

# Modeling of weak polyelectrolyte hydrogels under compression – Implications for water desalination

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## ABSTRACT

Hydrogels immersed in salty solutions induce partitioning of small ions that can be exploited for water desalination. This partitioning also affects the  $H^+$  ions, leading to a decrease of the pH in the gel as compared to supernatant solution. When using weak polyelectrolyte gels, this lower pH may decrease their ionization degree, and hence diminish their desalination capacity. Using the recently developed grand-reaction ensemble, we performed particle-based computer simulations of a gel in contact with a reservoir of salt solution at  $pH \approx 7$ . We showed that the effect of ion partitioning on the ionization degree is negligible, as long as the salinity of the reservoir is high. However, when the reservoir salinity approaches that of fresh water, the ionization degree of weak polyelectrolyte gel is significantly decreased, thus making it a less efficient desalination agent. Furthermore, we demonstrated that the ionization degree of the gel is decreased upon compression. However, up to pressures of approximately 30 bar this does not significantly affect the ion partitioning. Our result predict that weak polyelectrolyte hydrogels, such as the often employed poly(acrylic acid), can be efficiently used to lower the salinity of sea- or brackish water, while they will be inefficient in desalinating water of low salinity.

## 1. Introduction

When immersed in an aqueous solution, polyelectrolyte hydrogels form a two-phase system, which consists of the swollen gel and of the supernatant solution. In thermodynamic equilibrium, the concentration of salt ions in the gel phase is lower than in the supernatant solution, which is why such hydrogels have been considered for applications in water desalination [1,2]. In a desalination experiment, an external stimulus is used to trigger a switch in the swelling degree of the hydrogel, thereby changing its salt rejection. This can be achieved, for example, by mechanically compressing the hydrogel [3–5], and collecting the water expelled upon compression. Recovery of the gel is then achieved by letting it swell freely in the original salt solution. Alternatively, polyelectrolyte hydrogels have been considered as possible draw agents for forward osmosis (FO) desalination [2,6–11]. Due to their high osmotic pressure and macroscopic size they can simultaneously act as draw agents absorbing water and as a FO membrane keeping the water

inside. Then their response to a different stimulus can be used for the water recovery stage of the FO process. The stimulus to cause gel shrinkage could be heating [12,13], an applied electric field [6,14] light [15], or a magnetic field [16] applied to hydrogel-based composites. Additionally, similar phenomena have been studied in the context of stimuli-responsive materials, i.e. for the design of gel based sensors and actuators [17,18], as well as for the use of hydrogels to extract energy stored in the salinity gradient of river estuaries [19,20]. Despite the broad varieties of polymer chemistry, experimental set-ups and various stimuli used in different hydrogels, their use for desalination purposes shares common physical principles.

The physics of using of polyelectrolyte (PE) hydrogels for water desalination is mainly based on the Donnan partitioning. The polyelectrolyte network is charged, and mobile ions of opposite charge (counterions) are confined in its volume to retain electroneutrality [21]. This generates a Donnan potential, resulting in a lower concentration of salt ions in the gel phase than in the supernatant solution. A change in

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swelling of the gel by either one of the stimuli mentioned above is exploited in the desalination process to change the Donnan potential. Upon compression of the gel (or its shrinkage induced by a different stimulus), the amount of confined counterions remains constant due to electroneutrality whereas the volume of the outer phase increases. Therefore, the concentration of ions in the outer phase decreases.

The simple concepts described above apply to a strong polyelectrolyte with a fixed amount of charge, whereas hydrogels used in most desalination experiments were based on poly(acrylic acid) (PAA), which is a cheap polyanion produced in vast quantities [4,9,10,16,19,22–24]. Other polyanions and polycations have been tested much less [3,25,26]. The degree of ionization of a weak polyelectrolyte depends on the  $pK$  value of its monomers and on properties of the outer solution such as the pH and the salinity. Using the Henderson-Hasselbalch equation one can estimate that a weak polyacid is fully ionized if  $pH - pK \gg 1$ , and it can then be treated as a strong polyelectrolyte. By assuming a neutral pH of the desalinated water, one would estimate that PAA ( $pK \approx 4.26$ ) is almost fully ionized at  $pH=7$  ( $pH - pK \approx 3$ ). However, the same Donnan effect which causes partitioning of salt ions affects also the  $H^+$  ions, making pH inside the gel significantly lower than outside [27–29]. Furthermore, the Coulomb repulsion between the ionized groups in the polyelectrolytes increases their  $pK$  as compared to the isolated monomer [30–35]. To distinguish this effect from the Donnan effect, it has been termed the polyelectrolyte effect [27]. Lastly, the pH-value of the desalinated water is not always exactly neutral. All the above mentioned effects can render  $pH - pK \lesssim 1$ , and therefore lead to a pH dependent ionization of the polyelectrolyte that can, in principle, have severe effects for the performance as desalination agent.

Even though both effects mentioned above have been known in the literature and investigated separately, there has been no theoretical study which has considered both of them simultaneously, and explored their consequences for desalination. Several theoretical studies and simulations investigated the partitioning of ions and swelling of strong polyelectrolyte hydrogels [21,36–39]. Another set of studies has addressed the ionization of weak polyelectrolytes in solution [32,33,40–42]. In our previous study, we have shown that the compression of a weak polyelectrolyte hydrogel discharges the polymer network, and thereby decreases its desalination capacity [43]. Under certain conditions, the Donnan partitioning coupled to the ionization of the gel can even reverse this process, causing the gel to capture ions upon compression, instead of releasing them. However, the model used in [43] was based on a mean-field approximation that fully accounts the Donnan effect but only partly models the polyelectrolyte effect.

More recently, we presented the grand-reaction Monte Carlo method (G-RxMC), which allows to fully account for both effects in particle-based simulations [27]. In that work we used the PE solution as a model system, showing that the Donnan and polyelectrolyte effects are additive, and that they can shift the effective  $pK$  by more than two units especially at low salinity. In our present work we apply the same method to study the swelling of a weak polyelectrolyte hydrogel and its ability to reject salt ions upon compression. Our treatment is generic, and therefore our results can be applied to any polyelectrolyte hydrogel if the  $pK$  of its parent monomer is known. For clarity, we have chosen to work with the  $pK$  value of PAA and discuss the circumstances when it can be used efficiently as a desalination agent, and when its weak nature degrades its desalination capacity.

The rest of the manuscript is organized as follows: We start by presenting the model and simulation methodology and continue with results on the pressure-volume relations. Next, we discuss how the degree of ionization of the gel is changed upon the applied pressure, and finally we show how this affects the amount of ions transferred between the gel and the supernatant solution. Finally we discuss their consequences for using PAA hydrogels as desalination agents, and followed by a discussion and the conclusions.

## 2. Model and method

### 2.1. Details of the model

To represent a desalination experiment, we consider a simulation model of a polyelectrolyte hydrogel exchanging ions with an infinite aqueous reservoir of constant salinity depicted in Fig. 1. The simulated system comprises of a tetra-functional (diamond) network of 16 polyelectrolyte chains, each of which is composed of 30 ionizable monomer units connected by 8 tetra-functional crosslinks, yielding a total number of gel monomer units  $N_{gel}=16 \cdot 30 + 8=488$ . The gel is made macroscopic by connecting it to itself via periodic boundary conditions applied to a cubic box of volume  $V^{gel}$ . The size of the box defines the monomer concentration. We emphasize that even though the network has a diamond-like topology, the network nodes are not fixed at their lattice positions but they are free to move, allowing for fluctuations in the network structure. Admittedly, the tetra-functional network is an arbitrary choice, however, there are good reasons why it is preferred not only in our study but also in other simulations of polyelectrolyte hydrogels [37,44]. Diamond is presumably the simplest regular structure with a low number of connections emerging from one node, resembling tetrafunctional network nodes that appear as a result of some common crosslinking procedures used in experiments. Other regular network models, ranging from single-chain in a cylinder to cubic lattice networks have been employed, yielding qualitatively very similar results [29,45–47]. Real hydrogel networks are typically irregular and full of defects, however, faithfully reproducing this irregular structure in a simulation model requires a too large system, unsuitable for our current problem [48]. Apart from network topology, it is also possible to vary the length of the strands connecting the network nodes, as we have done that systematically in an earlier publication [44]. Thus, we may conclude that the choice of the model network structure may affect the quantitative outcome of the simulations but it does not affect the qualitative picture.

The ionization equilibrium for the monomer units is characterized by the corresponding acidity constant  $pK$ . The hydrogel exchanges mobile ions,  $Na^+$  and  $Cl^-$ , with the reservoir, which represents an aqueous solution of a given salinity,  $c_{salt}$ . To investigate the desalination capabilities of the hydrogel, we consider two different salinities:

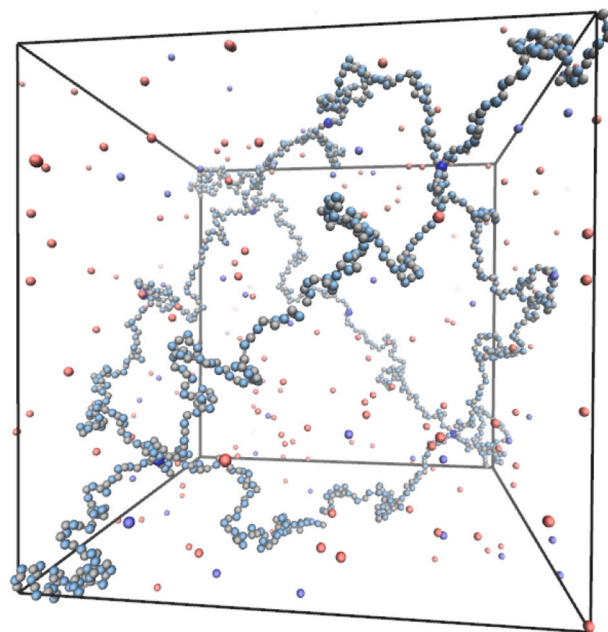


Fig. 1. Diamond-like network in box with periodic boundaries represents a cell of macro-size gel.

$c_{\text{salt}}=0.203\text{mol/l}$  which corresponds to brackish water, and  $c_{\text{salt}}=0.007\text{mol/l}$  which is approximately the salinity of drinking water. To investigate the role of the ionization of the weak polyelectrolyte, we varied the  $pK$  while keeping the  $pH$  constant, such that the difference  $pH - pK \in \{0, 2, 4\}$ . In the range  $3 \lesssim pH \lesssim 11$  and at the above-mentioned salt concentrations,  $pH - pK$  is an approximately universal control parameter [49]. In this range, the variation of  $pK$  at constant  $pH$  is (approximately) equivalent to the variation of  $pH$  at constant  $pK$ .

## 2.2. Interaction potentials

All particles interact via the same repulsive 6–12 truncated Lennard-Jones potential

$$V_{LJ}(r) = \begin{cases} 4\epsilon \left( \left( \frac{\sigma}{r-r_c} \right)^{12} - \left( \frac{\sigma}{r-r_c} \right)^6 \right) & , r < r_c \\ 0 & , r > r_c \end{cases} \quad (1)$$

where  $r$  is the distance between two particles,  $r_c = \sigma \cdot 2^{1/6}$  denotes the cut-off distance,  $\epsilon = kT$  is the depth of the potential well, and  $\sigma$  is the distance at which the inter-particle potential is zero.

All charged species interact via the Coulomb potential

$$V_{EL} = l_B k_B T \frac{q_1 q_2}{r} \quad (2)$$

where  $l_B$  denotes the Bjerrum length,  $l_B = 2\sigma = 0.7\text{nm}$ , which we set equal to the Bjerrum length of water at room temperature.

The bonds between the monomer units of the gel network are modeled via a Finitely Extensible Nonlinear Elastic (FENE) potential

$$V_{FENE}(r) = -\frac{1}{2} \Theta \Delta r_{\text{max}}^2 \ln \left[ 1 - \left( \frac{r-r_0}{\Delta r_{\text{max}}} \right)^2 \right] \quad (3)$$

where  $\Theta = 10.0 kT/\sigma^2$ ,  $\Delta r_{\text{max}} = 2.0\sigma$ ,  $r_0 = 1.0\sigma$  [50]. We simulate at constant temperature by using a Langevin thermostat or setting  $k_B T$  in the G-RxMC method.

With the above choice of monomer parameters, our model yields an average distance between ionizable monomers  $r \approx 1.05\sigma \approx 0.35\text{nm}$ . This value approximately matches the distance between two COOH groups of poly(acrylic acid) that could be estimated from the molecular geometry, assuming all-trans conformation. Nevertheless, it should be kept in mind that our model represents a generic polymer under good solvent conditions and its parameters have not been specifically tuned to reproduce the properties of poly(acrylic acid).

## 2.3. Acid-base ionization reaction and exchange of ions with the reservoir

In order to account for the ionization reaction we followed the scheme proposed in [27]. We also assumed that at neutral  $pH$  conditions the amount of  $H^+$  ions is so small that the ionization reaction



is most of the times accompanied by a simultaneous exchange for  $Na^+$  ions from the reservoir. The overall reaction is then



where

$$K' = K \exp(\mu_{H^+} - \mu_{Na^+}) \quad (6)$$

The use of Eq. (5) with the equilibrium constant  $K'$  allows us to perform the simulation also at  $pH \approx 7$  when the concentration of  $H^+$  is very low, as discussed in detail in Ref. [27].

We model the ion exchange with the bath as a reaction of an ion pair insertion (or deletion)



where the equilibrium constant of this exchange reaction is given by the chemical potentials of both ions in the reservoir,  $K_{NaCl} = \exp(\mu_{Na} + \mu_{Cl})$ .

## 2.4. Simulation protocol

We implemented the G-RxMC method for a gel in contact with a salt solution having  $pH=7$ , where the ionic strength of the reservoir is dominated by the salt. In the simulation there are three processes occurring simultaneously in the system: the movement of all the model particles, the ionization reaction of hydrogel monomer units, and the exchange of mobile ions between the gel phase and the reservoir.

In order to simulate a weak polyelectrolyte hydrogel in equilibrium with a reservoir we set the chemical potential of the ions,  $\mu = \mu_{Na} = \mu_{Cl}$ , and  $\mu_{H^+} = \mu_{H^+}^\ominus - kT pH / \log_{10} e$ , where  $\mu_{H^+}^\ominus$  is the chemical potential of  $H^+$  ions in the standard state, i. e. in the (hypothetical) state of a pure  $H^+$  component at the standard density of 1 mol/l, as defined by IUPAC (we set it to be equal to zero,  $\mu_{H^+}^\ominus = 0$ ).

Then we initialize the simulated system in the following steps:

1. Create the tetrafunctional network composed of 16 chains, each containing 30 monomer units, that are inscribed in a cubic box with periodic boundaries.

2. Add small ions to the simulation box, corresponding to the concentration predicted by Eq. (8).

3. Set the initial ionization state of the gel segments, such that the overall ionization degree approximately equals the value of  $\alpha$  predicted by Donnan theory (see Eq. (9) further in text).

Then we simulate three processes, occurring simultaneously in random order: Langevin molecular dynamics (LMD); ionization reaction of gel segments (RE); exchange of salt ion pairs with the reservoir (EX). The whole simulation procedure is then.

1. Choose randomly, which type of process to run: LMD, RE, or EX.

2. Simulate the chosen process, collecting 50 samples and obtaining the corresponding averages

LMD: pressure  $P$  and end-to-end distances of all the 16 chains,  $R_e^i$ ,  $i \in [1..16]$ ;

RE: number of ionized segments  $N_A$  and the degree of ionization,  $\alpha = N_A / N_{\text{gel}}$

EX: number of salt ions in the box,  $N_{Na^+}$  and  $N_{Cl^-}$ .

We checked the autocorrelation time of each process, requesting that the absolute value of the Pearson coefficient is smaller than 0.2, which was chosen based on our previous experience with similar simulations. Note that the choice of this value does not affect the simulation results, it only affects the efficiency of sampling. Sub-simulations continue until this requirement is fulfilled.

3. Repeat the procedure collecting at least 200 averages from each process.

The result of the whole simulation run is a set of arrays,  $\{P\}$ ,  $\{N_A\}$ ,  $\{N_{Na^+}\}$ ,  $\{N_{Cl^-}\}$ . We identified the observables  $R_e^i$  as the slowest evolving variables, therefore we used the arrays of  $\{R_e\}$  to indicate the autocorrelation time of the Langevin dynamics (see the flow chart in ESI Section 6).

In order to measure the resulting ion concentrations,  $c_{\text{salt}}$  and their osmotic pressure,  $P^{\text{res}}$ , which correspond to a given  $\mu$ , we also performed a simulation of a finite volume exchanging ions with the reservoir.

## 2.5. Ideal Donnan partitioning of ions

In our previous study, we used Donnan [43] theory to model the ionization of weak polyelectrolyte hydrogels. In the current work we use this theory as a reference model to which we compare the simulation result. We also use the Donnan predictions to construct the initial state of the system in order to speed up the equilibration of the simulation. Based on the ideal gas approximation the Donnan theory allows to

describe the thermodynamic equilibrium between the phase containing weak polyelectrolyte and the phase of bath aqueous solution.

$$\frac{c_{\text{Na}^+}}{c_{\text{Cl}^-}} = \frac{\alpha}{1-\alpha} 10^{pK-pH} = \sqrt{1 + \left(\frac{\alpha c_p}{2c_{\text{salt}}}\right)^2} - \frac{\alpha c_p}{2c_{\text{salt}}} \quad (8)$$

where  $c_{\text{Na}^+}$ ,  $c_{\text{Cl}^-}$ ,  $c_p$  are the concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$  ions, and the density of polyelectrolyte respectively;  $\alpha$  denotes the polyelectrolyte degree of ionization. This equation, together with the electroneutrality condition, translates into a cubic equation for  $\alpha$

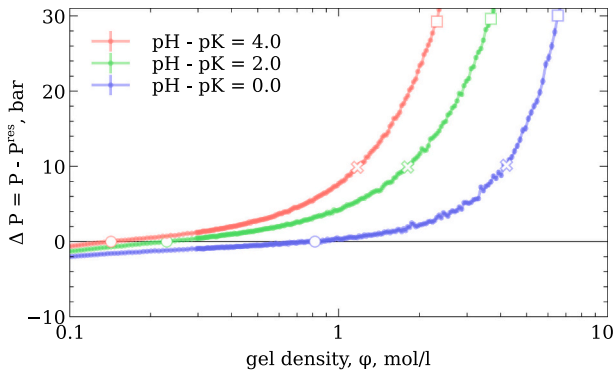
$$-\frac{\alpha^3 c_p}{c_{\text{salt}}} + \alpha^2 \left( \frac{c_p}{c_{\text{salt}}} + \theta - \frac{1}{\theta} \right) + \frac{2\alpha}{\theta} - \frac{1}{\theta} = 0 \quad (9)$$

where  $\theta = 10^{pK-pH}$ .

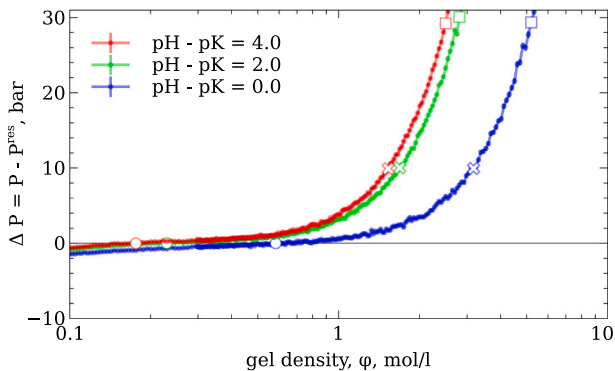
### 3. Results

#### 3.1. Compression of the gel

We performed the simulations by fixing the volume of the simulation box  $V^{\text{gel}}$  to various different values, and measured the pressure inside the simulation box,  $P$ , from which we subtracted the pressure of the reservoir,  $P^{\text{res}}$ . This pressure difference  $\Delta P = P - P^{\text{res}}$  corresponds to the external pressure that would have to be applied in order to compress the hydrogel to a given volume, while in equilibrium with the external reservoir. In the simulation protocol we fix the box volume,  $V$ , and measure the pressure  $P$ . Therefore, the values of  $P$  are not known a priori, and the resultant values of  $\Delta P$  are not exactly equal to the values  $\Delta P \in \{0, 10, 30\}$  bar that we highlight in Fig. 2. We obtain the pressure density



(a) low salinity,  $c_s = 0.007$  mol/l



(b) high salt  $c_s = 0.209$  mol/l

**Fig. 2.** External pressure which needs to be applied in mechanical equilibrium to compress the hydrogel and achieve a specific density at two different salinities of the reservoir solution, and three different values of  $\text{pH} - \text{pK}$ . High-lighted data points indicate the applied pressures  $\Delta P \in \{0, 10, 30\}$  bar.

curves shown in Fig. 2 and observe that in the initial stages of compression (around  $\Delta P=0$ ), a rather small pressure suffices to significantly increase the monomer density in the gel, i. e. to decrease the gel volume. Further compression requires higher pressures, as seen from the increasing slope of the curves in Fig. 2. At low salinity,  $c_{\text{salt}}=0.007$  mol/l we observe very different trends at each of the three values of  $\text{pH} - \text{pK} \in \{0, 2, 4\}$ , indicating that the acid-base equilibrium affects the pressure required to compress the gel. A lower value of  $\text{pH} - \text{pK}$  leads to a lower degree of ionization, and therefore to a reduced gel swelling (higher density) at free swelling equilibrium ( $\Delta P=0$ ). Additionally, gels which are less ionized (smaller  $\text{pH} - \text{pK}$ ) exhibit a steeper increase of pressure as the gel density increases.

At high salinity,  $c_{\text{salt}}=0.203$  mol/l the trends at  $\text{pH} - \text{pK} \in \{2, 4\}$  are very similar, whereas the trend at  $\text{pH} - \text{pK}=0$  is significantly different, indicating that the magnitude by which the acid-base equilibrium affects the pressure depends not only on the difference  $\text{pH} - \text{pK}$  but also on the salinity of the desalinated solution, as reported also in Ref. [51].

#### 3.2. Degree of ionization of the gel

The average degree of ionization  $\alpha$  of a weak polyelectrolyte gel is suppressed, as compared to that of the free monomer at the same value of  $\text{pH} - \text{pK}$ . This is caused by two effects [27,51]: (i) the Donnan partitioning of ions, which leads to the  $\text{pH}$  value in the gel being lower than the  $\text{pH}$  value in the reservoir,  $\text{pH}^{\text{gel}} < \text{pH}$ , termed the Donnan effect; (ii) the electrostatic repulsion between the charges on the chain, which decreases the ionization at the same value of  $\text{pH}^{\text{gel}}$ , termed the polyelectrolyte effect. Both these effects decrease the ionization degree, however, their magnitude can be very different depending on the salt concentration and on the strength of electrostatic interactions.

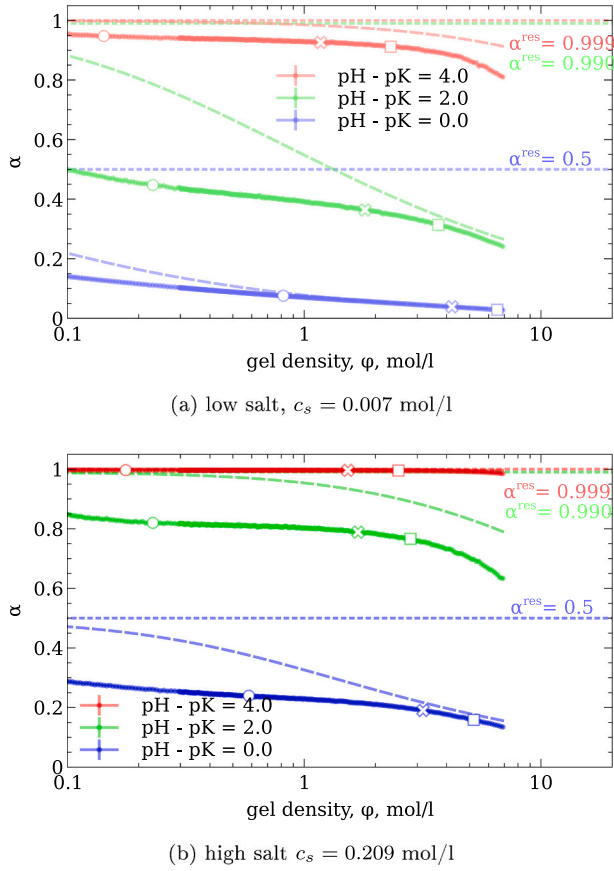
Fig. 3 shows how the degree of ionization of the gel varies upon compression. It is always lower than the ionization degree of the free monomer at the same  $\text{pH}$ , and it always decreases with increasing gel density. This effect was demonstrated also in our previous works [43,51,52].

For comparison, we included in Fig. 3 the ideal Donnan predictions, shown as dashed lines. The differences between the ionization of the gel predicted by the Donnan theory and ionization of the free monomer,  $\alpha^{\text{res}}$ , indicates how much the Donnan effect alters the ionization of the gel. On the other hand, the differences between the dashed lines and the simulation data in Fig. 3 indicate how much the polyelectrolyte effect changes the ionization of the gel, in addition to the Donnan effect. This additional effect is particularly strong at low salinity and  $\text{pH} - \text{pK}=2$ , lowering the ionization degree to half of its value for the free monomer. However, it only applies at sufficiently low densities of the gel, corresponding to moderate pressures. The Donnan model qualitatively predicts the observed suppression of ionization, however, a comparison with simulations shows that Donnan vastly underestimates the overall effect at low gel density, close to free swelling equilibrium,  $\Delta P=0$ . Donnan theory neglects the direct particle-particle interactions and ionic correlations therefore, it fails to quantitatively predict the suppression of ionization at low pressures (close to the free swelling equilibrium). Nevertheless, the mean-field Donnan models provide a good estimate of the ionization for weak polyelectrolyte gels under compression because the Donnan contribution dominates the suppression of ionization at higher gel densities. In contrast, computer simulations with explicit particles indicate the full scale of this effect and its impact on the desalination capabilities of weak polyelectrolyte hydrogels in the whole range of gel densities or applied pressures.

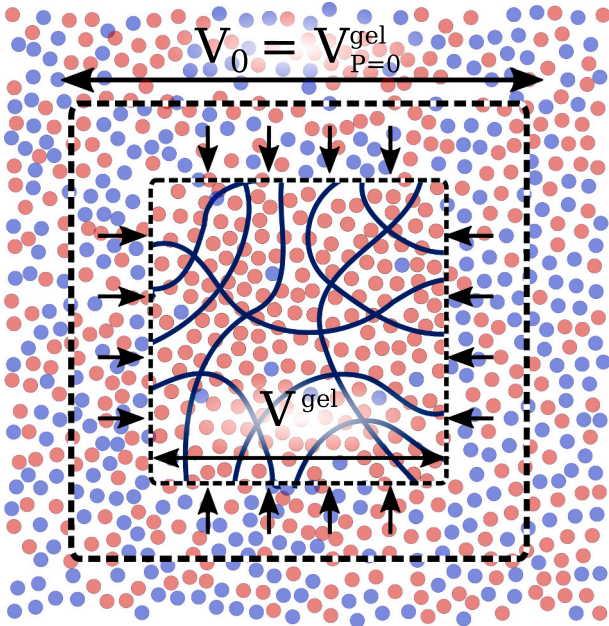
#### 3.3. Desalination effect

We now examine how the coupling between the degree of ionization of the gel, its state of compression, and the reservoir parameters ( $c_{\text{salt}}$ ,  $\text{pH} - \text{pK}$ ) affects the gel's ability to desalinate water, i. e. to transfer small ions between the gel and the reservoir. Fig. 4 illustrates the





**Fig. 3.** Degree of ionization,  $\alpha$ , as a function of hydrogel density at different salt concentrations in the reservoir, and different values of  $\text{pH}^{\text{res}} - \text{pK}$ . Dashed lines without markers represent the prediction of mean-field theory, accounting only for the Donnan effect using Eq. (9) highlighted data points indicate the applied pressures  $\Delta P \in \{0, 10, 30\}$  bar.



**Fig. 4.** Schematic illustration of the hydrogel being compressed isotropically by pressure  $\Delta P$  from the initial volume at free swelling equilibrium,  $V_0$  to a volume  $V^{\text{gel}}$ . Simultaneously, the gel exchanges small ions with a reservoir solution of salinity  $c_{\text{salt}}$ .

principle of desalinating water using a hydrogel. As the hydrogel is compressed from its initial volume  $V_0$  at free swelling equilibrium ( $\Delta P=0$ ) to a certain volume  $V^{\text{gel}}$ , the number of ions,  $N_i$ , in the initial volume  $V_0$  changes. This number is a sum of the ions inside  $V_{\text{gel}}$  and in the outer volume (which is left out after gel compression)

$$N_i = N_i^{\text{ingel}} + c_{\text{salt}} \cdot (V_0 - V^{\text{gel}}) \quad (10)$$

where the index  $i$  runs over the types of ions,  $i \in \{\text{Cl}^-, \text{Na}^+\}$ . Since the volume  $V_0$  is constant, the increase of the number of ions,  $N_i$ , in this volume implies, that ions from the reservoir enter this volume and vice versa. They leave the volume if  $N_i$  decreases.

To quantify this effect, we show in Fig. 5 the number of transferred ions per segment of the gel,

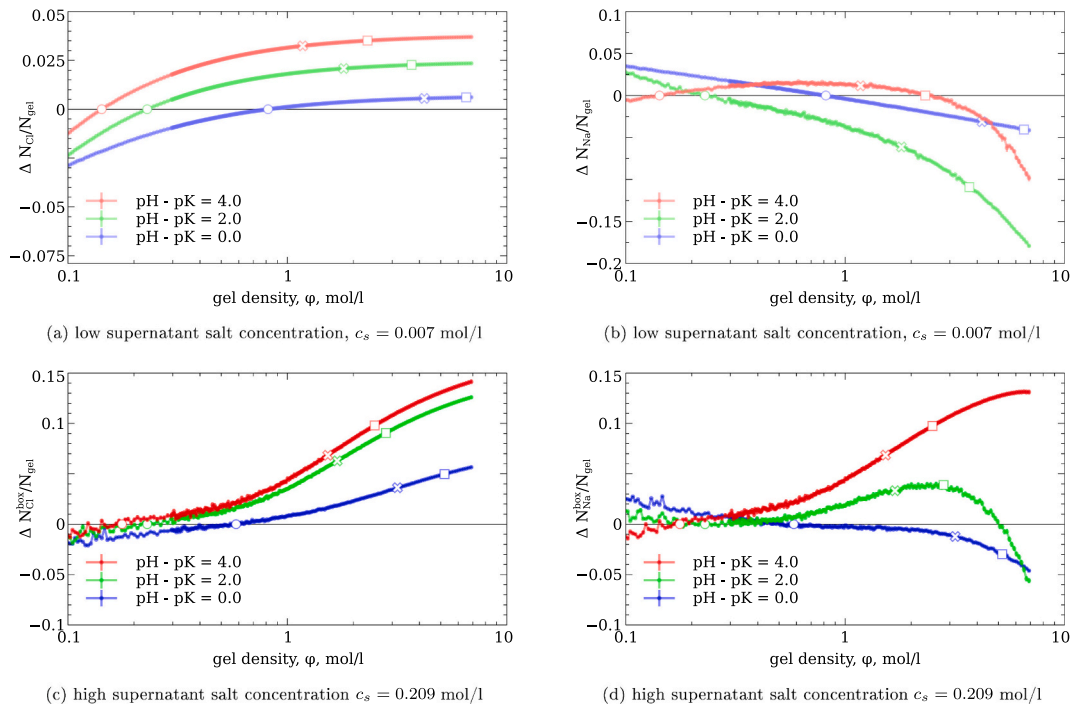
$$\frac{\Delta N_i}{N_{\text{gel}}} = \frac{N_i - N_i^{\text{ini}}}{N_{\text{gel}}} \quad (11)$$

which reflects how many  $\text{Na}^+$  and  $\text{Cl}^-$  ions are taken up by the volume  $V_0$ , when the gel is compressed to a state of given gel density,  $\phi$ , starting from its free swelling equilibrium, when it had volume  $V_0$  and contained inside  $N_{\text{Na}^+}^{\text{ini}}$  and  $N_{\text{Cl}^-}^{\text{ini}}$  ions of the corresponding type. Fig. 5 shows that, as the difference  $\text{pH} - \text{pK}$  decreases, the number of transferred ions decreases as well. At low salinity (Fig. 5a), the number of transferred  $\text{Cl}^-$  ions drops roughly by a factor of 2 in each step as  $\text{pH} - \text{pK}$  is decreased from 4 to 2, and to 0. At high salinity (Fig. 5c), there is very little decrease in the number of transferred  $\text{Cl}^-$  ions if  $\text{pH} - \text{pK}$  is decreased from 4 to 2, but there is a significant drop if  $\text{pH} - \text{pK}$  is decreased from 2 to 0.

To show how the number of transferred ions can be directly related to quantities measured in experiments, we use the data from Arens et al. [5] as an example. Arens et al. used PAA hydrogels to desalinate water, and in Fig. 3 of Ref. [5] they presented the salt concentration,  $c$  in the water expelled from the hydrogel as a function of total volume of the expelled solution,  $V$ , at a given applied pressure,  $P$ . Since they observed an almost linear variation of salt concentration with the gel volume, we can determine the mass of ions ( $\text{NaCl}$ ) transferred upon compression from  $P_0=1\text{bar}$  to  $P_1=30\text{bar}$  by calculating the area under the curve,  $m_{\text{NaCl}} = (c_1 - c_0)(V_1 - V_0)/2$ . Substituting  $V_1=270\text{ml}$ ,  $V_0=225\text{ml}$ ,  $c_0=10\text{g/l}$ ,  $c_1=8.4\text{g/l}$ , we obtain  $m_{\text{NaCl}}=0.035\text{g}$  that has been transferred using the gel with a dry mass of  $m_{\text{gel}}=7.4\text{g}$ . Using the molar masses  $M_{\text{NaCl}}=40\text{g/mol}$  and  $M_{\text{AA}}=86\text{g/mol}$ , we can calculate that  $\sim 0.01$  (moles of) salt ions per (one mol of) gel monomers have been transferred upon the compression to  $P_1=30\text{bar}$ . The compression to 10 bar lead to transfer of 0.003 mol of salt per (one mol of) gel monomers. In the more general case, if the dependence should be non-linear, the mass of transferred ions could be obtained by numerically integrating the experimentally determined dependence.

The drop in the number of transferred ions, observed in Fig. 5, correlates with the decrease in the ionization degree as  $\text{pH} - \text{pK}$  is decreased (Fig. 3). At low salinity the ionization degree at free swelling equilibrium ( $\alpha(\Delta P=0)$ ) changes gradually, approximately from 0.15 to 0.45 and then to 0.95. At high salinity the cases when  $\text{pH} - \text{pK}$  equals to 2 and 4 correspond to an almost fully ionized gel, i. e. to  $\alpha(\Delta P=0) \simeq 0.81$  and 0.99. In the case of  $\text{pH} - \text{pK}=0$  the gel is almost deionized,  $\alpha(\Delta P=0) \simeq 0.15$ . Qualitatively this effect can be understood even in terms of Donnan theory. At high salinity the ion partitioning is smaller than at low salinity, therefore the  $\text{pH}$  in the gel is closer to its value in the supernatant, and the ionization degree is closer the one predicted by the Henderson-Hasselbalch equation.

Furthermore, the ionization degree of the gel decreases with increasing gel density (pressure). In other words, the gel uses the mechanical work done by the compression to decrease its ionization, rather than to increase the Donnan potential. This effect shows up in the reversal of the trend in the number of transferred  $\text{Na}^+$  ions. Initially, it increases with compression but at a certain point it starts to decrease. At high salinity of the reservoir, this reversal occurs only at rather high



**Fig. 5.** Change in the number of  $\text{Cl}^-$  ions in the volume  $V_0$  (left column) and  $\text{Na}^+$  ions (right column) normalized by the number of hydrogel segments,  $N_{\text{gel}}$ . The gel is in contact with solutions of two different salinities and at three different values of  $\text{pH} - \text{pK}$ . Highlighted data points indicate the applied pressures  $\Delta P \in \{0, 10, 30\}$  bar.

pressures,  $\Delta P \gtrsim 30$  bar, but at low salinity this happens even at low pressures, at any  $\text{pH} - \text{pK}$ . In the pressure ranges where this dependence is reversed, the hydrogel may be used as a desalination agent where the roles of compression and swelling of the gel are swapped in the desalination cycle [43]. In our previous study [43], we have shown how the desalination cycle can be constructed using simultaneous compression of polycationic and polyanionic hydrogels, such that the difference of consumed amounts of cations and anion is compensated.

#### 4. Discussion

Based on the Henderson-Hasselbalch equation, the acidity constant of acrylic acid (PAA),  $\text{pK}=4.26$  [53], seems sufficiently low to make this cheap polyelectrolyte a good candidate for desalination applications. Indeed, if the desalinated solution would have a neutral  $\text{pH}=7$ , the difference  $\text{pH} - \text{pK}=2.75$  should be sufficiently big to ensure full ionization of PAA hydrogels, and hence PAA should retain its maximum desalination capacity down to the salt concentrations of drinking water. However, if the desalinated solution is slightly acidic, i. e.  $\text{pH} \lesssim 6$ , it will significantly suppress the ionization of the PAA hydrogel, thereby lowering its ability to act as a desalination agent. Such a suppression of the ionization will restrict the amount of transferred ions, especially at low salinity of the desalinated solution, while it will have a negligible effect if the desalinated solution has a higher ionic strength. Thus, our results demonstrate that weak polyacid gels, such as PAA, are not the optimal gels to desalinate water under all conditions. They work efficiently at neutral and slightly basic conditions while they fail to desalinate solutions of low salinity at slightly acidic conditions. Other polyacids with a lower  $\text{pK}$ , might work well at more acidic conditions, provided that  $\text{pK} < \text{pH} - 2$ . Because the investigated problem is symmetric with respect to changing the sign of charge of the polyelectrolyte, with only proviso that instead of cations it binds anions. Therefore, our analysis implies that polybases could be used for efficient desalination of water at neutral and acidic conditions because they bear cationic charge at a low  $\text{pH}$ , following the Henderson-Hasselbalch equation

$$\text{pH} - \text{pK}_A^{\text{base}} = \log_{10} \frac{1 - \alpha}{\alpha}. \quad (12)$$

where  $\text{pK}_A^{\text{base}}$  is the dissociation constant of the acid  $\text{BH}^+$ , conjugate to the base B, and  $\alpha$  is the degree of ionization of the base, corresponding to the following reaction:



Therefore, applying the symmetry with respect to the inversion of charge, we expect polybase hydrogels to be fully ionized at  $\text{pH} < \text{pK}_A^{\text{base}} - 2$ , and acting as efficient desalination agents in the respective  $\text{pH}$  range.

A simplified theoretical model, which considers only the Donnan effect, has predicted that the ionization of a weak polyelectrolyte hydrogel should be rather high at the initial stages of compression, and it should significantly decrease as the hydrogel is being compressed. On the contrary, our simulations show that, already at free swelling equilibrium, the ionization degree is much lower than that predicted by Donnan theory. However, the degree of ionization varies only weakly as the compression is increased. What is actually varied is the relative strength of the Donnan effect and the polyelectrolyte effect, keeping the ionization degree nearly constant up to rather high pressures of  $P \gtrsim 30$  bar. The Donnan model, previously used by ourselves and by other authors, qualitatively predicts the correct trends but it fails to capture important quantitative features, caused by direct electrostatic interactions. Predictions using such simple models are therefore overly optimistic when contrasted to experimental results. This underpins the need to use more sophisticated models for predictions of the desalination capabilities of polyelectrolyte hydrogels.

In the simulation model we have considered the desalinated solution as an infinite reservoir with a constant salinity and  $\text{pH} = 7$ , independent of the amount of ions captured or released by the hydrogel. In practice, the volume of the desalinated solution is always finite, although it is usually much greater than the volume of the hydrogel. In the case of a finite reservoir, changes in the ionization of the hydrogel upon compression would lead to a feedback loop, affecting the composition of

the reservoir [21,43]. If the  $\text{Na}^+$  ions would be released upon compression of the hydrogel, they would cause an increase of the pH of the reservoir solution. The overall effect then depends on the actual amounts of the hydrogel and the desalinated solution, and it is therefore hard to generalize. Nevertheless, if the amount of the desalinated solution is much greater than the amount of the hydrogel used for desalination, then the net result should be close to our predictions for the case of an infinite reservoir.

## 5. Conclusions

We employed the G-RxMC simulation scheme to model a weak polyelectrolyte network in equilibrium with an infinite reservoir of constant salinity and pH. We showed that the ionization of the hydrogel can be significantly suppressed as compared to predictions based on the Henderson-Hasselbalch equation. This is caused by two effects: (i) the Donnan partitioning of  $\text{H}^+$  ions; (ii) the electrostatic repulsion between charges in the gel. The magnitude of both effects depends on the difference  $\text{pH} - \text{pK}$  and on the salinity of the supernatant solution. The first effect is particularly strong at low salinity, and its magnitude decreases with increasing salinity of the supernatant. In contrast, the second effect is strong at high ionization degrees of the gel and its magnitude decreases as the ionization degree is decreased. Furthermore, our simulations also confirmed the previous prediction that the ionization degree decreases upon compression of the gel. However, they have shown that this decrease is much less significant than previously estimated using mean-field models. Finally, we also showed that decreasing the ionization of the gel upon compression may completely reverse the effect used for desalination, making the gel release counterions upon compression instead of absorbing them.

When considering poly(acrylic acid) (PAA  $\text{pK}=4.26$ ) as the most commonly used polyelectrolyte in desalination experiments, our results imply that PAA should be fully ionized at neutral pH of the supernatant. However, in a slightly acidic supernatant at  $\text{pH} \approx 5$  and low salinity  $c_{\text{salt}} \approx 0.007 \text{ mol/L}$ , the ionization of PAA should be much lower than expected from the Henderson-Hasselbalch equation, resulting in a decreased desalination capacity. Thus, PAA hydrogels could still be efficiently used for a pre-treatment of seawater or brackish water to lower its salinity, while they might be inefficient in desalinating water which already has a low salinity, or which has a slightly acidic pH. To overcome this deficiency, new polyelectrolyte materials should be sought. Polyacids with  $\text{pK} < 4$  or polybases with  $\text{pK} > 10$  should work well in the whole range of conditions relevant for desalination.

## CRedit authorship contribution statement

Oleg V. Rud: Data curation, Visualization, Investigation, Original draft preparation.

Jonas Landsgesell: Methodology and Software.

Christian Holm: Conceptualization, Formal Analysis:

Peter Košovan: Validation, Writing-Reviewing and Editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary data

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