

Lane formation in confined cation mixtures in strong DC electric fields

J. Marañón Di Leo^a and J. Marañón^{b*}

^aDepartamento de Aeronáutica, Facultad de Ingeniería, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina;

^bIFLP, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina

(Received 22 October 2010; final version received 6 February 2011)

On applying an external electric potential field at the ends of a flexible nanopore, the resulting onward current flow parallel to the field has been simulated with molecular dynamic simulation. This is suitable to study different effects of self-organisation, such as lane formation. The electrolyte model was composed of three Na⁺/K⁺ (30/70, 50/50 and 70/30) concentration ratios in aqueous solutions.

Keywords: cation flux; nanotube; electric field; lane formation

1. Introduction

The transport of electrolytes in nanopores is important for the areas of high technology and molecular biology. Non-equilibrium molecular dynamic simulations (NEMD) were performed to investigate the effects of confinement on structural and transport properties of the electrolyte in nanopores [1]. Most natural phenomena occur under non-equilibrium conditions. Many aspects of non-equilibrium systems are still not well understood, for example, non-equilibrium phase transitions in liquids and colloidal suspensions driven by an external field are far more complex than their equilibrium counterpart. By using NEMD with a kinetic thermostat, lane formation in liquids subjected to strong external fields was shown [2]. The effect of an external field applied to a binary colloidal mixture performing Brownian dynamics in a solvent was studied by means of non-equilibrium computer simulations. One half of the particles were pushed in the direction of the field and the other half in the opposite direction. When the field is increased, the system changes from a disordered state to a state characterised by the formation of lanes that are parallel and anti-parallel to the field direction. Lane formation increases particle transportation in the direction of the field and induces a drastic reduction of particle transportation perpendicularly to the direction of the field [3].

Recently, ionic lane formation has also been observed in cationic fluxes with (NEMD) simulation. By application of a high electrical field, a self-organisation of cations, Na and K, and their respective counter-ions, was formed, and a current lane was induced, where solvated ions and counter-ions flow parallel in the opposite direction, but without a perpendicular field component applied [4]. Additionally, without an external electric field, it is shown in [5,6] that,

for different Na⁺/K⁺ concentration ratios in aqueous solution, there is an anomalous behaviour of K⁺ ions in relation to radial distribution functions, hydration and residence time with respect to Na⁺. Thus, the aim of this work is to study the response of the system produced by an external electric field in a range that goes beyond the usual measurements applied to different Na⁺/K⁺ concentration ratios in aqueous solutions, as well as the anomalous behaviour of K⁺ ions in relation to lane formation with respect to Na ions.

2. Models and simulation methods

The simulation set-up was similar to that described in earlier articles [5,6]. Initially, we had 800 single-point charge/extended (SPC/E) [7] water molecules with an initial density of 0.928 g/cm³ as solvent inside the prismatic nanopore. Then, 200 water SPC/E molecules of the solvent were converted into 100 ions and 100 counter-ions as solute. As regard prismatic surface, it is a network (3.4 × 3.0 × 3.0 nm, net constant 0.131 nm) of 2484 van der Waals particles. Potential fields and configuration energies were computed using a modified GROMOS87 package [8] for all types of particles (cations, counter-ions, atoms and van der Waals particles).

By applying a constant uniform electric field E_x along the axial direction of the nanopore, the transport properties of ions and counter-ions were calculated. Under the external field, the charged particles move parallel to the field and, after some simulation time, the steps generate an average constant current. Since the external electric field works on the system as a consequence of the multiple collisions with water molecules, counter-ions and van der Waals particles, the heat generated by the external electric

*Corresponding author. Email: maranon@fisica.unlp.edu.ar

field was removed by adding a constraint parameter in non-Newtonian equations of motion [9–11].

3. Results and discussion

3.1 Density profiles

The fluid structure within the nanopore is best characterised on the basis of atom density profile. It is well known that solvation layers are found in water near the walls. The number of water molecules affected by the prismatic surface is substantially larger than in the corresponding systems near flat interfaces. This effect is due to packing. The presence of the wall aligns the water molecules parallel to the surfaces in the first layer close to the wall and isotropically orients the water molecules in the central region of the nanopore, partially breaking the water network. At the molecular level, the water structure is determined by hydrogen bond networks. The hydrogen bond distribution of the water in the central region is broad compared with pure water distribution. In the annular region, the distribution function is rather different from that of pure water, breaking the water network that is close to the wall [12].

The way in which the structure of the confined water is modified by the introduction of ions and the extent to which this determines the dynamical properties of the solution were studied.

The density profile of Na ions is distributed along the nanopore near the central axis and the density profile of K ions is close to the x -axis of the nanopore and farther away

from the walls than Na ions and water molecules. This is a consequence of ion interaction and ion hydration [13]. A series of simulations over an extended range of external voltages applied over Na and K ions shows that the density profiles of the ions are unfolded in two maximums [4].

To study the density profiles for three different Na and K ion concentration ratios in aqueous solutions over a wide range of external applied voltages varying from -15 to 15 V in the nanopore, density profiles were calculated normal to the x -axis of the nanopore, averaging the time frames over the last 120 ps of each simulation. However, the density displays quite similar pictures in all voltage ranges for each ion. Figure 1 shows the pictures for 1 and 15 V only.

For 1 V, the density profile of the K ion decreases by nearly one half when its concentration decreases, whereas the density profile of the Na ion slowly increases when its concentration increases. In the case of larger voltages, 15 V, this behaviour is more evident in both ions for 1 V as well. Furthermore, for each concentration, an incipient structure of ion density peaks is observed. These results complement the results of paper [5].

3.2 Current density distribution

The simple electrolyte model used is formed by ions, counter-ions and water molecules, so the displacement of the ions is to a large extent hindered by counter-ions and solvent water molecules. Consequently, the small external electric field strength applied produces a weak current

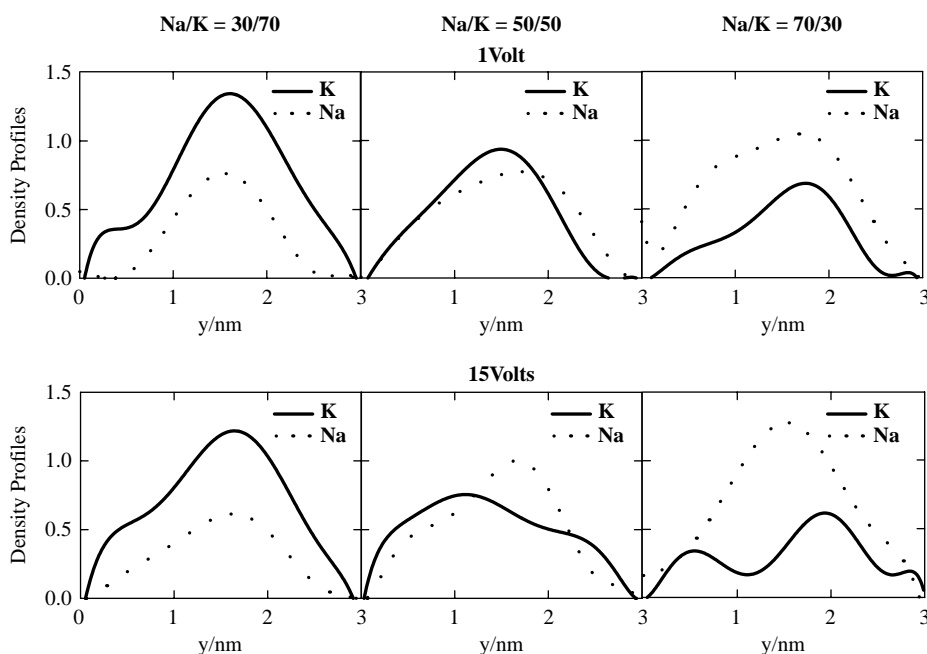


Figure 1. K and Na cation density profiles, for 1 and 15 V, for each of the three different Na/K concentration ratios: (solid line) K ions and (dotted line) Na ions.

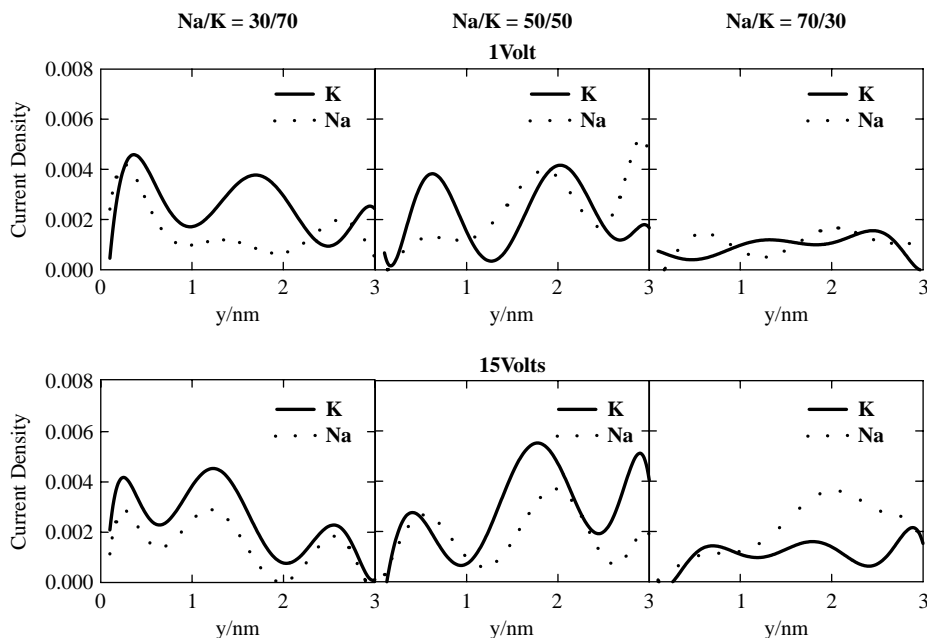


Figure 2. K and Na cation current density profiles, for 1 and 15 V, for each of the three different Na/K concentration ratios: (solid line) K ions and (dotted line) Na ions.

density with large statistical errors. Because ion currents are so small at the low applied potentials, it takes large amounts of simulation time out of our computation limits to gain reliable statistics. For this reason, values between 0.5 V and -0.5 mV were not considered in our simulation.

Following our study, we performed the calculation of current densities corresponding to three Na^+/K^+ concentration ratios (30/70, 50/50 and 70/30) under an external electrical field from 0 to 15 V and when applied in the reverse direction in the pore. A close look at Figure 2 shows only the current density of 1 and 15 V for three concentration ratios of Na^+/K^+ .

For 1 V, Figure 1 shows the current density of the three concentration ratios of Na and K ions; as it can be seen, there are no coincidences. Furthermore, when the concentration of Na ions increases, the intensity of current density decreases to a significantly low value for both ions. On the other hand, for 15 V, there is a greater coincidence with the current density of the lane. However, we note that a smaller coincidence was observed when the concentration ratio of the Na ion increased. The present results complement the results of paper [4].

4. Conclusions

Applying an external electric field at the ends of an elastic nanopore, formed by van der Waals particles like a prismatic surface, the results obtained using NEMD simulation of three Na^+/K^+ ions concentrations ratio (70/30; 50/50 and 30/70) in aqueous solution are reported.

To summarise, Figure 1 shows the increment of the density profile of both ions with the increase of their respective concentrations. This behaviour of the density profiles of Na and K ions for different concentration ratios indicates the presence of another force, such as the ion-ion interaction between hydrated ions of different size in aqueous media [6]. Finally, Figure 2 shows that, in general, for the concentration ratios, the intensity of the current density is larger for K ion than for Na ion for the two voltages. Therefore, we can lead cause this by increasing the intensity of the applied external electric field, by the K ion anomalous behaviour [5,6], the K ion current density rectify the Na ion current density. This situation is strongly related with the electric current rectification.

Acknowledgements

This work was partly supported by the CONICET, Argentina. JMDL is a Senior Researcher of CONICET, Argentina.

References

- [1] Y.W. Ai Tang, K.-Y. Chan, and I. Szalai, *Structural and transport properties of and SPC/E electrolyte in a nanopore*, J. Phys. Chem. B 108 (2004), pp. 18204–18213.
- [2] J. Delhommelle, *Should "lane information" occur systematically in driven liquids and colloids*, Phys. Rev. E 71 (2005), 016705.
- [3] M. Rex and H. Löwen, *Lane formation in oppositely charged colloids driven by an electric fields: Chaining and two-dimensional crystallisation*, Phys. Rev. E 75 (2007), 051402.

- [4] J. Marañón Di Leo and J. Marañón, *Cation transport in nanopores*, Mol. Simul. 35 (2009), pp. 280–286.
- [5] J. Marañón Di Leo and J. Marañón, *Confined Na⁺ and K⁺ ions in an aqueous solution*, Chem. Phys. Lett. 404 (2005), pp. 257–262, and reference therein.
- [6] J. Marañón Di Leo and J. Marañón, *Hydration and diffusion of cations in nanopores*, J. Mol. Struct. (THEOCHEM) 729 (2005), pp. 53–57.
- [7] H.J.C. Berendsen, J.R. Grigera, and T. Straatsma, *The missing term in effective pair potentials*, J. Phys. Chem. 91 (1987), pp. 6269–6271.
- [8] W.F. van Gusteren and H.J.C. Berendsen, *Groningen Molecular Simulation Package*. Available from Biomos n.v. Ninborgh 16, 4767 AG Groningen.
- [9] Y.W. Tang, I. Szalai, and K.W. Chan, *Diffusivity and conductivity of a primitive model electrolyte in a nanopore*, Mol. Phys. 99 (2001), pp. 309–314.
- [10] D.J. Evans and G.P. Morris, *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London, 1990.
- [11] I.M. Svishchev and P.G. Kusalik, *Dynamical properties of Coulombic systems at low densities: Computer simulation results*, Phys. A 192 (1993), pp. 628–646.
- [12] J. Marañón Di Leo and J. Marañón, *Confined water in nanotube*, J. Mol. Struct. (THEOCHEM) 623 (2003), p. 159.
- [13] J. Marañón Di Leo and J. Marañón, *Confined ions and water in nanotube*, J. Mol. Struct. (THEOCHEM) 709 (2004), pp. 163–166.