The Influence of Divalent Anions on the Rectification Properties of Nanofluidic Diodes: Insights from Experiments and Theoretical Simulations

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During the last decade, the possibility of generating synthetic nanoarchitectures with functionalities comparable to biological entities has sparked the interest of the scientific community related to diverse research fields. In this context, gaining fundamental understanding of the central features that determine the rectifying characteristics of the conical nanopores is of mandatory importance. In this work, we analyze the influence of mono- and divalent salts in the ionic current transported by asymmetric nanopores and focus on the delicate interplay between ion exclusion and charge screening effects that govern the functional response of the nanofluidic device. Experiments were performed using KCl and K_2SO_4 as representative species of singly and doubly charged species. Results showed that higher currents and rectification efficiencies are achieved by doubly charged salts. In order to understand the physicochemical processes underlying these effects simulations using the Poisson-Nernst-Planck formalism were performed. We consider that our theoretical and experimental account of the effect of divalent anions in the functional response of nanofluidic diodes provides further insights into the critical role of electrostatic interactions (ion exclusion versus charge screening effects) in presetting the ionic selectivity to anions as well as the observed rectification properties of these chemical nanodevices.

1. Introduction

The emergence of nanofluidics has produced a fundamental shift in the way transport phenomena in confined geometries is understood.[1–4] The particular transport features of nanopores, nanochannels and nanotubes, which depends on their surface characteristics pose interesting challenges both experimentally and theoretically.[5, 6] Most important among these features are concentration polarization, unipolar solutions and ionic current rectification.[7, 8] The understanding of these issues is of capital importance for a number of fields such as cation exchange membranes for fuel cells, nanofiltration, lab-on-a-chip applications and biosensors, among others.[9, 10]

Within the particular transport characteristics of nanopores, their ability to rectify ionic current or, equivalently, to show non-ohmic behavior, is nowadays one of the most relevant aspects to be understood due to its scientific and technological implications.[11–13] Up to date, several ways have been devised to tune this effect in order to control the magnitude and direction of the rectified current.[14–17] Therefore, nanochannels can be regarded as nanofluidic diodes with the distinctive advantage of being capable to finely tune the output current.[18, 19] This current rectification effect has been demonstrated to occur due to an asymmetry in the charge distribution along the main axis of the nanopore. This asymmetry can be obtained either by an asymmetric geometric shape, typically a conical shape,[20, 21] or by a gradient in the surface charge density inside the pore.[22] The first option is by far the most used to obtain a non-ohmic behavior from a synthetic nanopore, examples of different procedures can be found elsewhere in a large variety of materials such as SiN_x, glass or polymer foils.[12, 23, 24]

Even though the incidence of geometry and surface charge in the rectification behavior of nanopores has been thoroughly studied, there is still a lack of understanding of fundamental issues like the importance of the nature of the electrolyte in the current transport. Despite existing previous works that reported the use of different ions in the electrolyte solution, most of these reports studied the effect of monovalent and divalent cations.[25–31] The analysis of those results was not so straightforward, because the strong interactions between the inner surface of the nanopores, normally bearing a net negative charge, and the cations, were also associated with nanoprecipitation and charge reversal effects. We believe it is necessary to understand the influence of the transported ions nature on the transport properties of the rectifying nanofluidic devices.

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In the present work, we focus our attention on the nature of the anionic carriers using electrolytes with mono and divalent anions, namely KCl and K_2SO_4. The experiments were performed with negatively charged track-etched nanopores, thus introducing a scenario in which divalent carriers are primarily excluded from the pore. Our experimental results were simulated using a continuous model based on Poisson–Nernst–Planck (PNP) equations in order to characterize the mechanism underlying the changes in the ionic conductance and rectification features. Our analysis points to the interplay between ion exclusion, the effect of reducing the concentration inside nanopores due to strong electrostatic repulsion powered by nanoconfinement, and charge screening effects arising from counterions that are adsorbed over the pores surface also due to electrostatic attraction. We propose that this interplay ultimately define the dependence of the ionic selectivity and rectification properties on the amount of divalent anions present in the electrolyte. We observe that for our nanopores 0.1 M concentration of divalent salts is high enough to ensure that charge screening prevails and consequently doubly charged anions are not fully excluded at negative potentials.

Our results demonstrate that the rectification properties can be increased at intermediate bulk ion concentrations of divalent anionic species and this phenomenon arises from a combination of the electrical screening of surface charges (predominant at high concentrations) and the ion exclusion of divalent anions from the negatively charge pore (predominant at low concentrations). In a similar way we demonstrate that the magnitude of ionic current flowing through the nanopore and the rectification efficiency can be straightforwardly manipulat-

ed by changing the composition of the mixture in the bulk system. We consider that this combined theoretical–experimental approach provides additional insights into the origin and mechanisms lying behind the functional response of nanofluidic diodes in the presence of divalent anions.

2. Results and Discussion

During the different series of experiments, it was found that the ionic currents were higher for K_2SO_4 solutions with respect of the solution of KCl of equivalent concentrations, especially at $V > 0$ (Figure 1 a,c). Therefore the current rectification efficiencies were also higher for nanopores measured in divalent salt solutions, especially at lower concentrations. (Table 1)

This anion-valency-dependent behavior could have, in principle, two different contributions. The first one is related to the concentration of cations, which is higher for the divalent salt at a constant concentration. The second possible contribution to these differences in the current magnitude could correspond to the charge of the anions. Because the charge on the

Table 1. Rectification efficiencies calculated for each concentration from the experimental and simulated data.

Conc. [M]	KCl	K_2SO_4
0.1	7	8
0.1(PNP)	14	18
0.05	15	28
0.05(PNP)	12	20
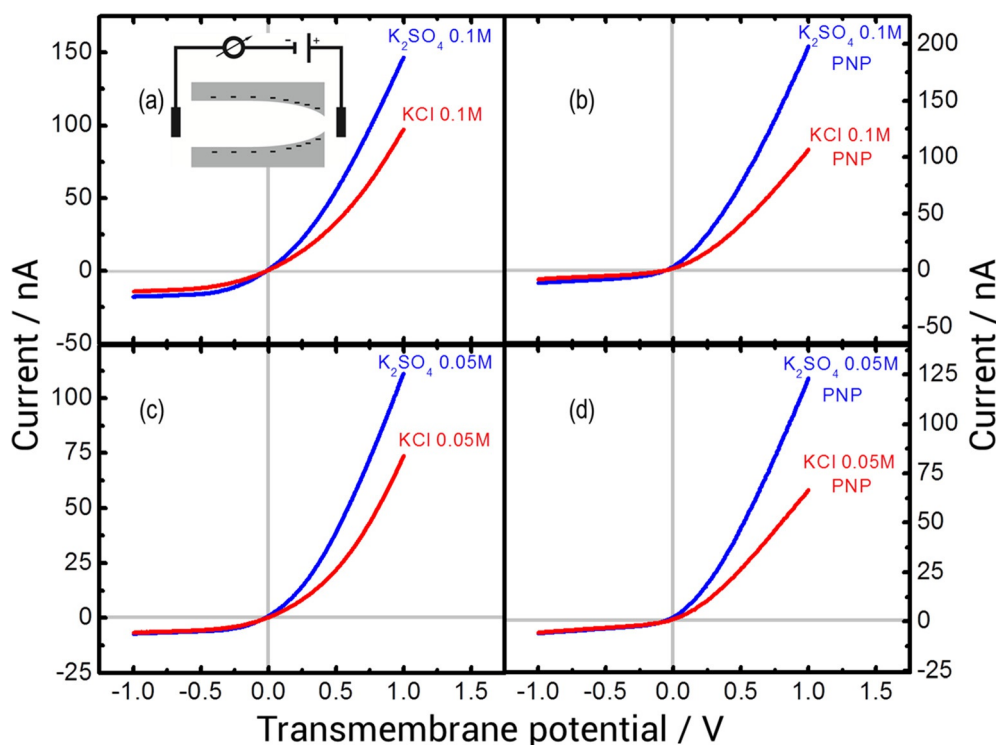
Figure 1. a,c) Experimental and b,d) theoretical current–voltage curves, using a total concentration of 0.1 M (a) and (b), 0.05 M (c) and (d). The inset shows the electrode convention used for the experiments, the voltage was applied towards the tip whilst the electrode placed on the base side was grounded.

sulfates is twice as high as that on the chlorides, the ionic current transported by sulfates is higher.

To ascribe the correct importance to either contribution we have measured current–voltage characteristics for each salt, maintaining the ionic strength constant,[32] instead of maintaining the concentration constant. Results revealed that the currents at $V > 0$ for the divalent salt were again higher with respect of the monovalent salt showing the same behavior to the experiments at constant concentration (Figure S1m Supporting Information). Consequently, it can be assumed as a first approximation that the main contribution is due to the charge of the anions instead of the difference between the cation concentrations.

To qualitatively analyze and understand the difference between the current–voltage characteristics of the two salts involved we use the Goldman constant field approximation for a cylindrical pore, which provides a way to calculate the conductivity G [nS] of a pore of radius R from the sum of the conductivities of all mobile ions. These in turn are calculated using the respective diffusion coefficients for each ion and their average concentration inside the nanopore [Eq. (1)]:

$$G = I/V = \frac{2\pi F^2}{LRT} \sum_i q_i^2 D_i \int_0^R C_i(r)\, r \, dr \qquad (1)$$

Assuming that the average concentration inside the pores is independent of the pore radius, and that the applied potential is the same for the two salts, the ratio between the conductivities of divalent and monovalent salts is given by Equation (2):

$$\frac{I_{divalent}}{I_{monovalent}} = \frac{z_{K^+}^2 D_{K^+} C_{K^+} + z_{SO_4^{-2}}^2 D_{SO_4^{-2}} C_{SO_4^{-2}}}{z_{K^+}^2 D_{K^+} C_{K^+} + z_{Cl^-}^2 D_{Cl^-} C_{Cl^-}} \qquad (2)$$

where $I_{divalent}$ is the current transported by divalent species, $I_{monovalent}$ by monovalent species, z_i, D_i and C_i are the charge, diffusion coefficient and the concentration of ion i, respectively.

Thus, if at negative potentials, the anions would be completely excluded from the nanopores, the ratio in Equation (2) would depend only on the cation concentration. Assuming electrical neutrality in the channel, the cation concentration should be equal for both salts; and the ratio should be close to one.

Figure 2 displays the $I_{Divalent}/I_{monovalent}$ ratio calculated from experimental data at negative potentials. The ionic current ratios are close to one and show an increase with increasing ion bulk concentration. This observation is in agreement with theoretical predictions (Figure 2b). We attribute this increase to an incomplete exclusion of anions at negative voltages, especially for higher concentrations. For the case of 0.1 M concentration, there is less exclusion of doubly charged anions at negative potentials due to a higher surface charge screening and, accordingly, the ratio between the divalent salt current and the monovalent salt is higher as well as the rectification rates (Table 1). The calculated ratios showed a transmembrane potential dependence. This tendency is more pronounced for a concentration of 0.1 M. We hypothesize that the higher concentration polarization at higher potentials can be the reason of this behavior. At low transmembrane potentials, the few anion carriers present inside the pores can contribute to the transport of current but increasing the potential forces more anions to access the channels. Since they are impeded to do so due to electrostatic repulsion of the channel, the contribution of anions to the current decreases and the $I_{divalent}/I_{monovalent}$ ratio approaches values closer to unity.

In order to gain further inside into the mechanism underlying the anion-dependent behavior of the current transport in nanopores, we have performed computational simulations using a continuous model based on the coupled equations of PNP (Figure 1).[33,34]. We applied the PNP formalism to model current–voltage curves to calculate the concentration profile of each ionic species across the pores (Figure 3).

Figure 3 shows the concentration profile of cations throughout the pores. It can be observed that at negative transmembrane potentials and up to a distance of 3 μm from the tip, that is $x = 0$, the profiles are similar for both types of electro-
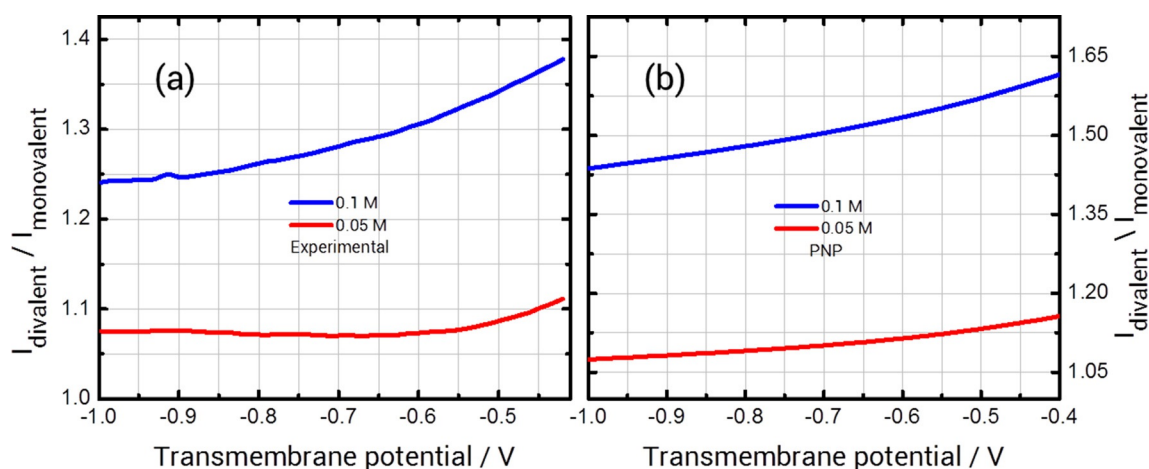
Figure 2. a) Experimental and b) theoretical results corresponding to divalent salt/monovalent salt ionic current ratios measured at different overall concentrations.
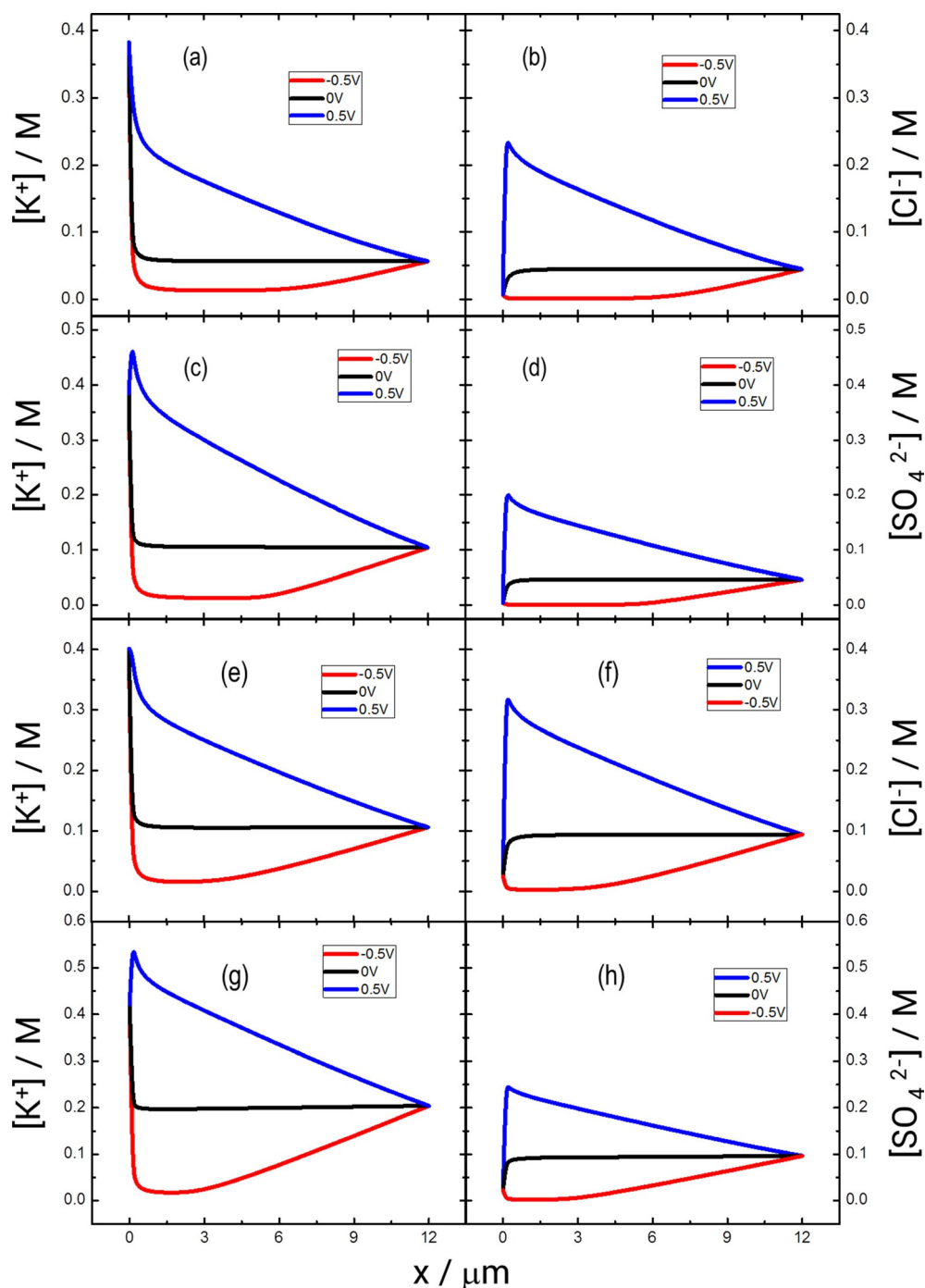
Figure 3. Concentration profiles of each ion across the length of the pore x; $x = 0$ corresponds to the position of the tip. (a) and (b) corresponds to a bulk concentration of 0.05 M KCl and (c) and (d) to 0.05 M in K_2SO_4. (e) and (f) corresponds to a bulk concentration of 0.1 M KCl and (g) and (h) to 0.1 M in K_2SO_4.

lytes and for the two different concentrations, 0.05 M and 0.1 M. This can be explained in terms of the electroneutrality. Figures 3 b,d show that for 0.05 M concentration and $V < 0$ there is an almost complete exclusion of anions. Under these conditions, the main charge carriers are cations, whose concentration is governed by the surface charge of the pore. This causes the cation concentration at $V < 0$ to be approximately the same for both cases, as seen in Figures 3 a,c.

On the other hand, at $V > 0$ we observe an effect similar to that described by Cervera et al.[35] where the electric field drags the cations to the pore's tip. Accordingly, anions are forced toward the nanopore tip also in order to preserve the electroneutrality. As a consequence of this effect, the concentration of charge carriers increases with the potential difference V, seen in IV curves as a steep increase in the ionic current (Figure 1).

Figures 3 a,b and 3 e,f display the concentration profiles for both cations and anions in the monovalent salts at 0.05 and 0.1 M respectively. It is observed that the concentration values throughout the pores are higher at 0.1 M as expected. Never-

theless, it is interesting that this difference is not as high as in the bulk solution were one concentration is twice as high as the other. This effect is related to the nanoconfinement of the solution. Since the diameter of the nanopores is small, especially towards the tip ($x=0$), there is a significant overlapping of the double layer of the nanopores surface that causes that the concentrations of species become closely related to the surface charge of the nanopore. The concentration ultimately depends on the surface charge instead of the bulk concentration.

At a concentration of 0.1 M, we see that there is less exclusion of anions at $V < 0$ towards the tip of the nanopores than for a concentration of 0.05 M, for both salts. This can be expected because if the concentration is increased, the Debye length, which is the screening length of the surface charge produced by the counterions, decrease.

When the potential is positive, the cation concentration in the divalent salt is higher than in the monovalent salt (Figures 3 a,c). However, the divalent anion concentration is lower as fewer anions are needed to neutralize the positive charge into the pore (Figure 3 b,d).

Despite the excellent qualitative agreement between theory and experiments, a quantitative comparison demands much caution due to differences between experimental and calculated values. These differences are possibly given by the uncertainties in the determination of the pore small opening (tip) radii and the surface charge density. The major difference is for divalent anions, being the theoretical current higher than the experimental which is also traduced in higher rectification efficiencies (Table 1). This might be caused by ion-pair formation in the experiment, being this an effect that is not taken into account in the theoretical model.

To analyze in more detail the contribution of the different species to the ionic current we use PNP simulations. Figure 4 shows the current transported by only one type of ion at different transmembrane potentials. It was found that the contribution to the ionic current of the divalent anion is almost double than the contribution of the monovalent anion. This fact can be analyzed taking into account that even though the mobility of the sulfates is half that of the chloride, the term corresponding to the anions increases with the charge and linearly with the diffusion coefficient [Eq. (1)].

With the aim of assessing the contributions of each ionic carrier to the total current, namely the quantity of current transported for each type of ion, the fractions of current transported by each ion, that is, the transport numbers (*t*), were calculated as a function of the transmembrane potential (Figure 5).
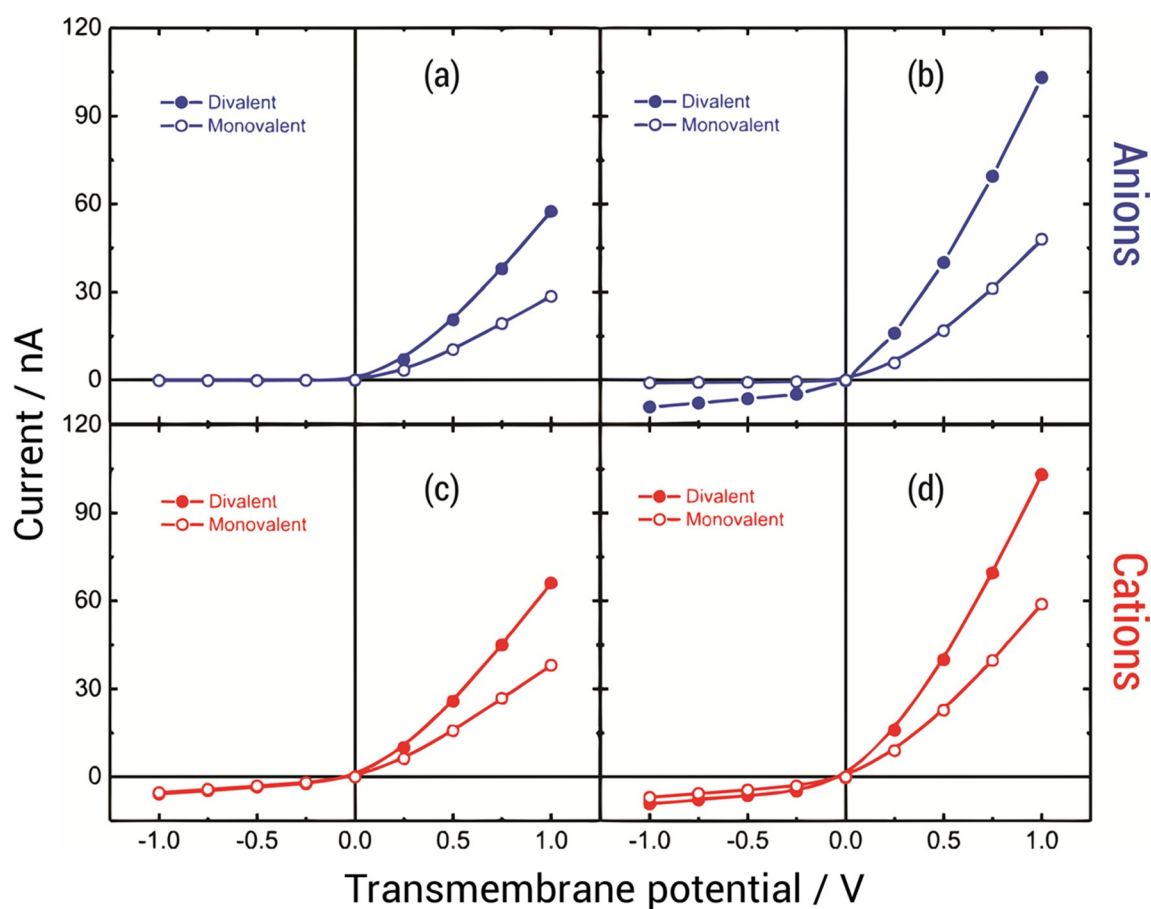
Figure 4. Individual ion contribution to the ionic current. Blue curves represent the contribution of anions at a concentration of a) 0.05 M and b) 0.1 M. Red curves represent the contribution of cations at a concentration of c) 0.05 M and d) 0.1 M.
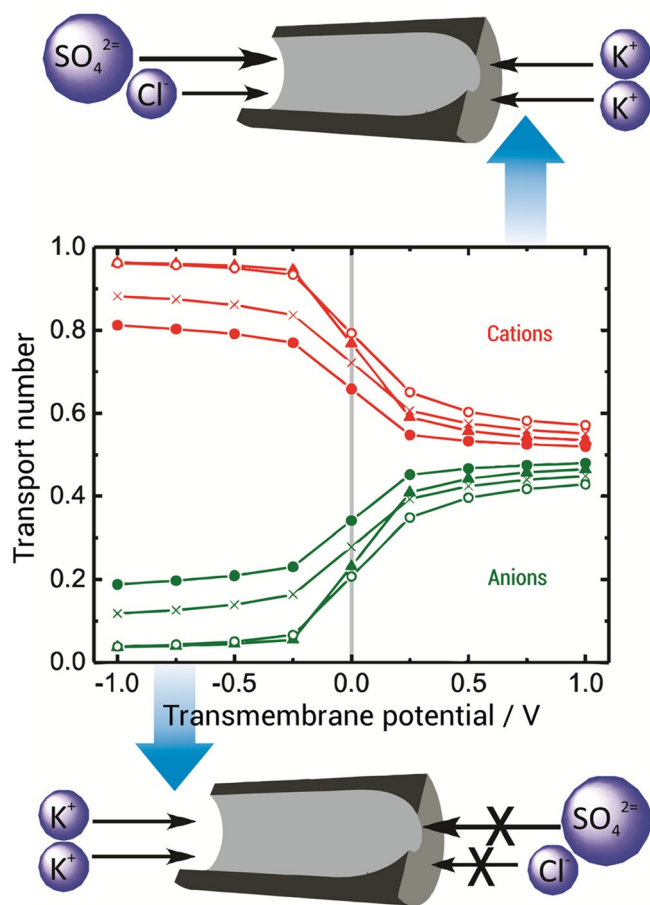
Figure 5. Fraction of ionic current transported, that is, transport number (t), for anions and cations. Each curve was calculated using either K₂SO₄ (full triangles for 0.05 M and full circles for 0.1 M) or KCl (empty circles for 0.05 M and crosses for 0.1 M), as electrolyte. Cartoons show the ionic transport for positive (above the plot) or negative (below the plot) applied potentials.

The fraction of the total current was calculated with Equation (3):

$$f = \left| \frac{I_i}{I} \right| \qquad (3)$$

Where [Eq. (4)]:

$$I_i = z_i F \pi a^2 J_i \qquad (4)$$

in which I_i is the current transported by the ion, z_i is the charge of the ion, F is the Faraday constant, a is the pore radius and J_i the ionic flux.

It can be seen in Figure 5 that for low concentrations more than 95 % of the current for $V < 0$ is transported by cations, either for the monovalent or the divalent salt. This is a very important point observed experimentally at $V < 0$ where the currents are similar for both salts. Both groups of curves asymptotically reach the limit of $t \approx 0.5$ for positive voltages, indicating a decrease in the selectivity of the nanochannels to cations. On the other hand, at negative voltages, the nanopore

selectivity towards cations increases, as observed from the decrease in t_- and the concomitant increase in t_+.

There are other important remarks to be made from of these results. First, the fraction of current transported by cations at $V > 0$ is lower for divalent salts, with the 0.1 M K₂SO₄ solution having the lowest t_+ and the 0.05 M KCl solution the highest t_+. It is important to note that the fraction of current can be qualitatively related to the selectivity of the nanopore towards a particular ionic species. Second, at $V < 0$ and 0.1 M concentration, the transport number of divalent anions is higher than that of monovalent anions, implying that in the case of divalent salts, anions transport more current at negative voltages. However, this tendency is suppressed at lower concentrations (0.05 M KCl). This reveals that under conditions of low ionic strength, ion exclusion has a predominant effect on the transport number of the anionic species regardless of the valency of the ion.

Next, in order to fully explore the influence of doubly charged species on the rectification properties of the nanopore, I–V curves were measured using different proportions of KCl and K₂SO₄ at a fixed total concentration. In our experiments we used two fixed total concentrations: 0.05 M and 0.1 M. By these means, we have attained a gradual change in rectifying properties in which the behavior observed in monovalent and divalent salts are the asymptotic limits (Figure 6). These experiments proved a facile strategy to finely tune the transport features of a nanofluidic diode without any further chemical modification the nanopores surface as it is commonly done in many approaches.

An estimation of the rectification efficiency (f_{rec}) for each mixture of salts revealed a monotonic decrease upon increasing the content of monovalent salt in the electrolyte (Figure 7, empty circles). The degree of rectification (f_{rec}) is defined as the ratio between currents measured at voltages of the same amplitude but opposite polarities,

For the sake of comparison all the rectification efficiencies were normalized with respect to the current measured in the corresponding K₂SO₄ solution in the absence of KCl, which exhibits the higher current value. Normalizing the rectification factor allowed us to compare results with the theoretical predictions obtained from the PNP model (Figure 7, filled circles). It can be observed from Figure 7 that there is a good agreement between theory and experiment, thus reinforcing the idea that PNP simulations not only provides a good description of ionic transport in the nanopore system but also gives an accurate depiction of the changes occurring in the rectification efficiency as a function of the concentration of monovalent and divalent carriers. This is important in order to design experiments that require the use of more than one type of salt and predict the outcome using the PNP theoretical framework.

It is interesting to note that the rectification efficiency decreases upon increasing the concentration of monovalent salt, this effect being more pronounced under low concentration conditions. This fact could be interpreted in the light of the experimental results described in Figure 1 and PNP simulations results described in Figure 5. Under low-concentration conditions, at negative potentials, the ionic current has a negligible
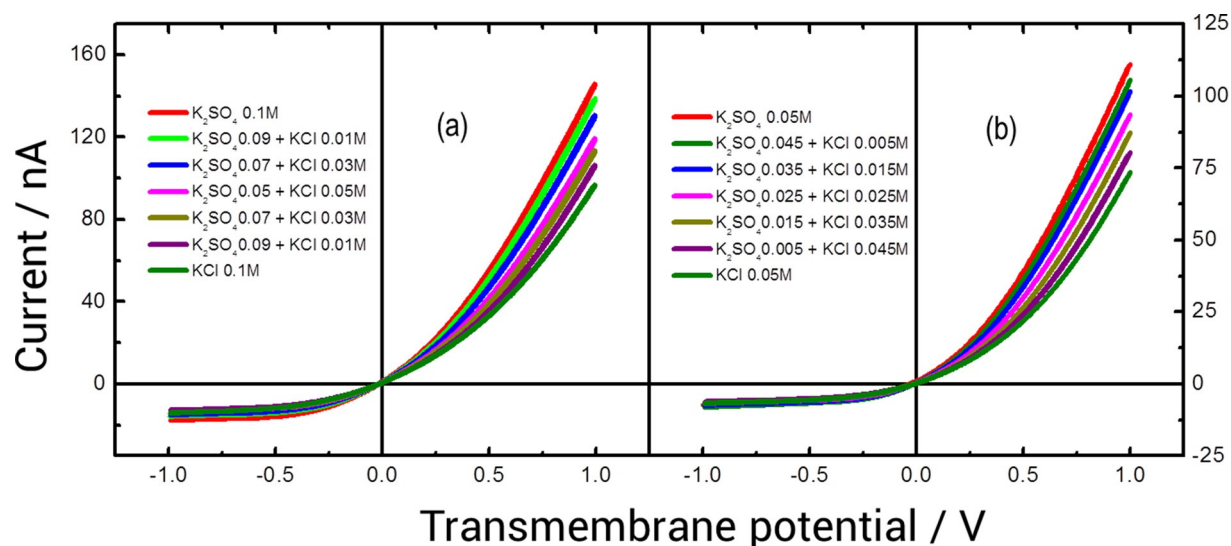
Figure 6. Current–voltage curves for different mixtures of KCl and K_2SO_4. The proportions for each mixture are indicated in the graphs. The total concentrations are a) 0.1 M and b) 0.05 M.
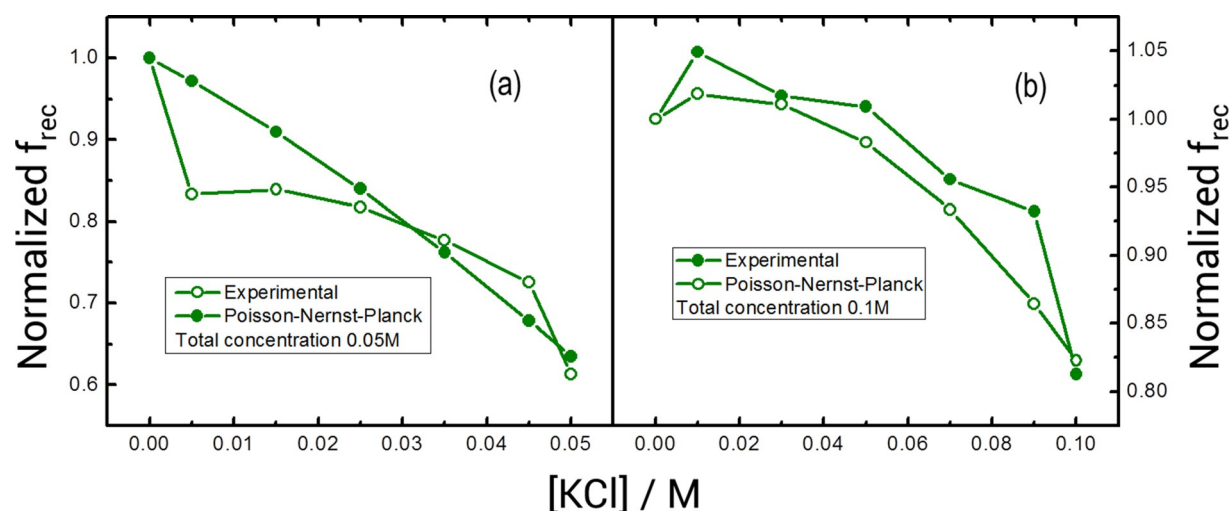
Figure 7. Normalized rectification factors versus the concentration of KCl for each mixture. Total concentrations are a) 0.05 M and b) 0.1 M.

contribution from the anions regardless of the electrolyte valency (divalent or monovalent), and the cations constitute the main carriers contributing to the ionic current. In this scenario, the concentration of cations at negative potentials is purely dominated by the electrostatic interaction with the pore walls and consequently their surface charge density defines the concentration of cations in the interior of the nanopore. The predominance of this effect is evidenced by the ionic current values at $V < 0$. Despite the fact that the bulk concentration of K^+ ions is higher in 0.05 K_2SO_4 than in 0.05 M KCl, the cationic currents are similar, which indicates that the concentration of cationic carries in the interior of the pore is nearly the same. When the potential increases, the anions are allowed to entering inside the pore where they can contribute to the ionic transport. Finally, the magnitude of this contribution is given by the composition of the system.

When the concentration of the electrolyte mixture is higher anions can then enter into the pore, even at negative poten-

tials. This causes an increment in the contribution of the anions and, consequently, the current at negative potentials also depends of the composition of the electrolyte mixture in the bulk. As expected, the extent of the ionic exclusion is higher in the divalent anions than in the monovalent anions due to the more repulsive electrostatic interactions.

3. Conclusions

In this report, we have described the effect of using salts with divalent and monovalent anions on the ionic conductance and rectification efficiency of asymmetrical nanopores. To this end, solutions of different concentrations of K_2SO_4 and KCl were used. We observed an increase in ionic currents when electrolytes constituted of divalent anions are used instead of monovalent anions. These differences are mostly observed for positive currents, and consequently have an impact on the rectification efficiency, i.e.: f_{rec} is also increased by the presence of di-

valent anions in the electrolyte solution. In order to have a broader view of the physicochemical nature of this effect theoretical simulations using the Poisson–Nernst–Planck formalism have been performed. It was found that the reason of the differences in currents was related mainly to the presence of double charged species. It was due to a larger loss of selectivity of the channels both at positive and negative voltages. Furthermore, several mixtures of both types of salts were measured finding a tendency going from the divalent behavior towards a monovalent behavior. We have shown therefore that both the magnitude of ionic current flowing through nanopores and the degree of current rectification can be finely manipulated in a facile way by changing the composition of the mixture in the bulk system. These experiments and theoretical insights shed light on the mechanisms of ionic transport in nanopores when multivalent species are present in solution and highlight the critical role of the interplay between ion exclusion and charge screening effects in defining the ionic selectivity to anions and rectification behavior of ionic diodes.

Experimental Section

Nanopores in poly(ethylene terephthalate) were fabricated using swift heavy-ion irradiation followed by an anisotropic chemical etching procedure to obtain highly tapered, bullet-like, nanopores. The etching was carried out as explained by Pérez-Mitta et al.[36,37] As reported elsewhere, bullet-shaped nanopores present an enhanced non-ohmic behavior with respect to typical conical nanopores, mainly due to the increased aspect ratio close to the small opening of the pores.[38]

In order to explore in a comprehensive manner the effect of valency of anions in the electrolyte on the ionic transport characteristics of the nanopores, we used solutions of K_2SO_4 and KCl of two different concentrations, 0.05 M and 0.1 M, as representative divalent and monovalent species, respectively. The pH was within the range of 5–6 for every solution. Concentrations of both salts were the same on both sides of the membrane for each experiment.

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