

Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modeling

RUD O., LAKTIONOV M., NOVÁ I.

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Czech Republic

*corresponding author:

e-mail: oleg.rud@natur.cuni.cz

Abstract. Polyelectrolyte hydrogels possess the remarkable ability to efficiently absorb large volumes of water through an osmotic membrane by exerting swelling pressure. Conversely, the insoluble cross-linked structure of the gel allows for dewatering when triggered by external stimuli such as temperature or mechanical forces. Moreover, from a thermodynamic perspective, polyelectrolyte hydrogels act as osmotic membranes, effectively preventing the passage of ions between external and internal solutions. These unique properties make these gels highly promising for desalination applications, offering an alternative to expensive membranes. In this study, we present our recent investigation into the utilization of polyelectrolyte hydrogels for water desalination. We developed a model to analyze the thermodynamic equilibrium between the gel and the supernatant aqueous salt solution. Our findings demonstrate that as the gel undergoes compression, the salinity of the supernatant phase decreases due to the release of absorbed solution with lower salinity from within the gel matrix. Furthermore, we conducted a series of simulations to replicate the continuous reduction of solution salinity until freshwater concentrations were achieved.

Keywords: polyelectrolyte hydrogel; simulation; desalination

1. Introduction

Hydrogels are intricate networks of polymer chains, connected either through physical or chemical bonds, that have the remarkable ability to retain substantial amounts of water due to the presence of hydrophilic groups. When a dehydrated or shrunken hydrogel absorbs water, its polymer chains elongate, resulting in the generation of swelling pressure. For instance, in a study by Wack et al. [Wack2009], it was observed that weakly crosslinked poly(acrylic acid) (PAA) copolymers, with polymer volume fractions ranging from 0.03 to 0.30, exhibited swelling pressures varying from 0.20 to 4.23 MPa. Polyelectrolyte hydrogels, which contain ionic groups within their comonomer units (similar to PAA), possess the capability to repel salt ions from the solution and can absorb a solution with lower salinity compared to their initial equilibrium state.

From a thermodynamic standpoint, the polyelectrolyte hydrogel itself acts as an osmotic membrane, creating a Donnan potential that prohibits the movement of ions between external and internal solutions. This perspective on hydrogels has been extensively explored by Prof. Wilhelm's research group, as evidenced in the following publications [Arens2017, Fengler2020]. These studies propose the elimination of the osmotic membrane, opting instead for microfiltration to compress the hydrogel and expel the accumulated solution residing within its matrix. The methodology involves equilibrating the shrunken hydrogel with saline water during which it swells and absorbs water. Subsequently, the gel is removed from the feed solution and mechanically compressed using a microfiltration membrane. The expelled brine demonstrates lower salinity than the original feed water.

In the current study, we focus on modeling the compression of the hydrogel, primarily considering low compression rates below 5 bar, and investigating the impact of gel compression on the surrounding salinity. Additionally, we model the desalination process as a sequence of successive gel swellings and compressions, aiming to progressively reduce the salinity of the supernatant until it reaches a potable water level.

2. Our hydrogel model

In our model, we represent the hydrogel as a network consisting of 16 linear polymer chains, each comprising 30 monomer units. These chains are interconnected within a diamond-like polymer network structure through 8 crosslinking units. To facilitate simulations, we enclose the hydrogel within a simulation box with periodic boundaries, ensuring a continuous and consistent environment. Within the system, every unit of the polymer network carries a negative electric charge, precisely equivalent to the charge of an electron. Additionally, apart from the network particles, the simulation box contains monovalent co-ions (Cl^-) and counter-ions (Na^+). The combined electric charge of all particles in the box is neutral, meaning the number of Na^+ ions exceeds the number of Cl^- ions by the count of hydrogel units, which is calculated as $N_{\text{gel}} = 16 \cdot 30 + 8 = 488$.

In our simulations, we investigate the compression of the gel in two distinct ensembles:

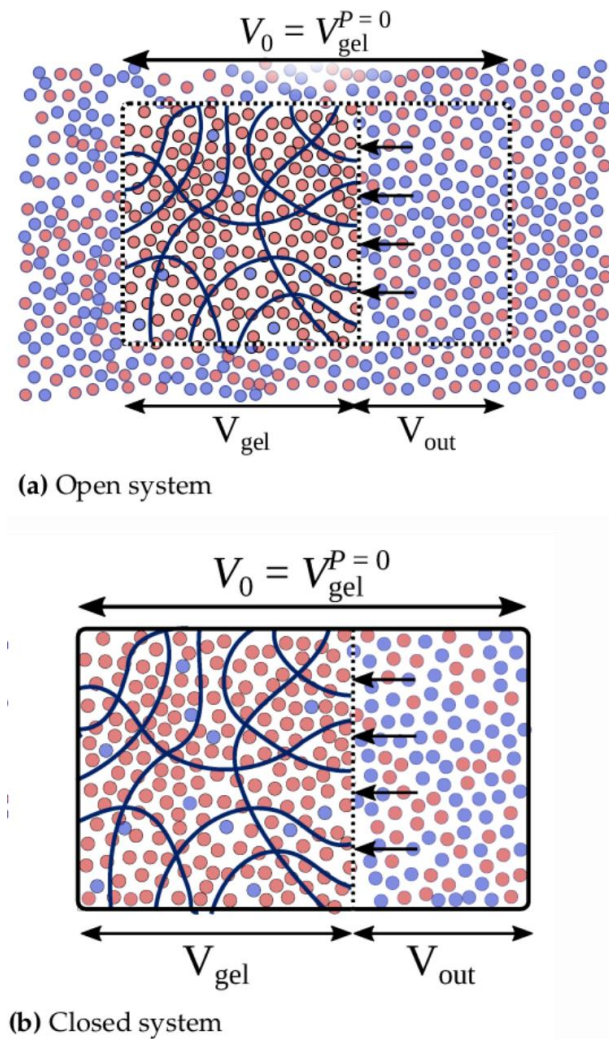


Figure 1. The hydrogel compressed in open and in closed system. Red and blue circles represent Na^+ and Cl^- ions. V_0 is the volume which gel has in free swelling equilibrium state.

1. The first ensemble is referred to as an "open system." In this setup, the simulation box containing the gel has the freedom to exchange ions with a substantial quantity of aqueous solution with a fixed and constant salinity referred to as c_s . As the gel undergoes compression, the surrounding salinity, represented by the density of ions outside the gel, remains unaffected and remains constant throughout the compression process (illustrated in Figure 1a). Therefore, the concentrations of Na^+ and Cl^- ions, denoted as c_{Na} and c_{Cl} , respectively, maintain a constant value equal to c_s .
2. The second ensemble is "closed system." Here, the gel is in equilibrium with a finite volume of aqueous solution. In this scenario, what remains constant is the total number of Na^+ and Cl^- ions present in both the gel and the external volume. This indicates that the sum of ions within the gel and the external volume, denoted as V_0 (as shown in Figure 1b), remains unchanged as the gel undergoes compression.

3. Desalination Scheme

In our study, we conducted simulations to model the compression of a polyelectrolyte gel in thermodynamic equilibrium with a limited amount of supernatant aqueous solution. Our findings revealed that as the gel undergoes compression, the salinity of the supernatant decreases. Exploiting this phenomenon, we devised a model for water desalination. The desalination was done as a sequential combination of two processes: (1) swelling of the gel in an open system, exchanging ions with a large reservoir at constant salinity; (2) compression of the gel in a closed system, during which the gel exchanges ions with a small reservoir, affecting its salinity.

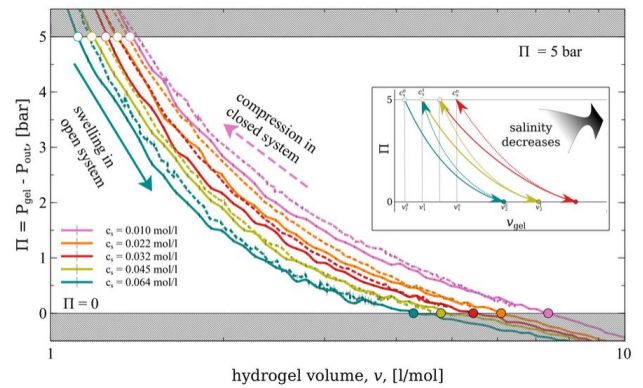


Figure 2. The gel partial pressure vs gel molar volume

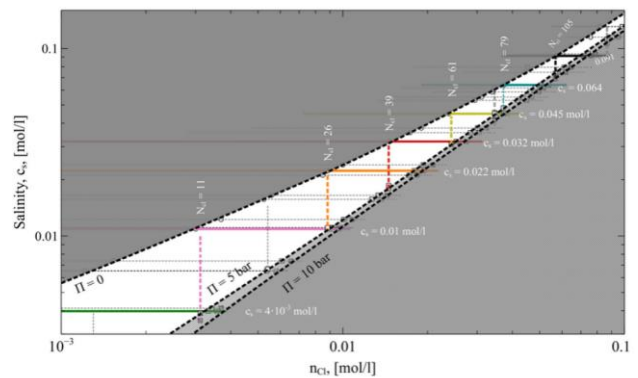


Figure 2. Supernate salinity versus the gel molar volume.

Figures 2 and 3 visually depict the desalination process using different coordinates. The highlighted colored lines on the plots within these figures represent a sequence of gel swellings and compressions. These processes occur successively, alternating between open and closed systems. In Figure 3, the depiction resembles a staircase, where the horizontal lines correspond to the open system processes, and the vertical lines represent the closed system processes.

The desalination process begins with the swelling of the gel in the open system, starting from a high salinity ($c_s =$

0.091 mol/L) represented by the solid black line. As the gel swells, it exchanges ions with a reservoir containing the same high salinity. Once the gel reaches its maximum swelling, it is then compressed in the closed system until the pressure reaches 5 bar, indicated by the dashed black line. Following this compression, the gel undergoes another swelling process in the open system. However, this time it swells in a reservoir with slightly lower salinity ($c_s = 0.064$ mol/L), depicted by the light blue line. Once again, after maximum swelling is achieved, the gel is compressed with 5 bar pressure in the closed system, represented by the dashed light blue line. This alternating pattern of swelling in the open system and compression in the closed system continues. The gel swells in reservoirs with progressively lower salinities: first in a reservoir with $c_s = 0.045$ mol/L (solid yellow line), then in a reservoir with even lower salinity, and so on. This sequential chain of alternating swellings and compressions continues until the salinity is reduced to $c_s = 4 \cdot 10^{-3}$ mol/L after the final compression in the closed system, indicated by the dashed magenta line. At this stage, the desalination process is completed, and the gel has achieved the desired low salinity level.

References

Wack, H.; Ulbricht, M. (2009) Effect of synthesis composition on the swelling pressure of polymeric hydrogels. *Polymer* **50**, 2075–2080.

Arens, L.; Albrecht, J.B.; Höpfner, J.; Schlag, K.; Habicht, A.; Seiffert, S.; Wilhelm, M. (2017) Energy Consumption for the Desalination of Salt Water Using Polyelectrolyte Hydrogels as the Separation Agent. *Macromol. Chem. Phys.* **218**, 1700237.

Fengler, C.; Arens, L.; Horn, H.; Wilhelm, M. (2020) Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation. *Macromol. Mater. Eng.* **305**, 2000383.