Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modelling and experiment

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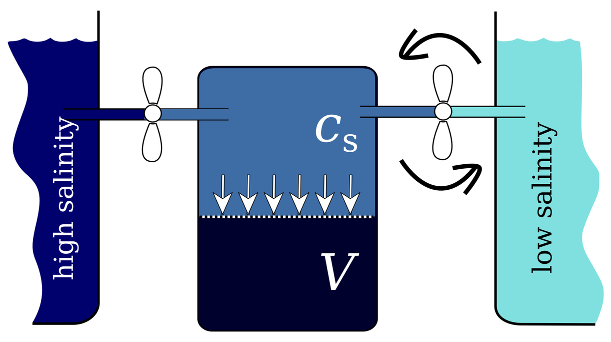
Polyelectrolyte hydrogels have the ability to absorb a big amount of water across forward osmosis membrane as a result of their swelling pressure. The insoluble cross-linked network of the gel enables dewatering under the influence of stimuli (thermal and/or mechanical). On the other hand, the network structure of a polymer hydrogel, from a thermodynamic perspective, is already an osmotic membrane. So hydrogel microparticles may allow to completely avoid the osmotic membranes in forward osmosis and use microfiltration instead. Here we present our recent study of the use of polyelectrolyte hydrogel for water desalination. We modeled the thermodynamic equilibrium of coexistence of the gel and the aqueous salt solution in the so-called closed ensemble, in which the total amount of ions is assumed to be constant. We modeled the compression of the gel and the associated with that release of the solution. We have shown that the squeezed out solution has a little lower salinity than that the gel was equilibrated with. Also, we performed a set of simulations modeling the process of continuous decrease of water salinity up to freshwater concentrations.

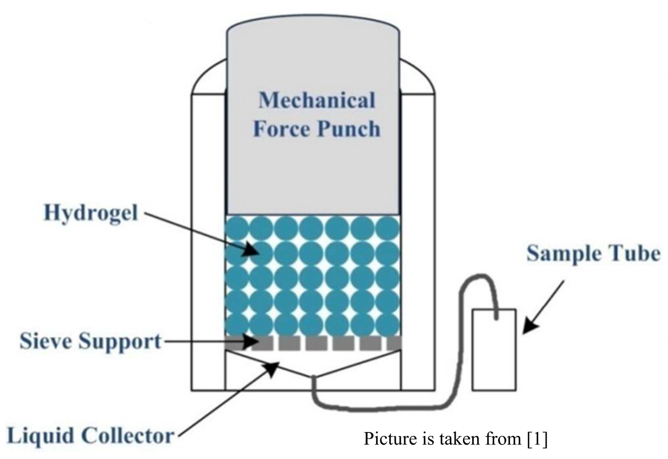
1. Hydrogels for desalination

1.1 Reverse osmosis



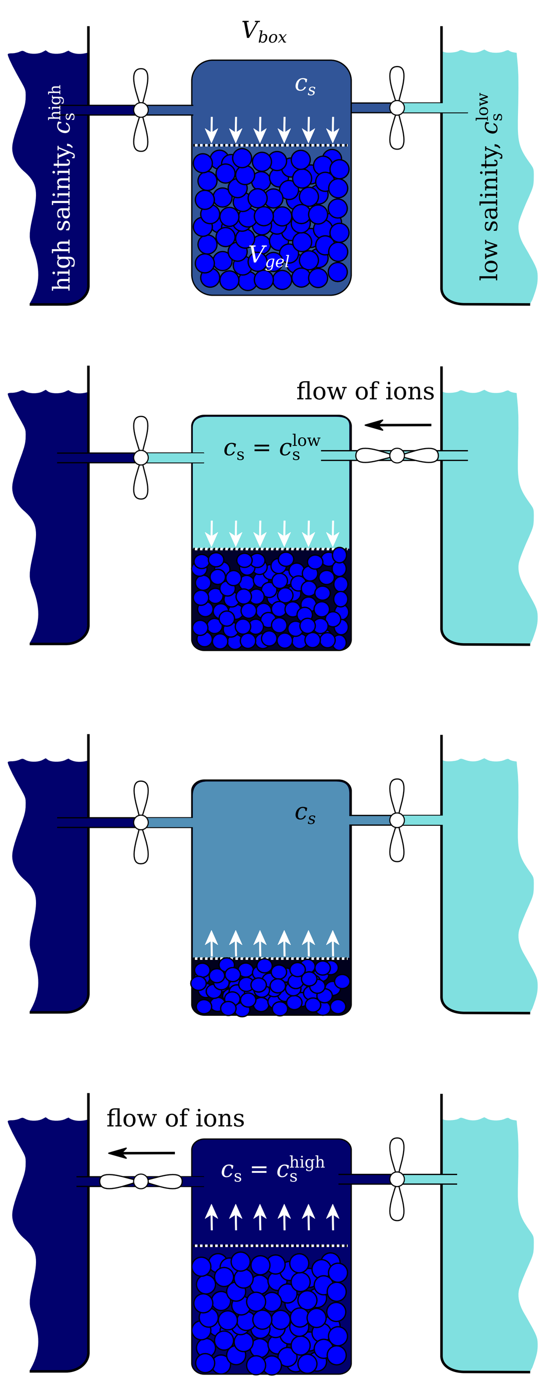
- Fully reversible, therefore works in ideal thermodynamic efficiency
- Membrane is expensive and sensitive to quality of feed water

1.2 The use of polyelectrolyte hydrogels

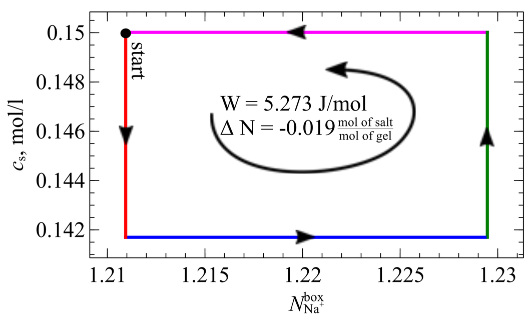


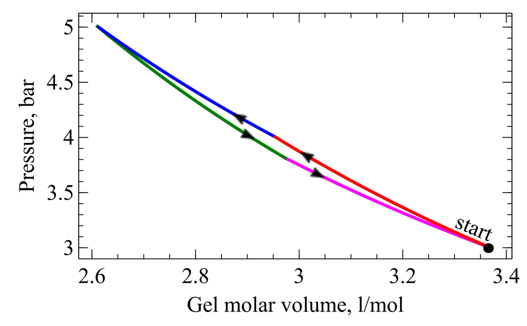
- The idea [1, 2] is
  1. let the gel swell in salt solution
  2. squeeze the gel and collect the excluded brine
  3. repeat
- The approach is free from the use o osmotic membraine
- But contains an irreversible process

1.3 Reversible (Carnot) desalination cycle



- A a fully reversible desalination cycle using polyelectrolyte hydrogels [3].
- The cycle is based on the analogy with the Carnot cycle for reversed heat engine



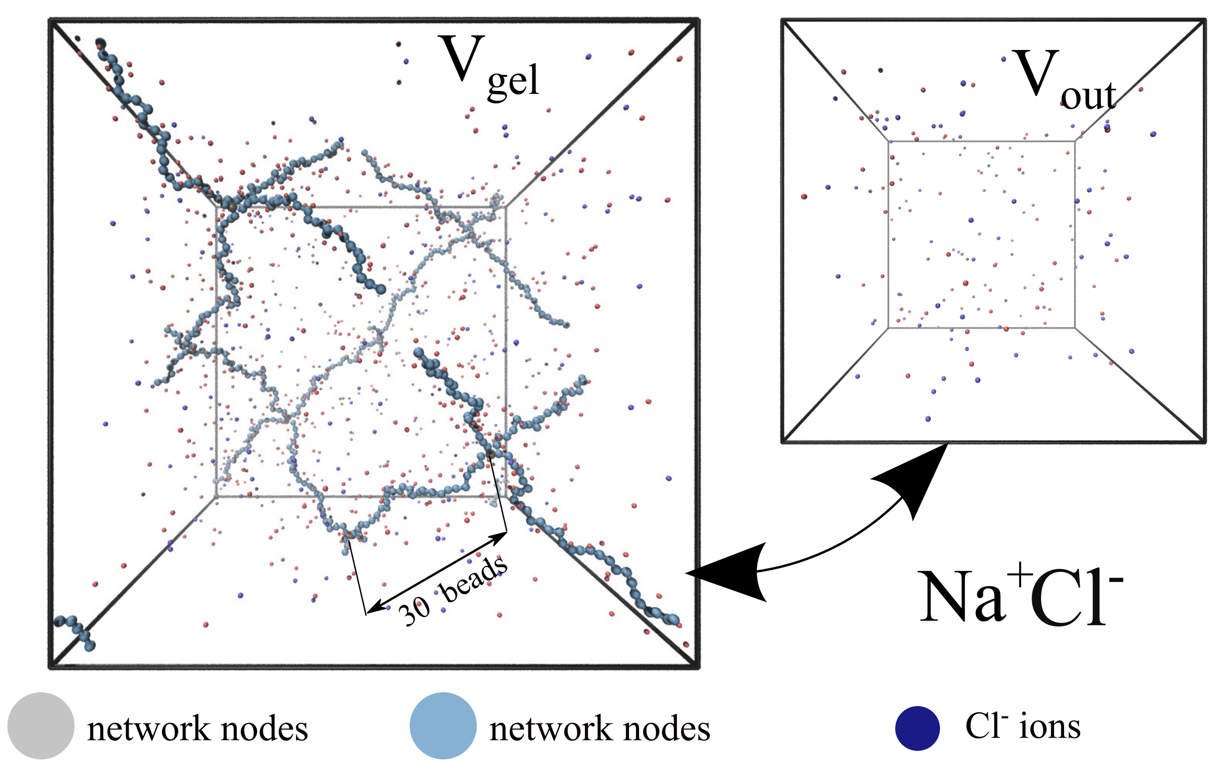


[1] Yu, C., et al. (2016). http://doi.org/10.1021/acs.est.6b03193
[2] Arens, et al. (2017). http://doi.org/10.1002/macp.201700237
[3] Rud, et al. (2018). http://doi.org/10.1016/j.desal.2018.05.002

2. The model of the gel

2.1 Diamond network

The model is a polyelectrolyte chains connected to a diamond lattice cell in periodic boundary conditions



N^{gel} = 16 chains × 30 beads + 8 nodes

2.2 Molecular dynamics (MD) simulation

- All the particles interact via Lennard-Jones potential

$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \epsilon = k_BT,\ \sigma = 0.35\text{nm}.$$

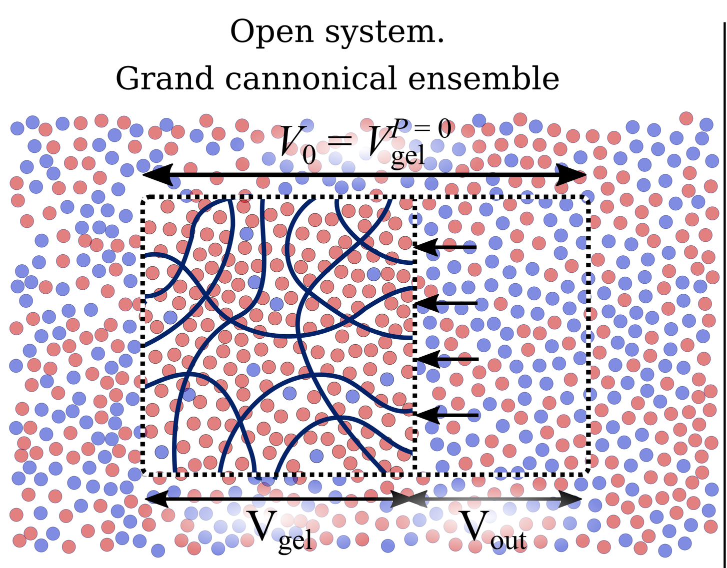
- The beads of gel network interact via FENE (finite extension nonlinear elastic) potential

$$V_{FENE}(r) = -\frac{1}{2}K\Delta r_{max}^2 \ln\left[1 - \left(\frac{r - r_0}{\Delta r_{max}}\right)^2\right] \qquad K = 10\epsilon,\ \Delta r_{max} = 2\sigma,\ r_0 = 0$$

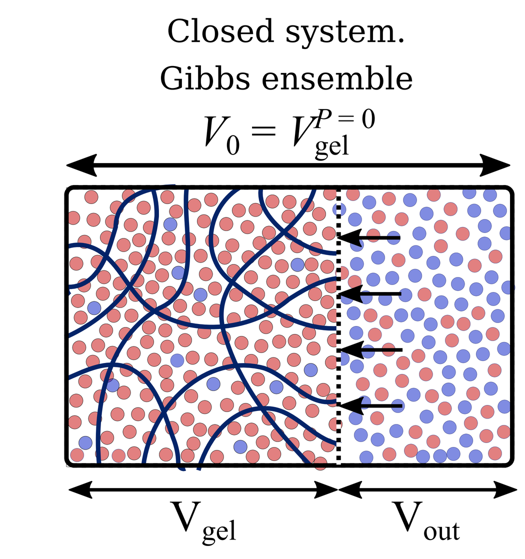
- The electrically charged species interact via Coulomb potential.

$$V_{EL} = l_B k_B T \cdot \frac{q_1 q_2}{r} \qquad l_B = 2\sigma \text{ --- is Bjerrum length, } q_1, q_2 = e$$

2.3 Monte Carlo (MC) sampling



μ_{Na} = Const μ_{Cl} = Const



N_{Na} = Const N_{Cl} = Const

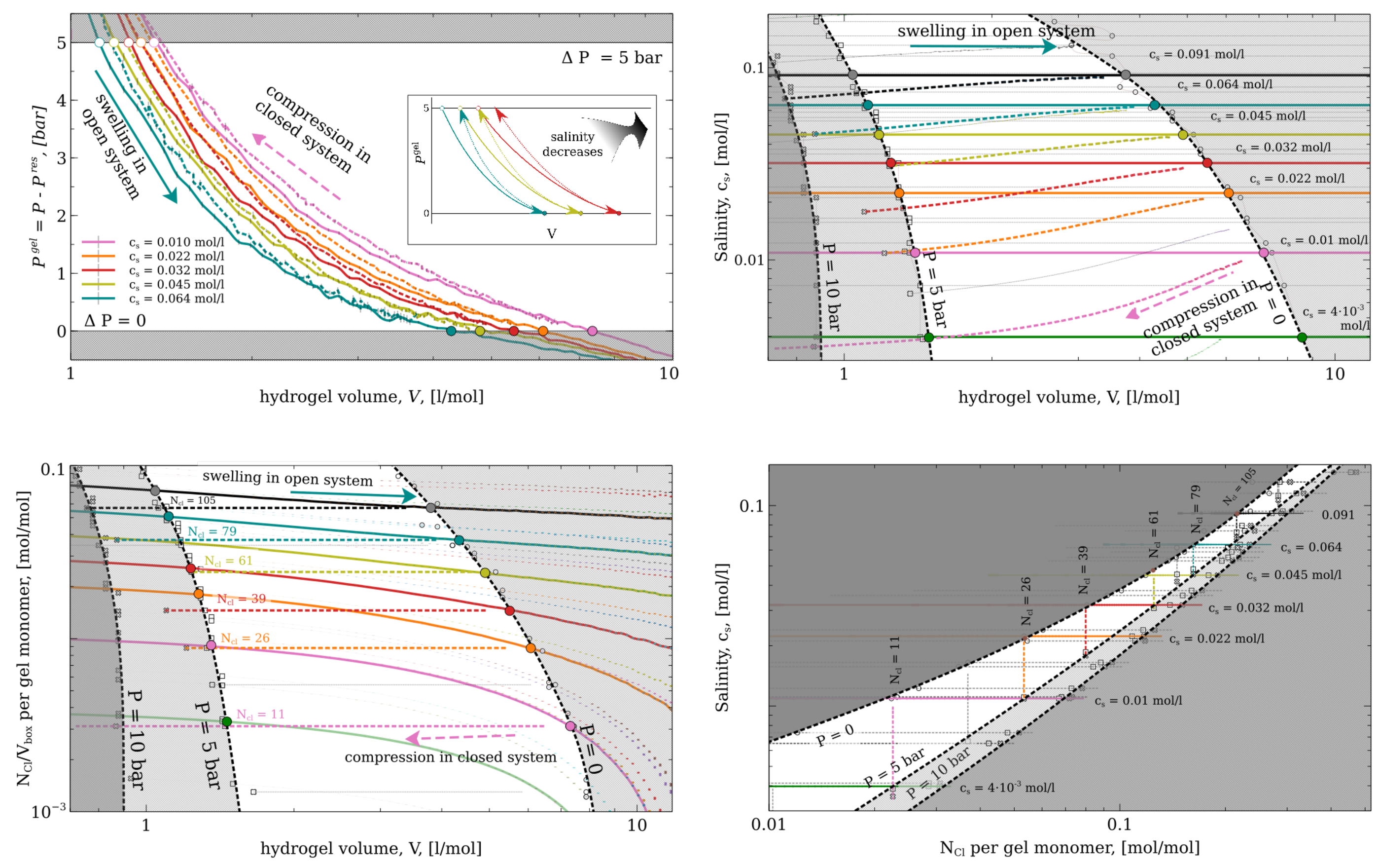
- perform a reaction with arbitrary ion pair

$$\varnothing \overset{K}{\leftrightarrows} \mathrm{Na}^+ + \mathrm{Cl}^- \qquad K = \exp\left(\mu_{\mathrm{Na}^+} + \mu_{\mathrm{Cl}^-}\right)$$

- accept new state if

$$\mathrm{rand}(0,1] < K^{\xi} \prod_{i=Na,\ Cl} \left[\frac{N_i!}{(N_i+\xi)!}\right] \exp\left(-\beta\Delta E_{pot}\right)$$

3. Simulation of the desalination process



The estimation of the desalination efficiency

c_s^0, M	c_s^5,M	$N^0_{\mathrm{Cl}^-}$	$N^5_{\mathrm{Cl}^-}$	Δv, l	$\lvert W\rvert$, J/L	W^{id}, J/L
0.092		0.057 →	0.072	2.74	95.4	
0.089 →	0.074	0.057		2.72	109.1	
0.064		0.037 →	0.051	3.26	100.9	W^{id} = (52.9) R_w = 0.54
0.062 →	0.048	0.037		3.18	107.4	
0.045		0.024 →	0.036	3.82	106.7	W^{id} = 38.2 R_w = 0.53
0.044 →	0.031	0.024		3.91	106.4	
0.032		0.015 →	0.025	4.20	107.9	W^{id} = 43.8 (41.0) R_w = 0.52 (0.46)
0.030 →	0.019 (0.022)	0.015		4.17 (3.22)	115.6 (57.3)	
0.022		0.009 →	0.018 (0.015)	4.75 (3.76)	108.1 (68.3)	W^{id} = 66.6 (22.0) R_w = 0.53 (0.49)
0.021 →	0.011	0.009		4.71	110.8	
0.011		0.003 →	0.009	6.08	106.9	W^{id} = 69.7 R_w = 0.55
0.010 →	0.004	0.003		5.78	119.4	

3. Experimental part

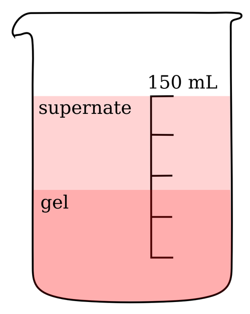
1. Prepare three solutions of c_s = 0.1, 0.05 and 0.01 mol/L.

Measure:
`(CND)` the conductivity
`(CLP)` potential pf Cl- ions

	0.1M	0.05M	0.01M
CND, µS/cm	10261 ±40.6	5547 ±12.1	1222.9 ±0.93
CLP, mg/L	3531 ±4.8	1829.9 ±1.41	345.9 ±0.21

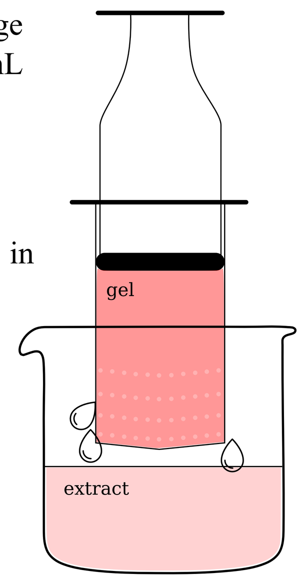
2. equilibrate PAA gel in 150 mL of solution

0.3 g in 0.01M | 69 mL
0.5 g in 0.05M | 67 mL
0.75 g in 0.1M | 70 mL



3. squeeze the gel in syringe to 45 mL

4. collect the extract and measure `CND` and `CLP` in
a) supernate phase
b) in gel phase
c) in extract



c_s = 0.1 mol/L

	gel	sepernate	extract
CND µS/cm	11516 ±58.0	10980 ±58.1	9183 ±29.4
CLP mg/L	3564.9 ±3.28	3650.8 ±3.60	3411.7 ±2.57
c_s mol/L	1.01e-1 ±9.2e-5	1.03e-1 ±1.0e-4	9.62e-2 ±7.2e-5

c_s = 0.05 mol/L

	gel	sepernate	extract
CND µS/cm	6313 ±39.6	6001 ±14.7	5154 ±11.1
CLP mg/L	(1765)	1851 ±1.0	1540.9 ±1.03
c_s mol/L	(4.98e-2)	5.22e-2 ±2.9e-5	4.35e-2 ±2.9e-5

c_s = 0.01 mol/L

	gel	sepernate	extract
CND µS/cm	10261 ±40.6	5547 ±12.1	1222.9 ±0.93
CLP mg/L	359.5 ±0.37	378.8 ±0.37	352.1 ±0.36
c_s mol/L	1.01e-2 ±1.0e-5	1.07e-2 ±1.0e-5	9.93e-3 ±1.0e-5

References

[1] Yu, C., et al. (2016). http://doi.org/10.1021/acs.est.6b03193
[2] Arens, et al. (2017). http://doi.org/10.1002/macp.201700237
[3] Rud, et al. (2018). http://doi.org/10.1016/j.desal.2018.05.002
[4] Turner, et al. Molecular Simulation, 34(2), 119 (2008).
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Acknowledgment

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