

# Thermodynamic model for a reversible desalination cycle using polyelectrolyte hydrogels

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## Abstract

We propose a novel desalination scheme which employs the hydrogels as a tool to draw salt ions from a brine with low salinity to a brine with high salinity. As a driving force we use the fact that the volume of polyelectrolyte gel does depend on the surrounding salinity. While the salinity defines the gel volume in open system, i.e. in equilibrium with big aqueous solution bath, in closed system (in equilibrium with small bath) salinity is defined by the gel volume. The compression and swelling in open and closed system processes are combined into four stages thermodynamic cycle working between two bathes of different salinities. The cycle implies reversibility at any stage, so, in principle, the method can achieve the maximum thermodynamic efficiency. We have shown that for weak polyelectrolyte gels the dependence between the salinity and gel volume appears to be non-monotonic. Depending on the model parameters the surrounding salinity may increase or decrease during compression. In both cases we consider the possible use of this relation in desalination cycle.

**Keywords:** *desalination, polyelectrolytes, hydrogels, forward osmosis*

## 1. Introduction

Polyelectrolyte hydrogels are the typical examples of “smart” polymer systems, which are able to change drastically their macroscopic properties by means of relatively small changes in their environment. For example, by changing the solution salinity and/or pH one may control swelling ratio of a hydrogel. Therefore there are many promising applications for the use of gels as mechanical actuators and sensors, reflecting on certain stimulus [Hersey2015].

Being immersed in aqueous solution gel forms a two-phase system, which consists of the swollen gel and of the surrounding solution. The properties of both phases are determined by thermodynamic equilibrium, so that the changes in solution phase affect the gel phase and vice versa. For example the outside solution salinity affects the volume of the gel phase as well as the gel internal ionic composition. The increase of outside solution

salinity may lead to 100% gel volume changes [Rud2017, Kosovan2015]. This phenomenon has been extensively studied in the context of stimuli-responsive materials, of design of gel based sensors and actuators as well as of the use of hydrogels to extract the energy stored in salinity gradient of river estuaries.

There are almost no studies addressing the reverse problem. Namely, how by compression of the gel to induce the gradients of salt concentration? Indeed, if the volume of the solution phase is comparable with the volume of the gel, than the phase equilibrium requires that changes of the gel volume affect the surrounding solution. For example, the compression of the gel made of strong polyelectrolyte decreases the outer solution salinity, that is *desalinate* the solution [Rud2017, Kosovan2015].

Recently, an alternative desalination method using polyelectrolyte hydrogels has been proposed [Arens2017, Yu2016]. The key idea of the method is that the salt concentration inside a polyelectrolyte hydrogel is lower than outside due to the Donnan partitioning of ions [Rud2017]. In the experiment gel particles were swollen and equilibrated in the solution of NaCl, and then compressed to squeeze out water with lower salt concentration.

## 2. Materials and Methods.

Being based on analytical mean-field theory of pH-sensitive polyelectrolyte hydrogel, and on the results of coarse-grained Monte-Carlo simulations we proposed the water desalination thermodynamic cycle similar to the Carnot cycle of reversed heat engine. Similarly to the Carnot cycle, the proposed one consists of alternating hydrogel compression and swelling steps in open and closed systems (see figures). While Carnot cycle transfers heat, the ours one transfers salt ions from the reservoir with low salinity solution to the reservoir with high salinity.

### 3. Results and Discussions.

The cycle presented on figures uses the feature of the strong polyelectrolyte hydrogel to decrease the surrounding salinity while compression. It consists of four steps resulting in,

1. uptaking the ions from the low salinity bath,
2. increasing the salinity of the brine surrounding the gel,
3. releasing the ions to high salinity bath and
4. decreasing the salinity of the brine back to the initial one.

Compression of *strong* polyelectrolyte gel always lead to decrease of the surrounding brine salinity, the compression of weak polyelectrolyte hydrogel affects its ionisation, which in turn, may lead to the release of ionic species form the gel. This may result in opposite effect, namely, in increase of outer salinity while cmpression .

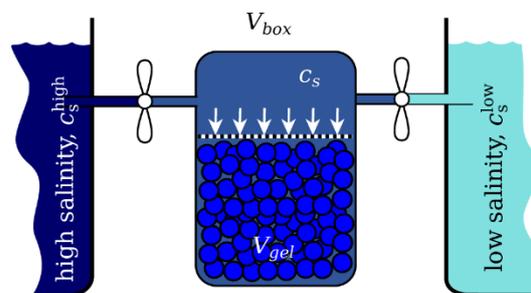
We proposed as well an alternative cycle for weak polyelectrolyte hydrogel by swapping the roles of compression and swelling steps. The designed cycles are fully reversible, so that these can in principle work gaining maximum thermodynamic efficiency.

### 4. Conclusions

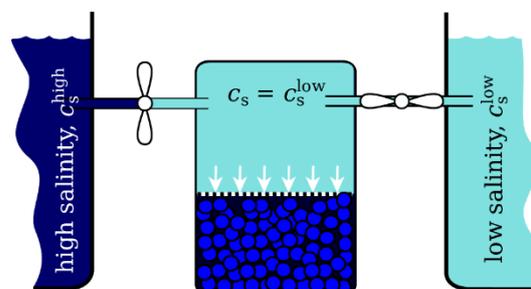
We modelled a fully reversible desalination cycles exploiting weak and strong polyelectrolyte hydrogels. We designed the cycles in analogy with the Carnot cycle of heat engine such that they transfer ions from a low salinity solution to a high salinity one. The change of salinity upon compression is exploited for desalination. The reversibility of cycles allows them to be as effective as the modern technologies based on reverse osmosis effect. In the same time the compression of hydrogel does not require the use of expensive osmotic membranes, which allows the proposed technique to be competitive with the reverse osmosis systems.

### References

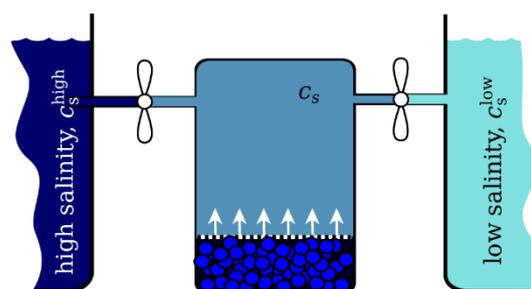
- Hersey, J. S., Meller, A., & Grinstaff, M. W. (2015). *Analytical Chemistry*, **87**(23), 11863–11870. [link](#)
- Rud, O., Richter, T., Borisov, O., Holm, C., & Košov, P. (2017). *Soft Matter*, **13**(18), 3264–3274. [link](#)
- Košovan, P., Richter, T., & Holm, C. (2015). *Macromolecules*, **48**(20), 7698–7708. [link](#)
- Subramani, A., & Jacangelo, J. G. (2015). *Water Research*, **75**, 164–187. [link](#)
- Arens, L., Albrecht, J. B., Höpfner, J., Schlag, K., Habicht, A., Seiffert, S., & Wilhelm, M. (2017). *Macromolecular Chemistry and Physics*, **218**(24), 1700237. [link](#)
- Yu, C., Wang, Y., Lang, X., & Fan, S. (2016). *Environmental Science & Technology*, **50**(23), 13024–13031. [link](#)



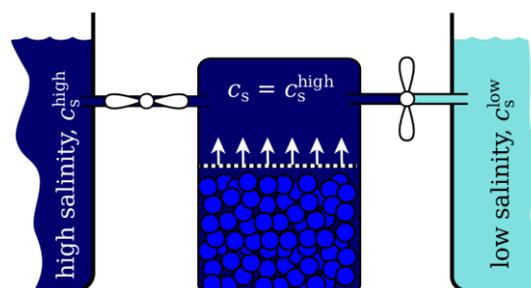
**Step 1:** Compression of the gel in a closed system starts at  $c_s = c_s^{\text{high}}$  and continues until  $c_s = c_s^{\text{low}}$



**Step 2:** Compression in an open system at  $c_s = c_s^{\text{low}}$  continues up to certain pressure  $p = p_{\text{end}}$ . In this steps ions are transferred from the right vessel to the box.



**Step 3:** Swelling in a closed system starts at  $p = p_{\text{end}}$  and ends when  $c_s = c_s^{\text{high}}$ .



**Step 4:** Swelling in an open system at  $c_s = c_s^{\text{high}}$  continues until pressure becomes equal to the initial one,  $p = p_{\text{ini}}$ . In this steps ions are transferred from the box into the left vessel.