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Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modeling

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Abstract:	<p>Recently polyelectrolyte hydrogels have been proposed as draw agents for reverse osmosis desalination techniques. Indeed, polyelectrolyte hydrogels have the ability to absorb a big amount of water across forward osmosis membrane as a result of their swelling pressure. On the other hand, the insoluble cross-linked network of the gel enables dewatering under the influence of a stimulus (thermal and/or mechanical). Moreover, from a thermodynamic perspective, the polyelectrolyte hydrogel is already an osmotic membrane rejecting ions between external and internal solutions. These three properties of the gels make it possible to use them for desalination and at the same time avoid the use of expensive membranes. In this article, we present our recent theoretical study of the use of polyelectrolyte hydrogel for water desalination. We modeled the thermodynamic equilibrium between coexisting phases of the gel and supernate aqueous salt solution. We have shown that the salinity of the supernate phase decreases during compression of the gel due to the release of absorbed in gel solution of lower salinity. Finally, we performed a set of simulations modeling the process of continuous decrease of solution salinity up to freshwater concentrations.</p> <p>p, li { white-space: pre-wrap; }</p>
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Mikhail Laktionov: Methodology, Software, Data curation

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Oleg V. Rud: Conceptualization, Methodology, Writing - Original draft preparation.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Prague, July 19, 2022

Dear Professor Ravi Naidu,

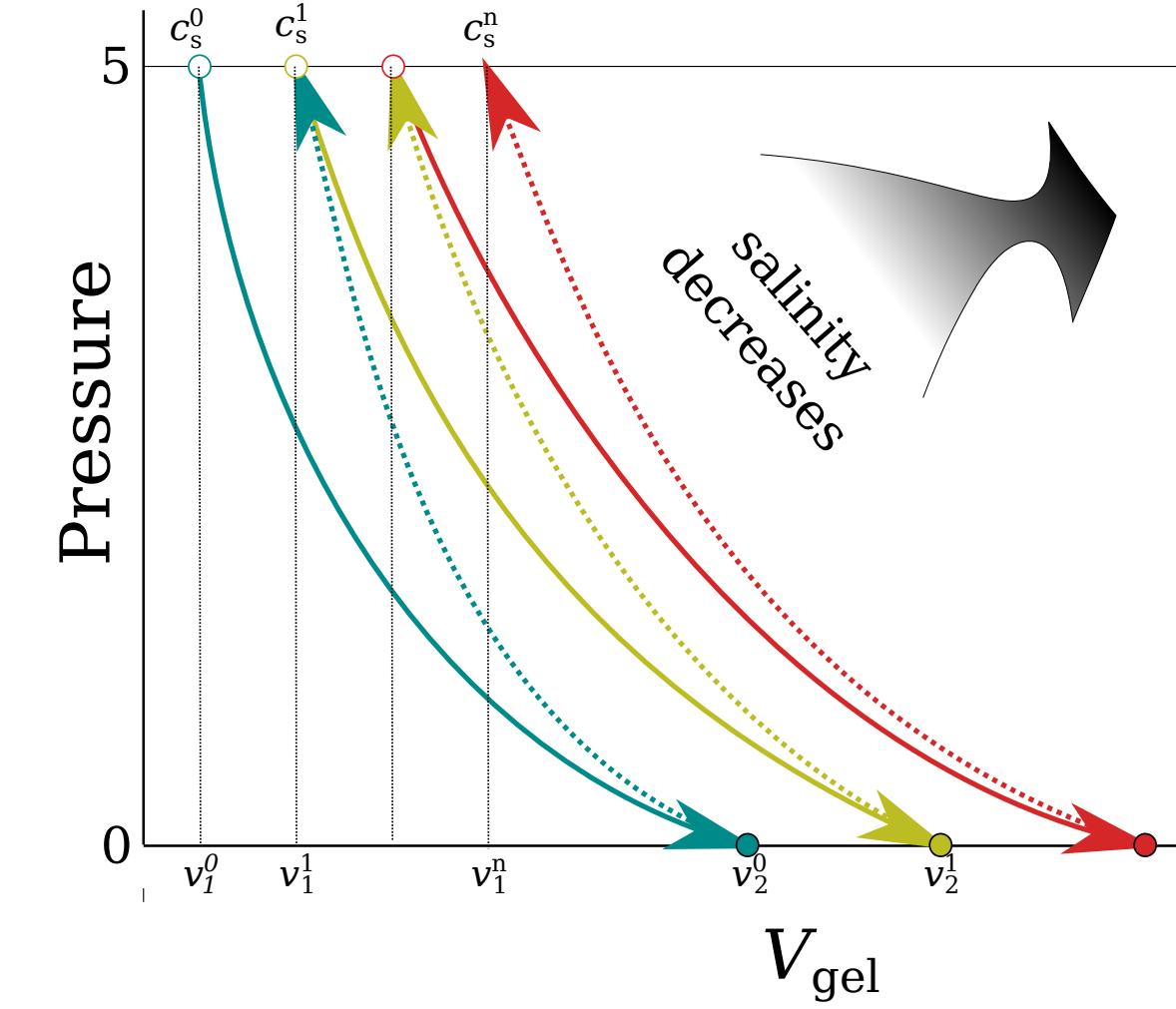
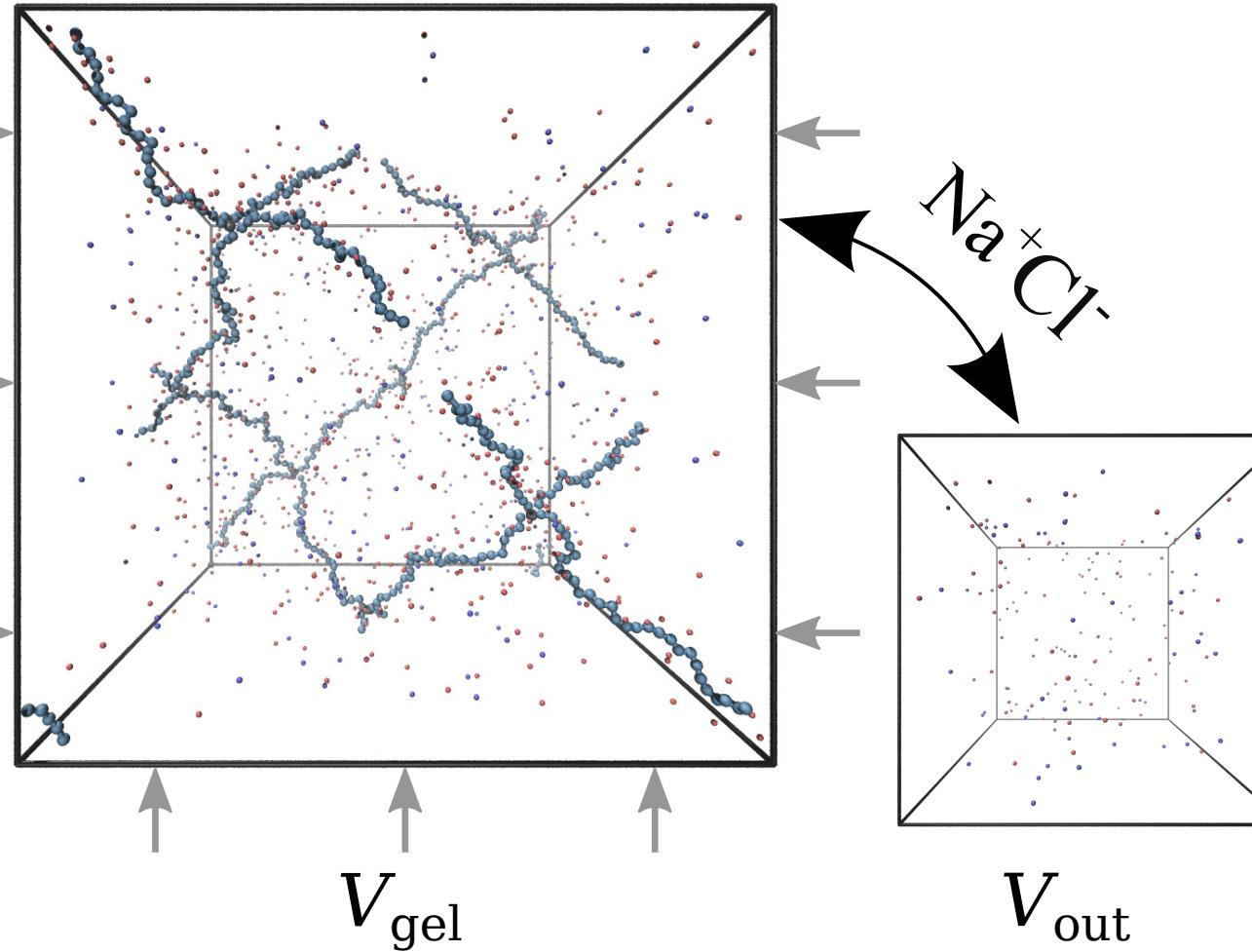
Herewith we would like to submit our manuscript: *Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modeling* authored by Mikhail Laktionov, Lucie Nová and Oleg V. Rud, to be considered for publication in *Environmental Technology & Innovation*. In the submitted manuscript we modeled hydrogel in Gibbs ensemble, *i. e.* in equilibrium with a small amount of aqueous solution, and demonstrated that the compression of the gel in such an ensemble slightly decreases the salinity of the outside solution. We employed this phenomenon and modeled the process of water desalination as a cascade of hydrogel swellings and compressions changing the outside salinity from ~ 0.1 to 0.01 mol/l .

We believe that our work brings new insights into the complex problem of seawater desalination that fits within the scope of *Environmental Technology & Innovation*, and that it will be of interest to its broad readership.

Yours sincerely,
on behalf of all co-authors,

O.V. Rud

Graphical Abstract



Highlights

1. Modelled the use of polyelectrolyte hydrogel for water desalination
2. Hydrogel compression causes changes in ionic composition of surrounding solution
3. It pumps out ion pairs from the solution of lower salinity
4. And pushes out them to the a solution of higher salinity

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Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modeling

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Abstract

Recently polyelectrolyte hydrogels have been proposed as draw agents for reverse osmosis desalination techniques. Indeed, polyelectrolyte hydrogels have the ability to absorb a big amount of water across forward osmosis membrane as a result of their swelling pressure. On the other hand, the insoluble cross-linked network of the gel enables dewatering under the influence of a stimulus (thermal and/or mechanical). Moreover, from a thermodynamic perspective, the polyelectrolyte hydrogel is already an osmotic membrane rejecting ions between external and internal solutions. These three properties of the gels make it possible to use them for desalination and at the same time avoid the use of expensive membranes. In this article, we present our recent theoretical study of the use of polyelectrolyte hydrogel for water desalination. We modeled the thermodynamic equilibrium between coexisting phases of the gel and

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4 supernate aqueous salt solution. We have shown that the salinity of the supernate
5 phase decreases during compression of the gel due to the release of absorbed in gel
6 solution of lower salinity. Finally, we performed a set of simulations modeling the
7 process of continuous decrease of solution salinity up to freshwater concentrations.
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15 Introduction

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18 **Water desalination technologies.** Two basic approaches for separating water from salt
19 are present in modern desalination technology.^{1,2}

22 The first approach is distillation, which uses heat to cause a phase change of the water
23 to vapor. The vapor phase is separated from the brine and condenses to liquid fresh water.
24 The released condensation energy is directed back to heating the feed solution. Distillation
25 processes were the first desalination techniques conducted on a large commercial scale and
26 still account for a large portion of the modern world's desalination capacity.
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33 The second approach is to physically separate the brine components using an osmotic
34 membrane transparent only for water molecules, which move in response to a water chemical
35 potential difference. In the context of our study, we will mention the reverse osmosis process
36 (RO) — the major process of all the modern desalination industry, and the newly emerging
37 membrane technology — forward osmosis (FO).³ In RO, the difference in water chemical
38 potential originates from a difference in pressures applied to the feed and to product solutions.
39 In FO, the chemical potential difference is due to an addition to solution from one side of the
40 membrane (draw solution) the so-called draw solutes, which are lowering the water chemical
41 potential in draw solution.
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52 Distillation is easy and cheap technology but it is characterized by relatively high energy
53 costs due to the dissipation of thermal energy. On the contrary, RO uses expensive osmotic
54 membranes, which need to be replaced regularly because of scaling and fouling. Moreover,
55 RO requires very high operating pressures, ranging from 20 to 200 bar, to let the water pass
56 through the membrane. But in terms of energy losses, it works close to the thermodynamic
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limit. Thus, theoretically, per one ion pair transferred from freshwater to salty water, it consumes only the energy equal to the difference between the chemical potentials of the transferred ions.

The absence of large hydraulic pressure in FO process (unlike in RO) allows to reduce the energy consumption in pumping, reduce membrane scaling and fouling, and therefore significantly increase the lifetime of the membranes. In FO, the draw solutes (agents) are dispersed and/or dissolved in water form homogeneous draw solutions. The correct choice of the draw agents is a task of paramount importance. As an osmotically driven process, the draw solute is expected to significantly reduce the water chemical potential, and consequently generate a high osmotic pressure. On the other hand, the draw solute is expected to be easily separated from water.⁴

Hydrogels for desalination. Hydrogels are three-dimensional networks of polymer chains that are crosslinked by either physical or chemical bonds. They are able to entrap large volumes of water attracted by the high concentration of hydrophilic groups. When a dehydrated or deswollen hydrogel uptakes water, its polymer chains extend, creating a swelling pressure. For example, as reported in⁵ weakly crosslinked poly(acrylic acid) (PAA) copolymers with polymer volume fractions between 0.03 and 0.30 exhibit a swelling pressure ranging from 0.20–4.23 MPa. Polyelectrolyte hydrogels, which are carrying ionic groups on the comonomer units (like PAA), are able to reject salt ions from the solution, they absorb a solution of lower salinity than that they are equilibrated with.

An important, advantageous aspect of polymer hydrogels is that they can undergo reversible volume change, *i. e.* solution — gel phase transitions in response to environmental stimuli. This aspect causes hydrogels to be labeled as ‘smart’ hydrogels. Many physical and chemical stimuli have been applied to induce various responses of such smart hydrogels, in particular, to change them from hydrophilic to hydrophobic, thereby releasing water. The physical stimuli include: temperature, solvent composition, light, mechanical pressure,

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4 sound, electric and/or magnetic field, whilst the chemical (or biochemical) stimuli include
5 pH, ionic strength, and specific molecular recognition.^{6–9}
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8 The smart properties of hydrogels were utilized for desalination in a recent study by Li
9 *et al.*,¹⁰ where hydrogels have been considered as draw agents for FO. In this study authors
10 have shown, that hydrogels, are able to absorb water across the FO membrane due to their
11 swelling and osmotic pressure and allow dewatering under the influence of stimuli (thermal
12 and/or mechanical), due to their insoluble cross-linked polymer network. For instance, Li *et*
13 *al.* proposed the use of hydrogel made of thermoresponsive polyelectrolyte — copolymer of
14 poly-N-isopropyl acrylamide (p-NIPAAm) and polyacrylic acid (p-AA). Depending on the
15 temperature the network of the gel appears to be either hydrophilic or hydrophobic. In the
16 hydrophilic state, the gel is used as a draw solute accumulating water inside, then in the
17 hydrophobic state, the water releases out.
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19 Moreover, from a thermodynamics perspective, the polyelectrolyte hydrogel itself is an
20 osmotic membrane generating Donnan potential, which rejects ions between outer and inner
21 solutions.¹¹ Such a view on hydrogels was employed in a series of works by the group of
22 prof. Wilhelm (see for example^{12,13}). The authors of these works proposed to get rid of the
23 osmotic membrane and simply use only micro filtration to compress the hydrogel squeezing
24 out the accumulated inside the gel solution. In their method first, the deswollen hydrogel
25 was equilibrated with saline water feed. During equilibration, the gel was swelling absorbing
26 water. Then it was taken out from the feed solution and mechanically squeezed by means
27 of a microfiltration membrane. The squeezed out brine was obtained to have lower salinity
28 than the feed water.
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30 A similar approach was used by Ali *et al.*¹⁴ In their study the thermosensitive gel was
31 used (based on copolymers p-NIPAAm and p-AA), so instead of physical compression, the
32 dewatering was done by an external heating stimulus (sunlight). At night the gel was equili-
33 brating with feed water and at daytime, under sunlight, the gel was shrinking and releasing
34 the collected inside solution.
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4 **Physics behind the desalination process.** Since the polyelectrolyte gel has its own
5 charges and its own neutralizing counterions, the density of mobile ions (which are able to
6 freely enter and leave the gel) in gel appears to be smaller than their density outside the gel.
7 Therefore the internal solution of the gel has a lower density of mobile ions than that in the
8 solution outside. In that sense, the gel acts as an osmotic membrane separating solutions.¹⁵
9 The driving force of the separation is the Donnan potential originated from the charges of
10 the hydrogel network. The density of mobile ions difference between ions concentrations in
11 the internal and external solutions is defined by Donnan law¹⁶
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$$\frac{c_{\text{Cl}^-}^{\text{gel}}}{c_s} = \frac{c_s}{c_{\text{Na}^+}^{\text{gel}}} = \sqrt{1 + \left(\frac{\alpha}{2c_s V_{\text{gel}}} \right)^2} \pm \frac{\alpha}{2c_s V_{\text{gel}}}$$

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27 where $c_{\text{Cl}^-}^{\text{gel}}$ and $c_{\text{Na}^+}^{\text{gel}}$ are the internal concentration of monovalent anions and cations, c_s is the
28 salinity of external solution, V_{gel} is the gel molar volume (inverse density of gel segments)
29 and α is ionization degree (in the case of our study $\alpha = 1$). The \pm sign in the formula
30 accounts for the change between the cases of gel made of polyanion or polycation.
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The lower salinity solution can be extracted from the gel by means of compression and/or
other stimulus providing that the charge of the gel remains constant. In the case of gel made
of weak (pH-sensitive) polyelectrolyte, the compression discharges the gel, therefore the
neutralizing counterions leave out the gel diminishing the desalination effect.¹⁶

44 One can argue that the sole Donnan effect is insufficient to achieve a high salt rejection⁴
45 and the salinity of the water squeezed from hydrogel under a very high hydraulic pressure
46 (up to 100 bar¹³) turns out to be not much different from the initial. Indeed, the use of high
47 hydraulic pressure diminishes all the advantages of this method over RO, and the reversibility
48 of hydrogel swelling after strong compression remains questionable. Nevertheless, in the
49 current study, we model the compression of the gel limiting ourselves to low compression
50 rates, less than 5 bar, and studied how the compression of the gel affects the surrounding
51 salinity. We modelled also the desalination process, as a cascade of following one by each
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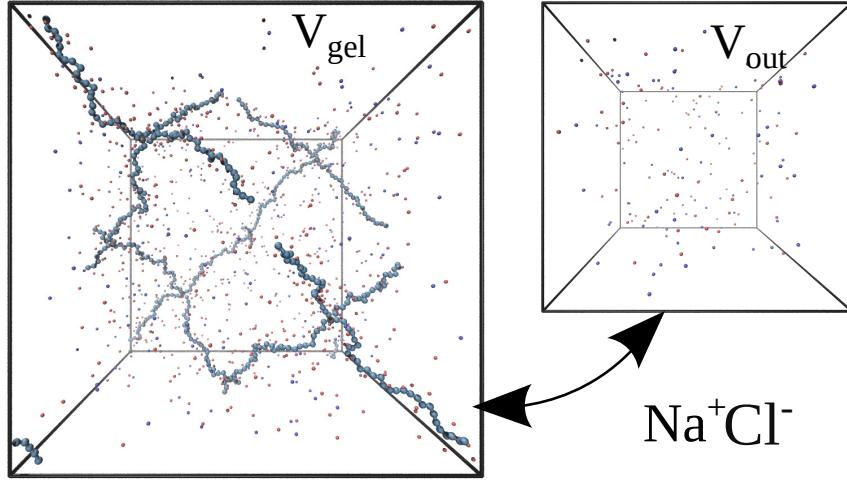


Figure 1: Diamond-like network in the simulation box. Color code represents the individual ion types (red: Na^+ , blue: Cl^- , yellow: Ca^{2+}) and the hydrogel (gray: neutral segment (AH), cyan: charged segment (A^-)).

other gel swellings and compressions driving the salinity of supernate down to drinkable water.

Theory behind the simulation

Model

We model the gel as a network of 16 linear polymer chains, each by 30 monomer units. The chains are connected to a diamond-like polymer network through 8 crosslinking units, and put into a simulation box with periodic boundaries (see Figure 1). Each unit of the network carries a negative electric charge, which is equal to the charge of electron. Except the particles of the network, the monovalent co- and counter-ions ions, Cl^- and Na^+ , are present in simulation box. The total electric charge of all the particles in the box is zero, therefore the amount of Na^+ ions is bigger than that of Cl^- by the number of hydrogel units, $N_{\text{gel}} = 16 \cdot 30 + 8 = 488$.

We simulate the compression of the gel in two ensembles.

1. The first is so called *open system*, when the simulation box with gel freely exchanges

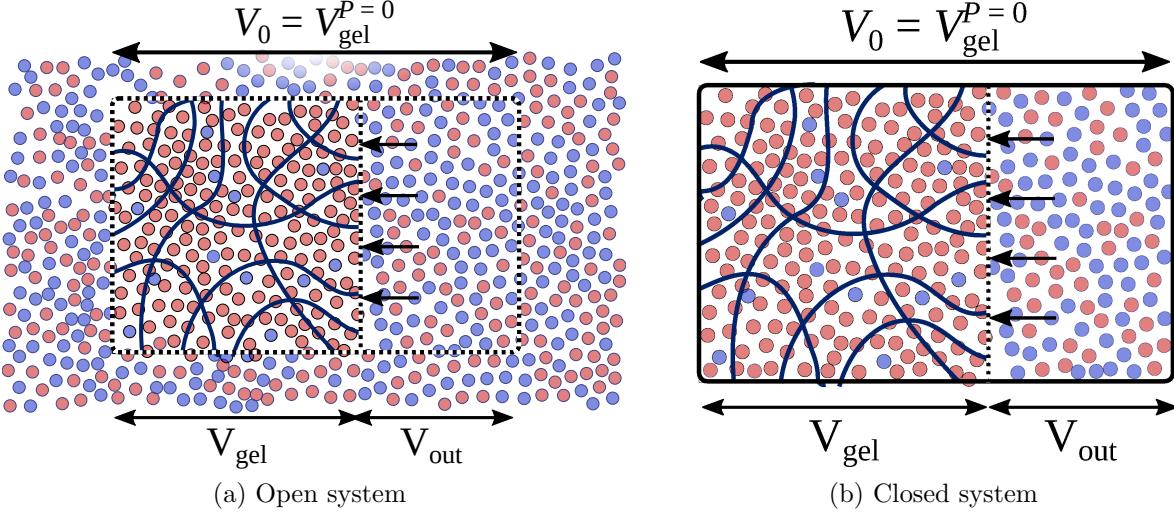


Figure 2: Diamond-like network in the simulation box. Color code represents the individual ion types (red: Na^+ , blue: Cl^- , yellow: Ca^{2+}) and the hydrogel (gray: neutral segment (AH), cyan: charged segment (A^-)). .

ions with a big amount of aqueous solution of certain constant salinity, c_s .

2. And in *closed system*, when the gel is in equilibrium with a finite volume of aqueous solution.

The compression of the gel in the *open system* does not affect the surrounding salinity, thus the density of ions outside the gel remains constant $c_s = c_{\text{Na}^+} = c_{\text{Cl}^-} = \text{Const}$ (Figure 2a). On the contrary, what remains constant in the *closed system*, is the total number of Na^+ and Cl^- ions, that are contained in the gel and in the external volume, *i. e.* in the volume V_0 (Figure 2b).

$$N_i = N_i^{\text{gel}} + c_s \cdot (V_0 - V_{\text{gel}}) \quad (1)$$

where $i \in \{\text{Na}^+, \text{Cl}^-\}$, N_i is the amount of the corresponding ions in gel, V_{gel} — volume of the gel, V_0 — the volume in which the gel is compressed. As V_0 we choose the volume of the gel in the free swelling equilibrium state.

Open system. We simulate the open system using the grand reaction method.^{15,17} This method is a hybrid of molecular dynamics (MD) and Monte Carlo (MC). The whole simulation represents a chain of subsimulations of MD and MC followed one by each other. For MD simulation we used a standard Langevin dynamics¹⁸ which models the mechanical movement of all the system particles. Whereas MC simulates the thermodynamic equilibrium with reservoir, which exchanges ions with the simulation box. The insertion (and deletion) of ion pairs is considered as a reaction of creation (or annihilation) of an ion pair



with a reaction constant defined by the chemical potential of ions, $K = \exp(\mu_{\text{Na}^+} + \mu_{\text{Cl}^-})$.

Closed system. The similar scheme we use to simulate the gel in closed system. The procedure represents a chain of subsequent MD and MC simulation, but now the molecular dynamics is running in two simulation boxes simultaneously. The first box of the volume V_{gel} contains the gel with ions, and the second box, V_{out} — contains only ions. The total volume of both boxes is kept constant, $V_0 = V_{\text{gel}} + V_{\text{out}}$, so the compression of the gel implies the decreasing V_{gel} and increasing V_{out} . These two boxes are represented in Figure 1.

Algorithm. The thermodynamic equilibrium between the two volumes implies the exchange of ion pairs between them, which is done by means of MC procedure in a way similar to described in.¹⁹ The simulation algorithm is following:

1. Simulate molecular dynamics in both boxes; collect the observables, for example, values of pressure P , to an array;
 2. Perform Monte-Carlo procedure simulating ion pair exchange; collect the arrays of observables samples: number of ions in both boxes, $N_{\text{Cl}^-}^{\text{gel}}$ and $N_{\text{Cl}^-}^{\text{out}}$;
 3. Repeat the procedure until the desired length of sample arrays is reached.

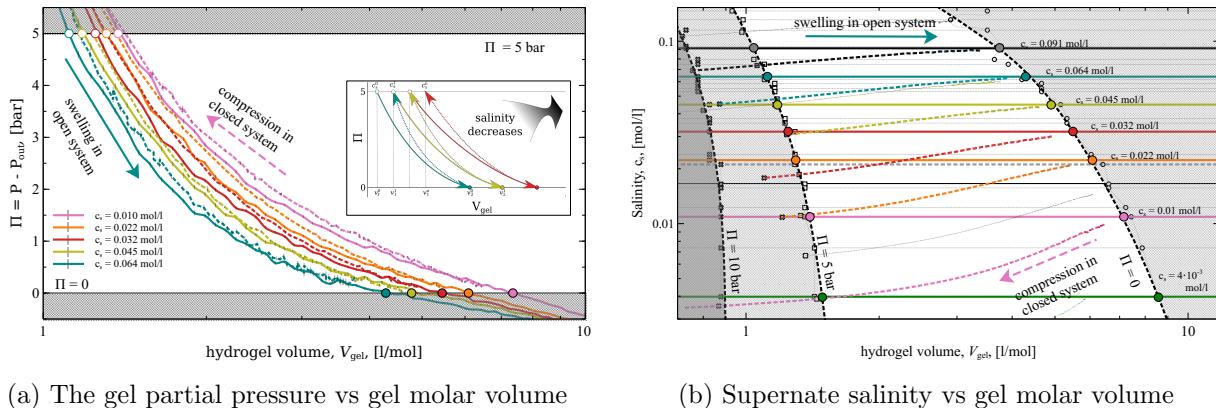


Figure 3: The compression of the gel in open system (solid lines) and in closed system (dotted lines). Each solid curve corresponds to different salinity of the reservoir c_s (see legend). Shadowed area limit the states with applied pressure below zero and above 5 bar.

Results and discussion

Compression in open system. First, we run a set of simulations modeling the gel compression in *open system*, *i. e.* in equilibrium with a big bath of certain salinity, c_s . The simulations are run for a set of different simulation box volumes. Each simulation returns the averaged pressure, P , and the number of Cl^- ions, which are present in the simulation box, n_{Cl^-} .

In order to get the partial pressure of the gel, we substitute from P the osmotic pressure of ions in the reservoir: $\Pi = P - P_{\text{out}}$. P_{out} , in turn, we calculate by running a separate simulation of a reservoir, containing ionic gas in equilibrium with the bath of the same salinity c_s . The gel partial pressure, Π , is the pressure that needs to be applied to the gel via a solvent permeable filter to compress the gel to a specific molar volume, V_{gel} . By gel molar volume V_{gel} we assume the volume of the gel calculated per mol of gel monomer units.

The dependencies of Π on V_{gel} are present in Figure 3a for a set of different salinities. These dependencies (the case of *open system*) are represented by solid lines. For example, the blue solid line illustrates the compression (or swelling) of the gel in equilibrium with a reservoir of salinity, $c_s = 0.063 \text{ mol/l}$. The points where the pressure equals zero, $\Pi = 0$, (indicated by filled circles) are the gel *free swelling equilibrium* states. These states shift

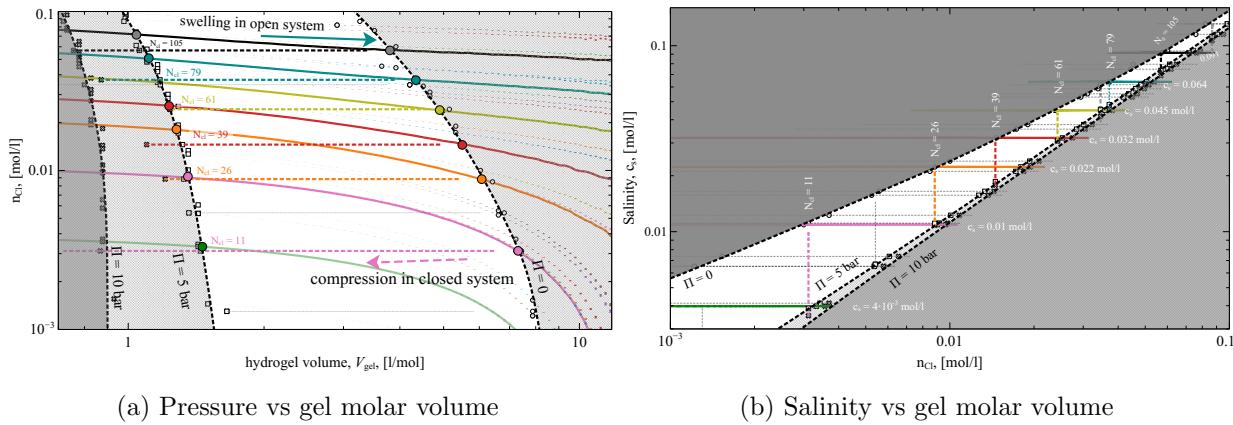


Figure 4: The compression of the gel in *open system* (solid lines) and in *closed system* (dotted lines). Shadowed area limit the states with applied pressure below zero and above 5 bar. The values N_{Cl^-} are the virtual numbers of present Cl^- ions in *closed system* simulation boxes.

towards smaller volumes with increase of salinity. In general, the increase of salinity shift all the $\Pi(V)$ curves towards smaller volumes. This effect is well known and is typical for all branched *strong* polyelectrolytes. It is caused by the decrease of ions osmotic pressure and by a screening of electrostatic interactions.^{17,20} 1

Compression in closed system. The free swelling equilibrium states are characterized by the corresponding molar volume of the gel, V_{gel}^0 and the amount of ions in gel $\{N_{\text{Na}^+}^0, N_{\text{Cl}^-}^0\}$ (Index “0” stands for zero bar applied pressure). We use these states as the starting ones for the gel compression in *closed system*. Thus, we simulate the compression of the gel in a closed volume, V_0 , which is equal to V_{gel}^0 , and contains $N_{\text{Cl}^-}^0$ of Cl^- ions and the Na^+ ions in the amount neutralizing the system, $N_{\text{Na}^+}^0 = N_{\text{Cl}^-}^0 + N_{\text{gel}}$.

We prepare two systems, one — simulating the gel of the volume V_{gel} , and another — simulating the supernatant solution of the volume $V_{\text{out}} = V_0 - V_{\text{gel}}$. Also, the ions of the amount $N_{\text{Cl}^-}^0$ and $N_{\text{Na}^+}^0$ are shared between the two volumes.

The processes of the gel compression in *closed* system are depicted in Figure 3a as dotted

¹The salinity dependence of the size of *weak* polyelectrolyte gel is in general non-monotonic. We discuss this case in.¹⁶

lines. In this plot, the blue dotted line, for example, illustrates the compression of the gel equilibrated with the solution of salinity $c_s = 0.063 \text{ mol/l}$, in a volume which gel has at zero pressure. Since, in this case, the volumes of the gel V_{gel} and of the supernate V_{out} are comparable, the compression of the gel decreases the salinity of supernate, c_s . This dependence is illustrated Figure 3b, where the same swelling/compression processes are displayed in different coordinates: *i. e.* salinity of supernate versus the gel molar volume, $c_s(V_{\text{gel}})$. In these coordinates, all the open system compressions show up as horizontal lines, which reflects the constant salinity, whereas the compressions in closed system demonstrate the change of c_s from $c_s^0 = 0.063$ at zero pressure Π to $c_s^5 = 0.045 \text{ mol/l}$ at $P^{\text{gel}} = 5 \text{ bar}$ (index “5” stands for 5 bar).

Although the salinity during compression in *open* system remains constant, the number of ions in a compression volume, *i. e.* in the volume where the gel is compressed (or swells), changes. In the Figure 4a we depicted the number of Cl^- ions in the volume V_0 , calculated per unit volume, $n_{\text{Cl}^-} = N_{\text{Cl}^-}/V_0$, as a function of the gel molar volume. The depicted value can be considered as the density of Cl^- ions averaged out over the compression volume V_0 .

As expected in the case of closed system compression these dependencies look like horizontal lines, whereas in an open system, the amount of ions in compression volume increases with compression. This implies, that the compression of the gel in the open system pulls out the ions from the bath to the compression volume, V_0 . And vice versa, the swelling of the gel pushes ions out to the bath.

Finally, in Figure 4b the same processes are depicted in coordinates $n_{\text{Cl}^-} — c_s$. In these coordinates, both ways of the compression, in *open* and in *closed* system, appear as straight vertical and horizontal lines correspondingly.

In our study, we modeled the compression of the gel in equilibrium with reservoirs of 40 different salinities, ranging from 0.001 to 0.5 mol/l. Every open system compression resulted in a defined free swelling equilibrium state, which we used as the initial ones for the compression in closed systems. All the corresponding dependencies are depicted in Figures 3

and 4 as thin grey dashed lines (some of them are highlighted and colored). The states corresponding to $P^{gel} = 0$, 5 and 10 bar pressure are marked by open circles, squares, and crosses respectively. The non-shadowed areas in the Figures highlight the states in which the gel partial pressure ranges between 0 and 5 bar.

Desalination scheme. As we have seen, the compression of the gel in a closed system affects the salinity, whereas the compression in an open system affects the amount of ions in a volume where the gel is compressed in. Here we show how to employ these phenomena for water desalination. The highlighted colored lines on plots of Figures 3 and 4 form a sequence of the following one by each other swellings and compressions of the hydrogel, correspondingly in *open* and *closed* systems. This sequence forms the water desalination process. Starting from swelling the gel in the *open* system at high salinity ($c_s = 0.091 \text{ mol/l}$, solid black line), the gel gets compressed in *closed* system until the pressure reaches 5 bar (dashed black line). Then the same gel swells in a reservoir of a bit lower salinity (*i. e.* $c_s = 0.064 \text{ mol/l}$, light blue line). After swelling, the gel is compressed again by the pressure of 5 bar in *closed* system (dashed light blue line). Then the gel is put swelling in a reservoir of even smaller salinity ($c_s = 0.045 \text{ mol/l}$, solid yellow line). And so on. The chain of alternating swelling and compression steps ends up when salinity gets equal to $c_s = 4 \cdot 10^{-3} \text{ mol/l}$ after compression in closed system (dashed magenta line).

The plots of Figures 3 and 4 depict the whole process in all the possible coordinates In all the plots the whole process looks like a staircase, especially in the Figure 4b, where open system processes are horizontal lines and closed system are vertical ones, a 'staircase' has rectangular steps

The efficiency of desalination. The theoretical minimum specific energy for seawater desalination ($c_s \simeq 0.6 \text{ mol/l}$ as for pure NaCl) is $\sim 3.9 \text{ kJ/l}$ (1.1 kWh/m^3) for 50% recovery.²¹

This value is calculated as follows

$$W = 2RT \left(\frac{c_f}{R_w} \ln \frac{c_b}{c_f} - c_p \ln \frac{c_b}{c_p} \right) \quad (2)$$

where R is a universal gas constant, c_f is the salinity of feed water, c_p — of product water and c_b — the salinity of the brine, which necessarily appears in any desalination process. R_w is a recovery ratio, *i. e.* the ratio between volume of produced water and the volume of the feed water. 50% recovery ratio means that one part of feed water divides into two equal volume solutions of the product water and of the brine. Of course, a significant amount of additional energy is required to operate the system.²² It has been reported that the specific energy consumption (SEC) of reverse osmosis (RO) process is 2.5 – 4.0 kWh/m³ (9 – 14.4 kJ/l), which is significantly higher than its minimum specific energy. The SEC of a real-scale RO plant is even higher, approximately 3.5 – 4.5 kWh/m³ (12.6 - 16.2 kJ/L), including pre-treatment and post-treatment processes.²³

In order to compare the efficiency of the process presented in 3 and 4 with provided values, we collect the corresponding data to the Table 1. The presented desalination process is a cascade of six swellings in open system, at six different (constant) salinities c_s , each followed by six compressions in closed system, at six different (constant) n_{Cl^-} . Each swelling and compression process is presented as a row of Table 1, which is colored by matching the lines in the Figures. The first column of the table contains values c_s^0 and c_s^5 , which stand for the supernate salinity at 0 and 5 bar compression; in open system, supernate salinity does not change, so c_s^0 and c_s^5 are presented by a single number. The second column contains values of n^0 and n^5 , which stand for the number of Cl^- ions in compression volume V_0 , at 0 and 5 bar pressure (divided by V_0). The number of ion does not change in closed system compression, thus n^0 and n^5 are the same in the corresponding rows. The third column shows the change of the gel volume in corresponding process, Δv . The fourth column contain the work needed for the compression in the corresponding process, calculated per volume of

extracted solution. This value is an integral of corresponding $\Pi(V_{\text{gel}})$ dependence

$$W = \frac{\int_{v^0}^{v^5} \Pi dV_{\text{gel}}}{\Delta v} \quad (3)$$

Here, in the table, we present the absolute values of the work, whereas one should keep in mind that the compression implies the work is done by external force and the swelling implies that the work is done by gel.

Table 1: The estimates of the efficiency of the desalination process. All the units are calculated per one mol of gel segments. Values in brackets are the estimates corresponding to crossection of 'red' and 'orange' lines on the plots of Figures 3 and 4

c_s^0 , mM	c_s^5 , mM	$n_{\text{Cl}^-}^0$, mM	$n_{\text{Cl}^-}^5$, mM	ΔV_{gel} , l	$ W $, J/l	W^{id} , J/l
91.47		$57.08 \pm 0.122 \rightarrow 71.75 \pm 0.024$		2.74	95.4 ± 1.9	
$89.41 \pm 0.23 \rightarrow 73.63 \pm 0.03$		56.90		2.72	109.1 ± 1.7	
63.93		$37.28 \pm 0.08 \rightarrow 50.579 \pm 0.013$		3.26	100.9 ± 1.7	
$62.05 \pm 0.15 \rightarrow 48.21 \pm 0.02$		37.17		3.18	107.4 ± 1.4	
44.91		$23.75 \pm 0.06 \rightarrow 35.911 \pm 0.010$		3.82	106.7 ± 1.5	
$43.46 \pm 0.12 \rightarrow 30.795 \pm 0.008$		24.27		3.91	106.4 ± 1.1	
31.93		$14.66 \pm 0.04 \rightarrow 25.297 \pm 0.006$		4.20	107.9 ± 1.4	
$30.03 \pm 0.08 \rightarrow 18.585 \pm 0.004$ (22.32)		14.55		4.17 (3.22)	115.6 ± 0.9 (57.3)	
22.30		$8.84 \pm 0.03 \rightarrow 17.945 \pm 0.004$ (14.56)		4.75 (3.76)	108.1 ± 1.3 (68.3)	
$20.74 \pm 0.06 \rightarrow 11.082 \pm 0.002$		8.83		4.71	110.8 ± 0.8	
10.90		$3.00 \pm 0.01 \rightarrow 9.011 \pm 0.002$		6.08	106.9 ± 1.1	
$9.83 \pm 0.05 \rightarrow 3.862 \pm 0.001$		3.12		5.78	119.4 ± 1.0	

To give a clue of comparison with ideal desalination process efficiency, in the fifth column

we provided the values of specific energy consumption, W^{id} , which are calculated by means of Equation 2 as follows. We consider, for example, the solution of concentration $c_s^f = 44.91$ mmol/l as a feed solution, and the solutions of $c_s^p = 31.93$ mmol/l and $c_s^b = 63.93$ mmol/l correspondingly as produced product and brine solutions.

1. first, the gel, equilibrated with feed solution, is getting compressed in a closed system.

The volume of the gel changes by $\Delta v^p = 3.69$ l and the salinity of supernate decreases from c_s^f to c_s^p . The volume of product solution equals Δv^p

2. Then the squeezed gel is put back into the feed solution and is getting equilibrated there under pressure, so it does not swell.

3. After equilibration the gel is let to swell in a closed system such that the salinity of the external solution increases reaching the value of c_s^b .

4. Finally, the gel is taken out and squeezed by 5 bar in an open system in equilibrium with the bath of the brine. The change of the gel volume in this process is $\Delta v^b = 3.26$ l/mol, which equals the volume of the produced brine.

Thus the recovery ratio $R_w = \Delta v^p / (\Delta v^p + \Delta v^b) \simeq 0.53$ and the theoretical minimum specific energy of desalination with corresponding c_s^f , c_s^p and c_s^b is $W^{\text{id}} = 38.2$ J/l (Equation 2).

Such estimations are provided in the fifth column of the table, for five triplets of values c_s^f , c_s^p , and c_s^b . W_{sim} is the energy calculated by integration of $\Pi(V_{\text{gel}})$ dependencies — sum of corresponding compressions in closed and open systems, W_{id} — the estimate based on the equation Equation 2 and R_w — is the corresponding recovery ratio. Note that calculating the W_{sim} we accounted for only the work done on the gel during compression, whereas the work done by the gel itself during swelling was not taken into account. The ratio between W_{sim} and W_{id} ranges from 3.26 to 5.43, which is comparable to that of RO.

Conclusions

We have modeled the compression of the gel in thermodynamic equilibrium with the reservoir of the limited amount of water. We have shown that in the case of gel made of strong polyelectrolyte, the compression always decreases the surrounding salinity. We have modeled the process of water desalination by combining two processes: (1) the swelling of the gel in *open* system, exchanging ions with a big reservoir at constant salinity. (2) the compression of the gel in *closed* system, when the gel affects the salinity in the surrounding solution. We estimated the energy needed to produce one liter of water and have shown that the method may compete with the modern technologies used in modern industry.

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