulting from the action of the tangential electric field upon the space charge of a quasiequilibrium diffuse double layer. Electroosmosis of the second kind (EO2) invoked by Dukhin [8] results from the action of the tangential electric field upon the extended space charge of the nonequilibrium double layer. This latter develops at a permselective interface in the course of concentration polarization under the passage of normal electric current [9].

The stability problem corresponding to EO1 implied that no hydrodynamic instability could result from EO1 for a realistic low molecular electrolyte [10]. EO1 is accepted widely to explain the current density towards the limiting value which happens at concentration polarization resulting from the vanishing interface electrolyte concentration at the permselective membranes.

EO2 which is related to the extended space charge developing in the nonequilibrium electric double layer at a permselective interface was invoked by Dukhin as mentioned above [9]. Unfortunately, in his theory of this phenomenon, Dukhin disregarded the very same effects of double layer polarization which he had used to explain the quasiequilibrium electrokinetic phenomena (which resulted in the formula for the EO1 [11]). This led to a fundamental inconsistency of his theory of EO2. This inconsistency is modified by Rubinstein and Zaltzman who analyzed polarization of the nonequilibrium double layer by the tangent components of the external gradients, gaining a correct condition for EO2 [3]. According to this condition, electroosmotic slip velocity at a flat permselective membrane is proportional to the tangential derivative of the normal component of the current density through the permselective interface with the squared voltage, resulting in the expression

$$\tilde{u}_s = -\frac{1}{8}\tilde{v}^2 \left. \frac{\partial^2 \tilde{c}}{\partial \tilde{y} \partial \tilde{z}} \right|_{\tilde{z}=0} \quad (1)$$

However, there is no work to examine experimentally or numerically the EO2 formula of Rubinstein and Zaltzman before. If this formula is proven to be believable, it will help to confirm the relationship between the EO2 and the instability in concentration polarization at electro dialysis membranes, which in turn clarifies the mechanism of the over-limiting conductance phenomenon.

In this paper, we use our numerical solver which is developed in the OpenFOAM platform to simulate the phenomena that occurred at near permselective membrane. By using the obtained data, we also present a clear explanation for these phenomena. The most important part of the paper is the examination of the EO2 formula suggested by Rubinstein and Zaltzman.

2. Model and Numerical Method

2.1. Model

We consider a model system of a permselective membrane in contact with a symmetric, binary electrolyte solution as sketched in Fig. 2. In the model, bulk space where the concentrations of both anion and cation are maintained at constant is at a distance H from the membrane. Electric current is driven through the membrane by a bias voltage between the bulk space and the membrane.

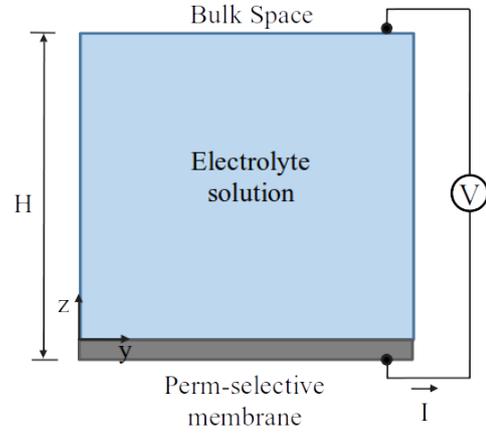


Fig. 2. Model of a permselective membrane in contact with a quiescent electrolyte solution. A bias voltage V is applied between the membrane and bulk space to drive ion current through the membrane.

2.2. Equations

The two-dimensional model problem for concentration polarization mentioned above is described by following equations [1], [12] (tilded notations are used below for the dimensionless variables, as opposed to their untilded dimensional counterparts):

$$\frac{1}{\tilde{\lambda}_D} \frac{\partial \tilde{c}_\pm}{\partial \tilde{t}} = -\tilde{\nabla} \cdot \tilde{\mathbf{j}}_\pm \quad (2)$$

$$\tilde{\mathbf{j}}_\pm = -\tilde{D}_\pm \cdot (\tilde{\nabla} \tilde{c}_\pm + Z_\pm \tilde{c}_\pm \tilde{\nabla} \tilde{\Phi}) + Pe \tilde{U} \tilde{c}_\pm \quad (3)$$

$$\tilde{\lambda}_D^2 \tilde{\nabla} \cdot (\tilde{\nabla} \tilde{\Phi}) = -\tilde{\rho}_e \quad (4)$$

$$\tilde{\rho}_e = Z_+ \tilde{c}_+ + Z_- \tilde{c}_- \quad (5)$$

$$\frac{1}{Sc} \frac{\partial \tilde{\mathbf{U}}}{\partial \tilde{t}} = -\tilde{\nabla} \tilde{P} + \tilde{\nabla}^2 \tilde{\mathbf{U}} - Re(\tilde{\mathbf{U}} \cdot \tilde{\nabla}) \tilde{\mathbf{U}} - \frac{1}{\tilde{\lambda}_D} \tilde{\rho}_e \tilde{\nabla} \tilde{\Phi} \quad (6)$$

$$\tilde{\nabla} \cdot \tilde{\mathbf{U}} = 0 \quad (7)$$

The Nernst-Planck equations (2) and (3) describe convective electro-diffusion of cations and anions, respectively. Equation (4) is the Poisson equation for the electric potential, where $\tilde{\rho}_e$ is the space charge due to a local imbalance of ionic concentrations. The Stokes equation (6) is obtained from the full momentum equation. Finally, equation (7) is the continuity equation for an incompressible solution. Spatial variables in equations (2-7) have been nondimensionalized as follows:

$$\tilde{v} = \frac{\nabla}{l_0}, \tilde{t} = \frac{t}{\tau_0}, \tilde{C}_{\pm} = \frac{C_{\pm}}{C_0}, \tilde{\Phi} = \frac{\Phi}{\Phi_0}, \tilde{\mathbf{U}} = \frac{\mathbf{U}}{U_0}, \tilde{P} = \frac{P}{P_0}$$

where $l_0, \tau_0, C_0, \Phi_0, U_0$ and P_0 are the reference value of spatial coordinate, time, ion concentration, electric potential, velocity field and pressure, respectively. The value of l_0 is the characteristic geometrical length scale, C_0 is the bulk salt concentration, the other values are defined as follows:

$$\tau_0 = \frac{\lambda_D l_0}{D_0} \quad (8)$$

$$\Phi_0 = \frac{k_B T}{ze} \quad (9)$$

$$U_0 = \frac{\epsilon \Phi_0^2}{\eta l_0} \quad (10)$$

$$P_0 = \frac{\eta U_0}{l_0} \quad (11)$$

where $\tilde{\lambda}_D = \lambda_D/l_0$ is the dimensionless thickness of the Debye layer.

$$Pe = \frac{U_0 l_0}{D_0} = \frac{\epsilon \Phi_0^2}{\eta D_0} \quad (12)$$

is the Peclet number defined as the ratio of the convective to the diffusive ion flux.

$$Sc = \frac{\eta}{\rho_m D_0} = \frac{\nu}{D_0} \quad (13)$$

is the Schmidt number defined as the ratio of the momentum diffusion to the ionic diffusion in the electrolyte. The Reynolds number, Re , is defined as

$$Re = \frac{Pe}{Sc} = \frac{U_0 l_0}{\nu} \quad (14)$$

\tilde{D}_{\pm} are the dimensionless diffusivity of cation and anion,

$$\tilde{D}_{\pm} = \frac{D_{\pm}}{D_0} \quad (15)$$

where D_0 is the average diffusivity

$$D_0 = \frac{2D_+ D_-}{D_+ + D_-} \quad (16)$$

2.3. Boundary Conditions

To close the governing equation, boundary conditions must be applied. No-slip boundary condition is applicable at the membrane surface. The common boundary conditions for ion concentrations at ion exchange membrane [12] are employed: fixed

value for the concentration of counter-ions ($C_m = 2C_0$), and no-flux for co-ions. The control parameter in our simulation is the bias voltage applied between the bulk space and the membrane. Periodic boundary conditions for all variables are assumed at the left and right boundaries. The simulation is conducted with bulk concentration $C_0 = 0.01M$, diffusivity of cation and anion $D_+ = D_- = 1 \times 10^{-9} m^2/s$, characteristic length $l_0 = 100 \mu m$.

2.4. Numerical Method

In this work, we employed the coupled method proposed by Pham to solve the sets of equations [12]. The finite volume method, a locally conservative method, is used for the discretization of the equations. The nonlinear discretized PNP equations are solved using the Newton-Raphson method [12]. To resolve the rapid variations of the ion concentrations and electric potential near charged surfaces, the mesh near the membrane is extremely refined toward the surfaces. To avoid solving the large system of linear equations and guarantee the strong coupling of the PNP equations, we make use of a coupled method for solving the sets of PNP and NS equations [12]. Starting with a velocity field from the previous iteration or initial condition, the potential and concentrations are simultaneously solved from the PNP equations. Then, electric body force is calculated and substituted into the NS equations. The velocity field obtained by solving the NS equations is substituted back into the PNP equations. The process is repeated until convergence is reached.

3. Results and Discussions

In our simulation, we apply the increasing voltages from $0V_0$ to $27V_0$ on the model described above. The obtained results include the I-V response of the electrolyte membrane system, the streamlines, and the ions concentration corresponding to the three distinguishable regions of this I-V curve. Specifically, we got the velocity obtained by simulation and EO2 velocity suggested by Rubinstein and Zaltzman gained through the data of ions concentration gradient and voltage distribution in the model; and the former is used to be as a reference for the latter to examine its accuracy.

3.1. Current-Voltage (I-V Curve) Response

As shown in Fig. 3 the Ohmic region starts at $0V_0$ and ends at $7V_0$. Following the Ohmic region is the limiting region which corresponds to the range of voltage from $7V_0$ to $24V_0$.

The last region on I-V curve is the over-limiting one which begins at $24V_0$ and stops at $27V_0$. To clarify these regions, we consider thoroughly them by studying the streamlines and ions concentration near the perm-selective membrane in respective regions.

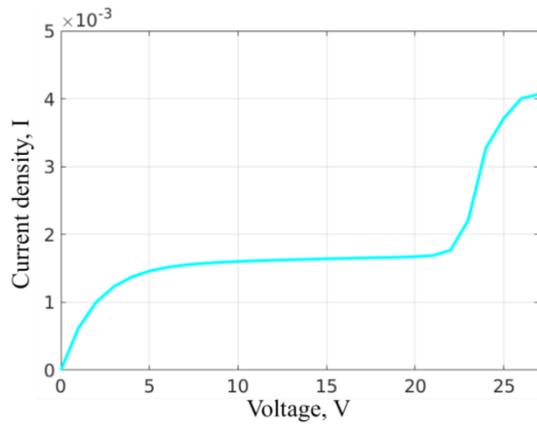


Fig. 3. The I-V curve of a permselective membrane when applying bias voltage from $0V_0$ to $27V_0$.

3.2. The Explanation of Ohmic Region

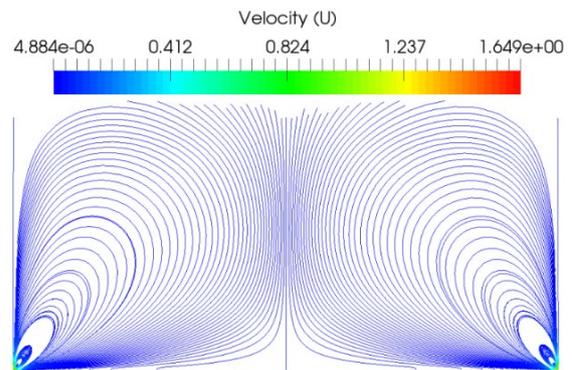
When the electric field is applied on the permselective membrane, counterion conducts through it, leading to a decrease in ion concentration near the membrane (Fig. 4b). This depletion causes an ion concentration polarization layer which is developed near the membrane and makes a gradient in the ion concentrations. The action of the electric field upon the net space charge in the electric double layer (EDL) produces a vortex pair formed above the surface (Fig. 4a). These vortices are referred to as seed vortices. These vortices rotate slowly, therefore they contribute insignificantly to the overall transport of ions. Ion in the system is mainly transported by diffusion where ion concentrations vary linearly with the distance from the membrane surface. As the bias voltage increases the ion concentration near the membrane is depleted further, making the electrolyte more polarized (Fig. 4c). As a result, the gradient of ion concentration increases, producing an increasing diffusive flux which is proportional to the external electric field. The current therefore increases with the bias voltage indicating the characteristics of Ohmic regime (Fig. 3).

3.3. The Explanation of Limiting Region

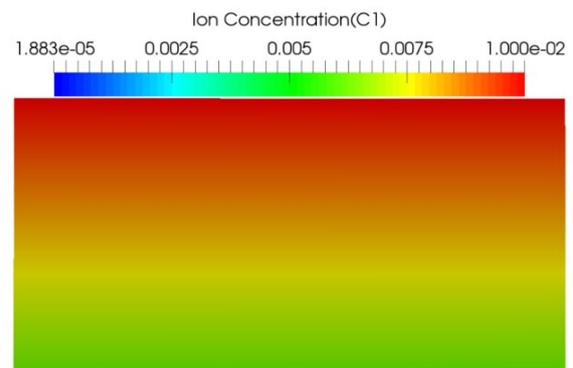
When bias voltage exceeds a critical value ($V_{cr1} = 7V_0$), ion concentration near the membrane surface approaches zero. Beyond this critical value, the concentration near the membrane does not reduce as increasing in bias voltage, but there is the development of an extended space charge layer next to the EDL of the membrane ($\rho_e = C^+ - C^-$). As can be seen in Fig. 5c, the thickness of the concentration polarization layer is about 0.1 (corresponding to bias voltage $V = 19V_0$).

The fluid flow is driven by electric body force which is determined by the electric field and the space charge. As the result of a larger space charge and

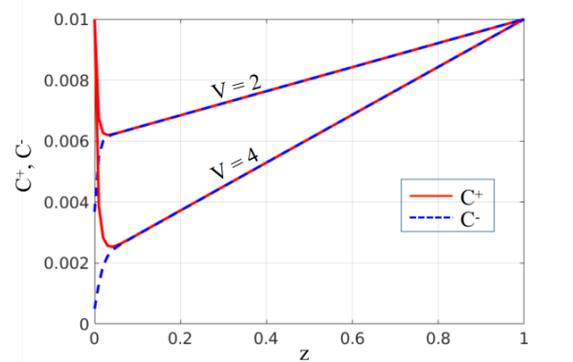
stronger electric field, fluid in the seed vortices rotates faster (Fig. 5a). However, the flow is not strong enough to significantly alter the ion concentrations. Therefore, the ion concentration is still uniform in the lateral direction. Due to the depleting of ions near the membrane, the current passing through the membrane is only slightly increased as bias voltages increase, corresponding to the limiting regime in the I-V curve (Fig. 3).



(a)

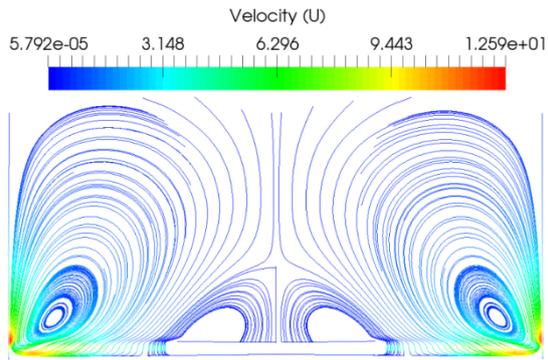


(b)

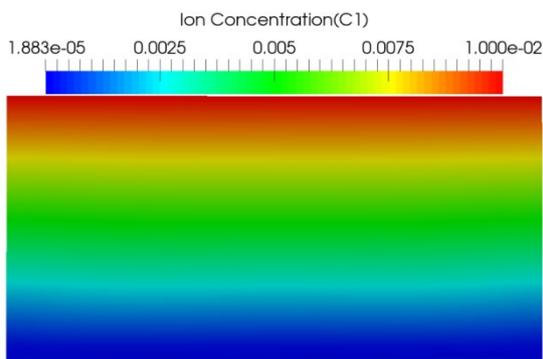


(c)

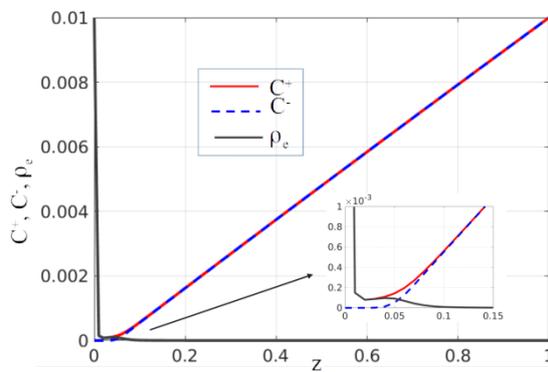
Fig. 4. The streamline (a), ion concentration (b), and concentration profiles (c) in Ohmic region at bias voltage $V = 2V_0$.



(a)

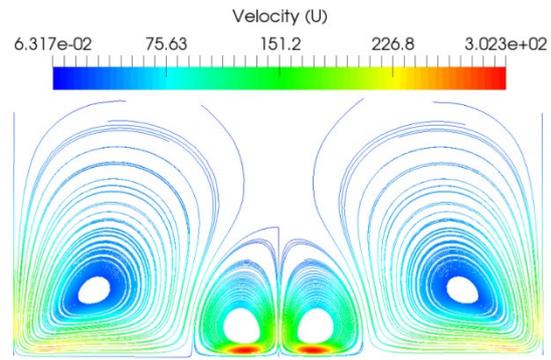


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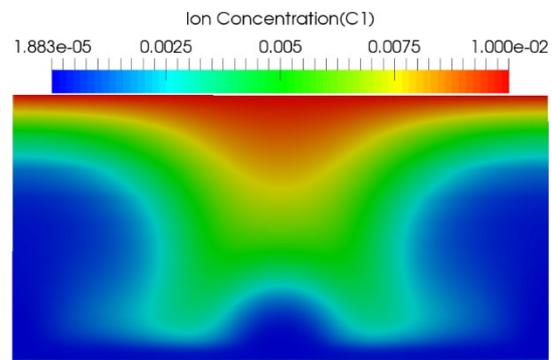


(c)

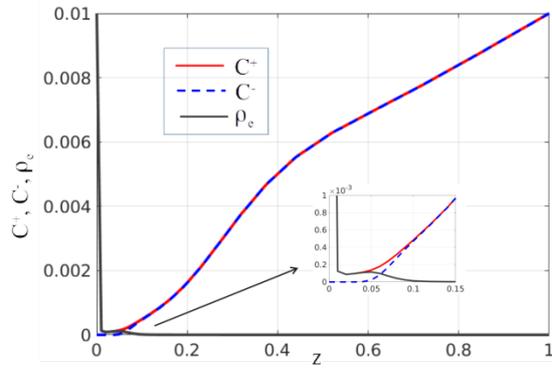
Fig. 5. The streamline (a), ion concentration (b), and concentration profiles (c) in limiting region at bias voltage $V=19V_0$.



(a)



(b)



(c)

Fig. 6. The streamline (a), ion concentration (b), and concentration profiles (c) in over-limiting region at bias voltage $V=27V_0$.

3.4. The Explanation of Over-Limiting Region

When the voltage exceeds a critical value ($V_{cr2} = 24V_0$), the seed vortices are broken up by the deformation effect caused by the action of an electric field on the space charge in the extended space charge layer. These broken seeds merge into each other and form large vortices which also rotate in a direction opposite to the adjacent vortices (Fig. 6a). Such large vortices make the fluid outside the depletion zone

where its high ion concentration is transported to the membrane surface. As higher bias voltage is applied, a faster rotation velocity of the vortices will be generated. The quicker flow carries more ions to the membrane surface to enhance the solution conductivity. Therefore, beyond the limiting current regime, the current passing through the membrane increases again with the increasing bias voltage, exhibiting the over-limiting current regime in the I-V curve (Fig. 3).

3.5. The Examination of EO2 Formula

The explanation of the I-V curve characteristics in Fig. 3 holds wide agreement in the Ohmic and limiting region. In contrast, the over-limiting region is confronted by long debate. One hypothesis is given to relate it to the instability in concentration polarization at electro dialysis membranes through electroconvection. The key feature of this new structure is an extended space charge added to the usual one of the quasiequilibrium EDL which generates EO2. The velocity EO2 which relates to this extended space charge renders the quiescent conductance unstable. Based on the unstable electroconvection theory, Rubinstein and Zaltzman suggested their EO2 formula (1) as mentioned above. In order to develop this EO2 formula, they claimed that although the velocity field is controlled by a gradient of pressure, diffusion and convection effects, the contribution of the electric field is the most significant in the over-limiting region. This is completely exact due to the combination of strong electric field and the high space charge in the extended space charge layer. Therefore, the EO2 calculated by their formula is the highest value on the velocity curve at the hump position of the extended space charge layer.

Consequently, there are two aspects to examine the accuracy of Rubinstein and Zaltzman's formula, including velocity magnitude and the position where it obtains the highest value. While the first aspect can be solved successfully by comparing the value of velocity calculated by their formula and the one got from the numerical simulation, the second one is much difficult due to the exact position where the highest space charge occurs cannot be determined analytically. In reality, this position can be only found by numerical simulation. As shown in Fig. 7, the space charge hump is approximately at the position of 0.05 corresponding to the bias voltage of $24V_0$, $26V_0$, and $27V_0$, respectively.

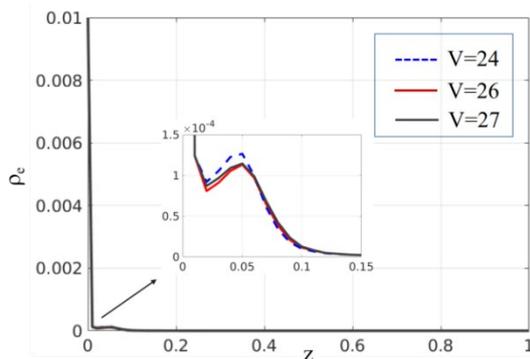
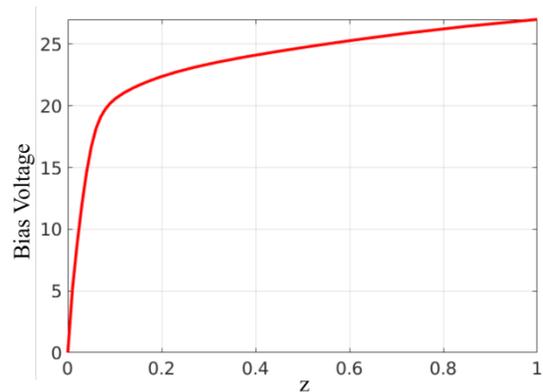
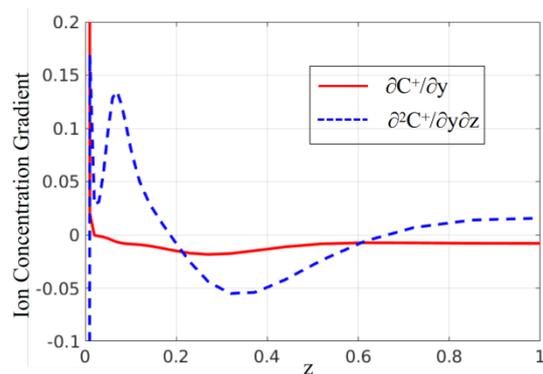


Fig. 7. The extended space charge layer corresponding to $V=24V_0$, $26V_0$, $27V_0$.



(a)



(b)

Fig. 8. The voltage distribution (a) and the ions concentration gradient (b) at $V=27V_0$.

In order to calculate the EO2 velocity suggested by Rubinstein and Zaltzman, we use the data of ions concentration gradient and the contribution of bias voltage through the simulated area. This data is plotted in Fig. 8.

Fig. 9a shows that when the top curve of the velocity calculated by Rubinstein and Zaltzman's formula (U_s) and the one obtained by numerical simulation (U) is coincident, their magnitude is the same. It is also obvious that when the bias voltage increases, the velocity magnitude raises correspondingly as shown in Fig. 9. However, in Fig. 9b, c, d there is a slight difference between the highest value of velocity got by Rubinstein and Zaltzman's formula and the one gained by numerical simulation. More specifically, the U_s is lower gradually compared to U when the applied voltage is increasing. This course of difference is caused by the non-coincident position of the maximum velocity U and U_s . As shown in Fig. 9b, c, d the top curve of U_s is moderately father from the one of U where the electric force is strongest. Consequently, the U_s velocity calculated by Rubinstein and Zaltzman is smaller than the one gained by numerical simulation.

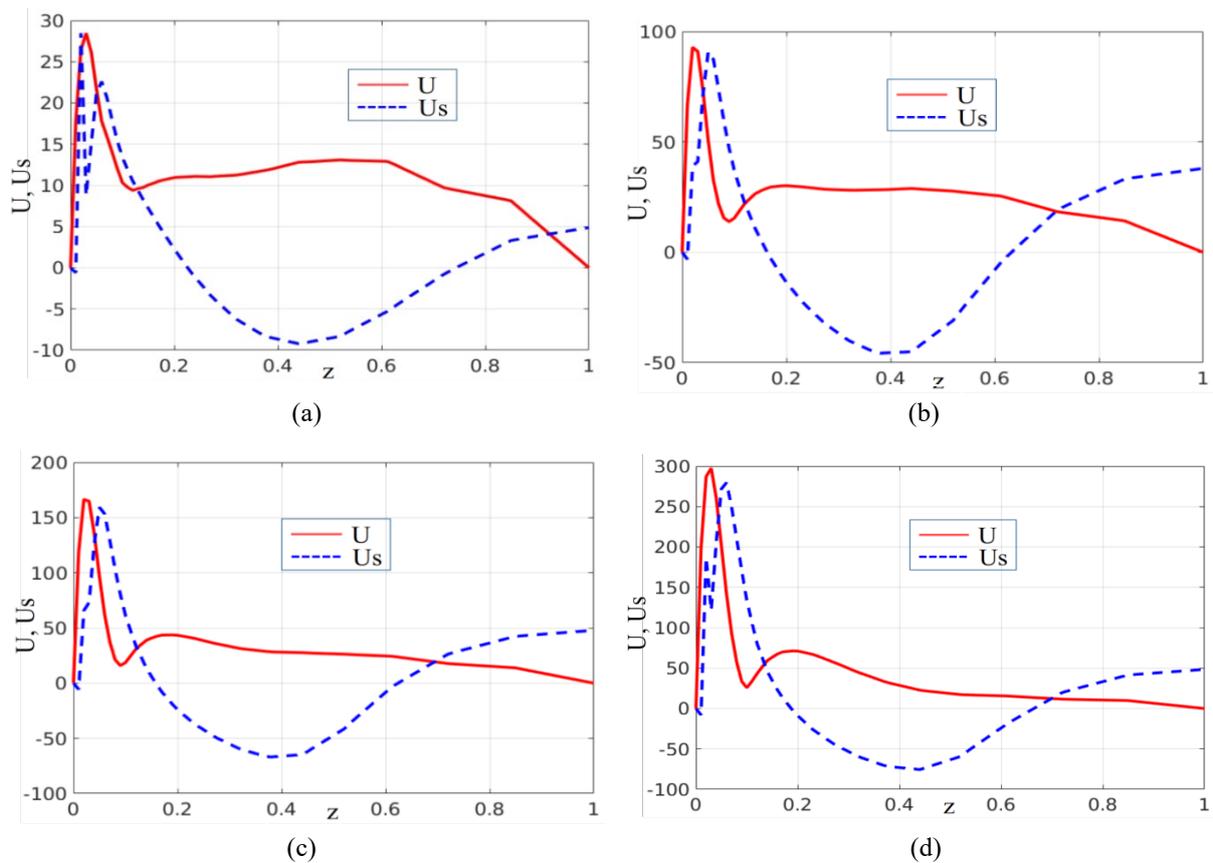


Fig. 9. The profile of U calculated by direct simulation and the profile of U_s calculated by Rubinstein and Zaltzman formula in over-limiting region at bias voltage $V=24V_0$ (a), $25V_0$ (b), $26V_0$ (c), $27V_0$ (d).

This drawback of their EO2 formula can be explained by the simplification in which Rubinstein and Zaltzman used to develop their formula as well as the difficulty of getting the exact position of space charge hump analytically as mentioned above. However, the difference between U_s and U does not exceed 6 percent of error in the whole examined over-limiting region.

4. Conclusion

In summary, we had used the direct numerical simulation solver which was developed in the OpenFOAM platform to study the phenomena that happened near the electro dialysis membrane of the planar model. From the simulation, three distinguishable regions on the I-V curve have been explained clearly. Importantly, the accuracy of the EO2 suggested by Rubinstein and Zaltzman was validated. We spotted that their formula is only applied with precise value at the exact space charge hump position. When their formula is calculated at father from this hump position, the magnitude of EO2 is smaller compared with our simulation result. This limitation of their formula is explained by simplification and assumption in the process of getting their formula as well as the difficulty of calculating

exactly the position of the extended space charge layer. Only by using direct numerical simulation, we can pinpoint exactly the space charge hump and the real EO2 at this position. Finally, our study on Rubinstein and Zaltzman's EO2 formula confirms numerically the theory of non-equilibrium electroconvection which is used to explain the mechanism of the interesting over-limiting region on I-V curve.

Acknowledgements

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