Ion Flux of Confined Ion Mixtures

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Abstract The transport of ions in a confined solution at nano-meter scale is critical for the function of inorganic and biological membranes. Then, it is important to study the effect of nano-confinement of ion transportation by computer simulation. To focus on the effect of nano-confinement, it is useful to investigate ion transport by that means. To reduce computational time, simple electrolyte models can be used. The structure of the water molecules surrounding an ion is described by the ion-atom radial distribution function (RDF). Ion size trends are those to be expected on intuitive grounds, in addition to the position and height of the first peaks. The height of the first peak diminished as cation size increased, thus implying a weakening of the cation. The purpose of this study was to apply an external electric field at the ends of a flexible nanopores contained configured as an electrolyte model under periodic boundary conditions, with molecular dynamics (MD). The results show several ion currents. The electrolyte model was composed of three Na^+/K^+ concentration ratios in aqueous solutions. For both cations, the radial distribution function (RDF) g(s) does not depend neither on voltage nor cation mixtures. Na^+ current-voltage (I-V) curves change for low Na^+ concentrations only.

Keywords Confinement; rectangular nanopore; external electric potential.

1. Introduction

The transport of ions in a confined solution at nano-meter scale is critical for the function of inorganic and biological membranes. Then, it is important to study the effect of nano-confinement of ion transportation by computer simulation. To focus on the effect of nano-confinement, it is useful to investigate ion transport by that means. To reduce computational time, simple electrolyte models can be used [1].

The structure of the water molecules surrounding an ion is described by the ion- atom radial distribution function (RDF). Ion size trends are those to be expected on intuitive grounds, in addition to the position and height of the first peaks. The height of the first peak diminished as cation size increased, thus implying a weakening of the cation-water interaction. However, it can be observed that when there are Na^+ and K^+ ions in the same aqueous solution, this trend is broken (anomalous behavior). The first peak of the K^+ RDF is higher and the position closer to the origin than the corresponding heights and positions of the Na^+ RDF first peaks. Recent papers [2-3] show for different Na^+/K^+ concentration ratios in aqueous solution, that there is an anomalous behavior of K^+ ions in relation to RDF, hydration, and residence time with Na^+. These results are due only to the relative responses of ion-water systems to constriction; thus, larger ions can fit more easily in a confined mixture [4].

The non-equilibrium molecular dynamic (NEMD) and periodic boundary conditions determine the transport constant of ion flux through a flexible nanopore under an axial electric field. Then, a quantitative explanation of

the (I-V) ion curves in a flexible nanopore for two mono-valent ions has been given. A novel law has been introduced, sinh function of the (I-V) (eq.1),

$$I = a. \sinh(b. V) \tag{1}$$

for confined ion currents driven by an electric potential, where I is the current, V is the electric potential, and a and b are two adjustable parameters [5].

Thus, the aim of this work is to study two issues. One is the anomalous behavior of K^+ ions in relation to RDF and hydration with respect to Na^+. The second objective is analyzing the I-V response curve 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.

2. Models and Simulation Methods

The simulation set up was similar to the description in earlier articles [2-4]. Initially, we had 800 SPC/E [6] water molecules with initial density of 0.928 g/cm^3 as solvent inside of the prismatic nanopore. Then, 200 water SPC/E molecules of the solvent were converted into 100 ions and 100 counterions as solute, with the object of maintaining the electro-neutrality of the system. The counterions of Na^+ and K^+ used were van der Waals particles with the same parameter and atomic mass, but with negative charge corresponding to the Na+ and K+ cations.

The prismatic surface is a network (3.4 x 3.0 x 3.0 nm, net constant 0.131 nm) of 2484 van der Waals particles (see reference [2]). Potential fields (force-field parameters) and configuration energies were computed using modified GROMOS87 and GROMOS96 packages [7] for all types of particles (cations, counterions, water molecules, and van der Waals particles).

Periodic boundary conditions were applied at both ends of the pore, and the axial direction of the pore was defined as the x-direction. Temperature was controlled by coupling the system to a thermal bath at 300 K and time constant of 0.5 ps. The covalent bonds length for water molecules, as well as the van der Waals particles of the prismatic network, were constrained by the SHAKE procedure (tolerance 0.0001 nm). Each simulation started after more than 600 ps, when the equilibrium period was reached, using a time step of 1 fs.

As regards ion and counterion migration, applying a constant uniform electric field E_x along the axial direction of the nanopore, the transport properties of ions and counterions were calculated. The external field causes the charged particles to move, and, after some simulation time, an average constant ion current is generated. Since the external electric field does work on the system as a consequence of the multiple collisions with water molecules, counterions and van der Waals particles, the heat generated by the external electric field was removed by adding a constraint parameter (Gaussian thermostat) in non-Newtonian equations of motion [8-10]. The induced electric current density, J_x, in the axial direction in response to the applied electric field is

$$J_x = \frac{1}{Vol} \sum_{i=1}^{N} q_i v_{x,i} \tag{2}$$

where q_i is the charge and, $v_{x,i}$ is the axial component of the *i-th* ion, *Vol* is the volume of the pore and N is the total number of ions. Despite that, the ionic concentration of the simulation cell is maintained by the axial periodic boundary condition, although fluctuations in current and motion of ions are detected over a long enough period of time.

Consequently, the ion current is averaged after some simulation time steps. The temperature *T* of the nonequilibrium iso-kinetic system is obtained through the constraint equation [3],

$$= \frac{1}{3Nmk_B} \sum_{i=1}^{N} \left(p_i - \left(T(m_i q_i J_x)/q_i \rho \right) e_i \right) \tag{3}$$

where p_i is the momentum vector of the *i-th* ion, e_i is the unit vector in the axial direction, m_i is the ion mass, *N* is the total number of ions in the system, $\rho = N/Vol$ is the density number, and k_B is the Boltzmann constant.

3. Results and Discussion
3.1. Radial distribution function and hydration

The structure of water molecules about an ion is described by the ion-atom radial distribution function (RDF) *g(r)*. The RDF *g(r)*, or pair correlation function, is a measure to determine the correlation between atoms within a system. Specifically, it is an average measure of the probability of finding an oxygen atom at a distance of *r* away from a given reference ion, relative to that for oxygen in liquid water. The first peak of the ion-oxygen *g(r)* (see Figure 1 and 2) corresponds to the radial distribution of the first nearest neighbour water molecules

around any given ion (the first solvation sphere). The appearance of a second peak in ion-oxygen $g(r)$ is much discussed and is taken as evidence for the presence of a tetrahedral ordered network in liquid water [11]. To study the RDF behaviour for Na and K ions and Na^+/K^+ concentrations ratios in an aqueous solution, a series of different simulations were performed. It was observed that cation-water interaction is larger for the K^+ ion than for the Na^+ ion when they are together in the same water solution [2-3].

As regards the anomalous behaviour of K^+ ions in the presence of Na^+ ions under an electric field, three Na^+/K^+ concentrations ratios (30/70, 50/50 and 70/30) were studied applying 1 electric volt to the ends of the nanopore. The results of this RDF calculation are show in Figure 1.
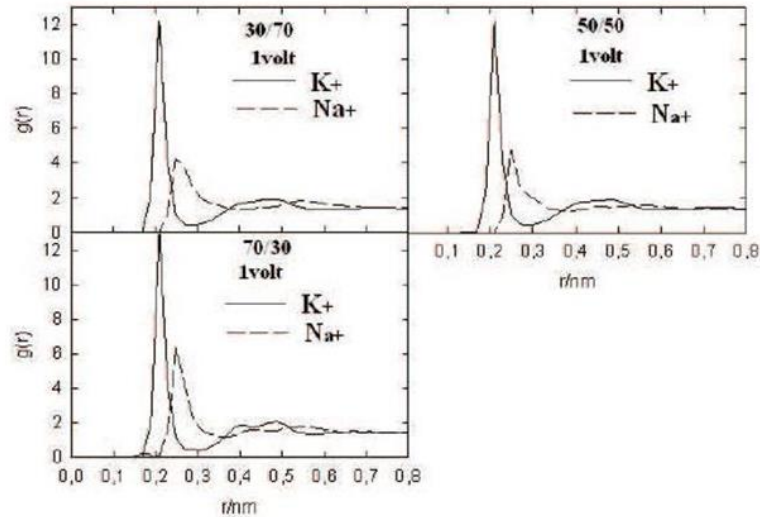

Figure 1: Radial distribution Function of Na and K ions for three different Na^+/K^+ concentration ratios in an aqueous solution for 1 volt.

The three graphics in Figure 1 show that the heights corresponding to K* first peaks are larger, and their position closer to the origin, than the corresponding heights and positions for Na^+; the same occurs for the three ratios. In other words, the anomalous behaviour of K ions for the same voltage does not change regardless of Na^+/K^+ concentration ratios.

The simplest quantities that reveal the structure of the solvation shell are the ion-oxygen radial pair correlation function $g(r)$ shown in Figure 1. The corresponding radial integration number is the hydration number $n(r)$ [11],

$$n(r) = 4\rho_0 \int_0^r s^2 \, g(s) \, ds \qquad (4)$$

where ρ_0 is the oxygen density number. This quantity represents the average number of water molecules that are found within a radius r centred on an ion. Table1 shows the hydration number of three Na^+/K^+ concentration ratios corresponding to the first solvation sphere of Na^+ ions gain approximately three water molecules, whereas K^+ ions lose the same numbers of water molecules with respect to the corresponding hydration values of its own water solution.

Table 1: Average hydration number n(r) of water molecules and the first r minimum of the RDF g(r) for 1 volts.

Na^+/K^+	Na^+		K^+	
Ratios	n(r)	r/nm	n(r)	r/nm
30/70	9.05	0.39	4.51	0.29.
50/50	8.57	0.39	4.51	0.29
70/30	8.78	0.37	4.63	0.31

These results confirm that the anomalous behaviour of K^+ does not change with different ion mixtures.

In much of what follows, we shall be concerned with Na and K ions RDF in an aqueous solution under the action of an electric field for all voltages between (1–15) and a comparison between them. Figure 2 shows four pictures for Na^+/K^+=70/30 ratio in an aqueous solution from 1 to 15 volts. Once again, the anomalous behaviour of RDF K ion persists for all voltage ranges. Thus, it can be concluded that the application of the electric potential to the end of the nanopore did not modify the structure of water molecules surrounding K ions as when the system is not subjucted to an external electric field [2].
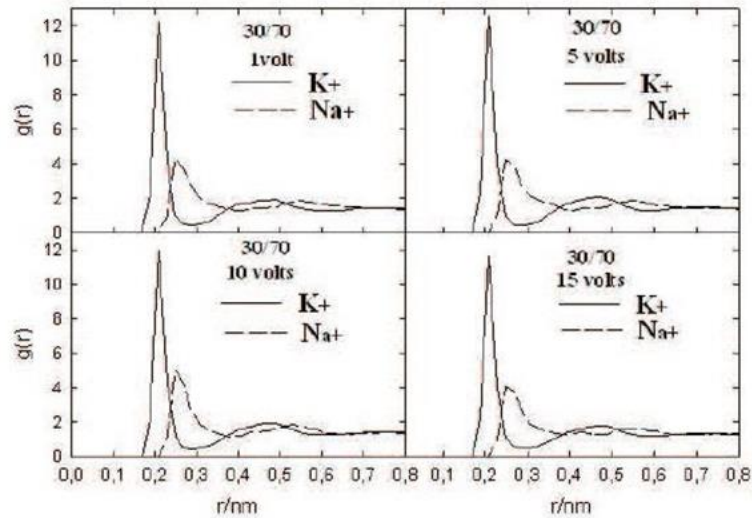
Figure 2: Radial distribution function of Na and K ions for $Na^+/K^+=70/30$ concentration ratios in an aqueous solution from 1 to 15 volts.

3.2. Current-voltage curves

The simple electrolyte model is formed by particles, and so ion displacement is to a large extent hindered by counter-ions and solvent water. Consequently, the small electric field strength applied produces a weak current 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 lower than 0.5 V and –0.5 mV are not considered. To obtain the I-V curve we proceeded in the following way. For each voltage V (1, 5, 10 and 15 volts) we simulated our system for a time of 1000 ps. To evaluate the corresponding current I for each ion, we used the expressions in reference [12] divided by factor 6.28×10^{18} electrons by second corresponding to one ampere. Calculations were not performed for reverse potential because the curve adjusted with function (1) was used. The curves attempt to fit by function (1) adjusting a and b parameters [5].

Following our study, we performed the calculation of the I-V curves corresponding to three Na^+/K^+ (30/70,

50/50 and 70/30) concentration ratios. Figure 3, Figure 4 and Figure 5 shows Na^+ and K^+ curves for three ratios, in the -15 to 15 volts range. It can be seen that K^+ curves are the same for all mixtures, regardless of K^+ concentrations.
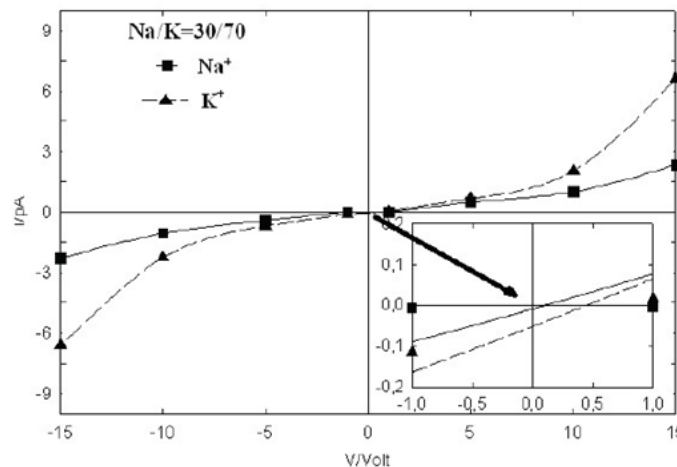

Figure 3: $Na^+/K^+=30/70$ concentration ratios. Na^+ and K^+ (I-V) current- voltage curves obtained with eq. (2). Na^+ (a = 0.532 and b= 0.144) and K+ (a = 0.541 and b = 0.213). Solid line, square: Na^+, long-dash line, triangle-up: K^+.

Meanwhile, the I-V curve for Na^+, starting from the lowest Na^+ value (30/70, Figure 3), increases as Na+ values increase (50/50, Figure 4 and 70/30, Figure 5), approaching to the I-V K^+ curve limit. An explanation could be given by using the hydration numbers from Table 1, Figure 1, Figure 2, and papers [2-3]. Since this is a volume problem, when the number of K^+ decreases in the mixture, the I-V curve is always the same, this volume is occupied by the increment of the Na^+, increasing their I-V curve as far as the K^+ I-V limit curve, because increasing the number of Na^+ ions imply the increase of Na^+ current values. In contrast, in spite of decreasing the number of K^+ ions, its anomalous behaviour [2-3] and consequently its great mobility, keep its current flux constant.
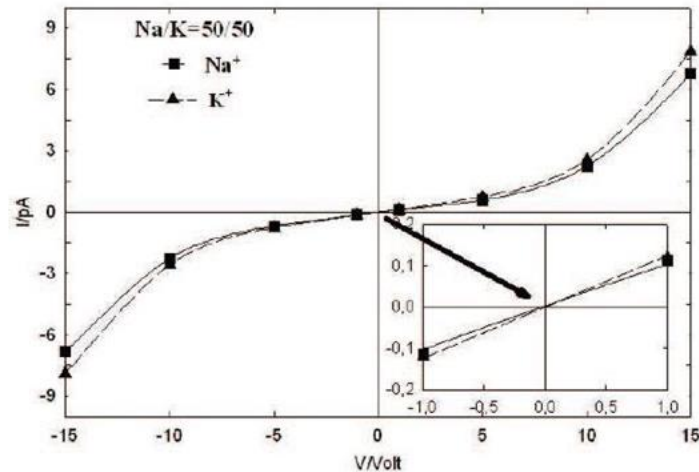

Figure 4: $Na^+/K^+=50/50$ concentration ratios. Na^+ and K^+ (I-V) current- voltage curves obtained with eq. (2). Na^+ (a = 0.510 and b= 0.219) and K+ (a = 0.560 and b = 0.223). Solid line, square: Na^+, long-dash line, triangle-up: K^+.

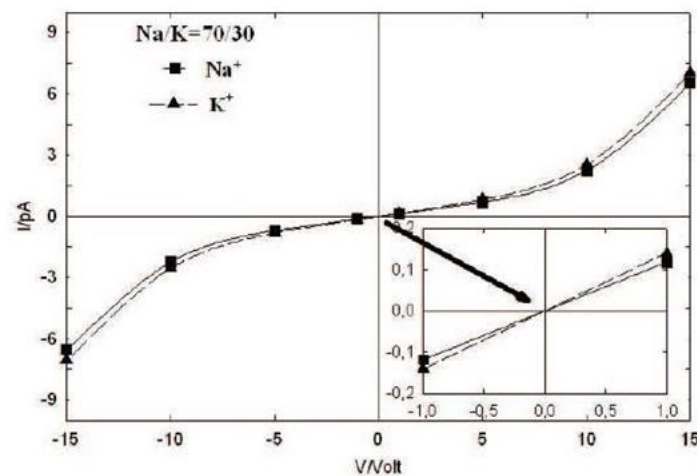*Figure 5: $Na^+/K^+=70/30$ concentration ratios. Na^+ and K^+ (I-V) current- voltage curves obtained with eq. (2). Na^+ (a = 0.551 and b= 0.211) and K+ (a = 0.691 and b = 0.201). Solid line, square: Na^+, long-dash line, triangle-up: K^+.*

To summarize, for the I-V curve of the Na and K ion mixture, only the Na^+ ion curve depends on the mixture of both ions.

4. Conclusions

Using an external electric field of pores, quantitative explanations were given of an anomalous behavior of K^+ ions in relation to RDF. The RDF for both cations is independent of cation mixture (Figure 1) and the applied voltage (Figure 2). The RDF for oth cations is similar in all cases without applying an external electric field [5]. Consequently, in relation to the (I-V) curves in a flexible nanopore for two mono-valent ions for different ratios

of the Na^+/K^+ mixture in aqueous solution, it was observed that the I-V curves are similar for both cations, except for Na^+ in low concentrations only (Figure 3, Figure 4 and Figure 5). This situation is strongly related with the electric current rectification.

Acknowledgement

References

[1]. Chan, K.Y., Tang, Y.W. & Szalai, I. (2004). Ion Transport in Simple Nanopores, Molecular Simulation, 30(2-3), 81-87. https://doi.org/10.1080/08927020031000152235

[2]. Marañón Di Leo, J. & Marañón, J. (2005). Confined Na^+ and K^+ ions in an aqueous solution. Chem. Phys. Letters. 404, 257-262. and reference therein.

[3]. Marañón Di Leo, J. & Marañón, J. (2005). Hydration and diffusion of cations in nanopores. J. Mol. Struc. (THEOCHEM), 729(1-2), 53-57.

[4]. Mauricio Carrillo-Tripp, M., Saint-Martin, H. & Ortega-Blake, I. (2003). A comparative study of the hydration of Na^+ and K^+ with refined polarizable model potentials. J. Chem. Phys. 118(15), 7062–7073. https://doi.org/10.1063/1.1559673

[5]. Marañón Di Leo, J. & Marañón, J. (2009). Cation transport in nanopores. Mol. Simulation, 35(4), 280-286.

[6]. Berendsen, H.J.C., Grigera, J.R. & Straatsma, T.P. (1987). The missing term in effective pair potentials. Journal of Physical Chemistry, 91(24), 6269-6271. https://doi.org/10.1021/j100308a038

[7]. van Gunsteren, W.F. & Berendsen, H.J.C. (1987). GROningen Molecular Simulation (GROMOS) package. Available from Biomos n.v. Ninborgh 16, 4767 AG Groningen, The Netherlands.

[8]. Tang, Y.W., Szalai, I., & Chan, K.W. (2001). Diffusivity and conductivity of a primitive model electrolyte in a nanopore. Mol. Phys., 99, 309–314.

[9]. Evans, D.J. & Morris, G.P. (1990). Statistical Mechanics of Nonequilibrium Liquids. London, Academic Press.

[10]. Svishchev, I.M., & Kusalik, P.G. (1993). Dynamical properties of Coulombic systems at low densities: computer simulation results. Physica A: Statistical Mechanics and its Applications, 192(4), 628–646. https://doi.org/10.1016/0378-4371(93)90113-I

[11]. Duh, D., Perera, D.N. & Haymet, A.D.J. (1995). Structure and properties of the CF1 central force model of water: Integral equation theory. J. Chem. Phys. 102(9): 3736–3746. https://doi.org/10.1063/1.468556

[12]. Coulson, C.A. (1958). Electricity, 5th edition, Oxford, University Mathematical Text.