Modeling of weak polyelectrolyte hydrogels under compression.

Implications for water desalination.

Oleg V. Rud

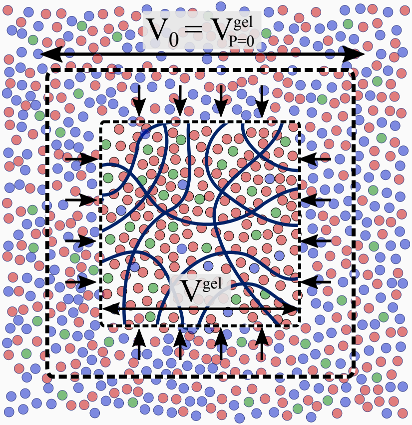
August 12, 2022

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, Praha 2 128 00, Czech Republic

Institute of Macromolecular Compounds of Russian Academy of Sciences, 199004, Bolshoy pr. 31, Saint-Petersburg, Russia

Intro

Introduction



- Desalination
- Hydrogels for desalination
- Forward osmosis
- Various stimuli: thermo-, pH-, electric-, magnetic-, light-indused gel collapse
- Manfred Wilhelm and Yu Chi experiment

Fengler, C., Arens, L., Horn, H., Wilhelm, M. (2020). **Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation.** Macromolecular Materials and Engineering

Yu, C., Wang, Y., Lang, X., Fan, S. (2016). **A Method for Seawater Desalination via Squeezing Ionic Hydrogels.** Environmental Science and Technology

Donnan prediction

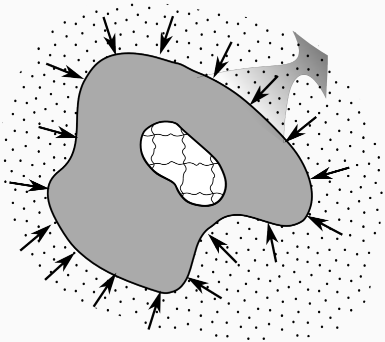


Figure 1: The compression of hydrogel affects the ionic composition of supernatant

- Donnan equilibrium $c_s^2 = c_{Na}^{in} \cdot c_{Cl}^{in}$
- Electroneutrality αN of self charges
  αN of neutralizing counterions
  c_{Cl}^{in} of free ion pairs
- By compression to the dry state one can exclude brine of concentration

$$N_{excl}/V = \begin{cases} c_s^{in} < c_s, \\ \\ c_s^{in} + \alpha N/V_{gel} > c_s, \end{cases}$$

The model of a polyelectrolyte gel.

Langevin dynamics.

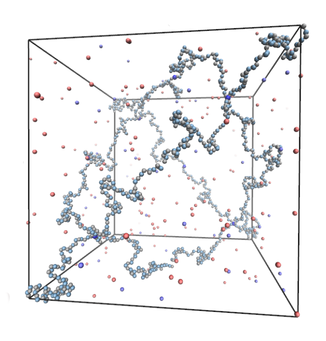


Figure 2: The snapshot of the hydrogel model for Langevin dynamics

- Diamond network of point particles
- Lennard–Jones interaction

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

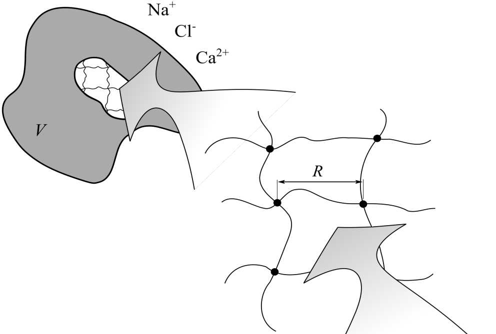
- FENE potential

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

- Electrostatic interaction

$$V_{EL} = l_B k_B T \cdot \frac{q_1 q_2}{r}$$

Grand-reaction ensemble.



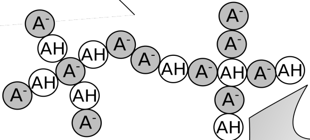
Constant salinity

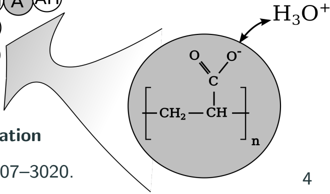
$$\boxed{c_s = c^-_{\mathrm{Cl}} = c^+_{\mathrm{Na}}}$$

The simulation box freely exchanges ions with reservoir as in **grand cannonical** ensemble

Ionization equilibrium in **reaction** ensemble

$$\boxed{\mathrm{pA}^- + \mathrm{H_3O}^+ \leftrightarrows \mathrm{pAH}}$$





Landsgesell, J., Hebbeker, P., Rud, O., Lunkad, R., Košovan, P., Holm, C. (2020). **Grand-Reaction Method for Simulations of Ionization Equilibria Coupled to Ion Partitioning.** Macromolecules, 53(8), 3007–3020.

Grand-reaction ensemble.

Grand canonical ensemble

The free energy of the grand-canonical ensemble for single particle type

$$\boxed{\Omega = E - TS + \mu N}$$

The entropy S expands via Boltzmann formula

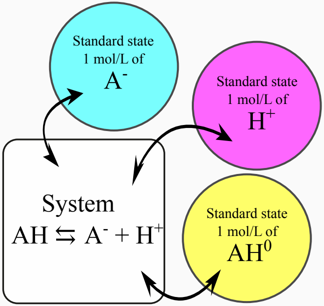
$$S = k_B \ln \frac{V^N}{N!} \qquad \Omega = E - k_B T \ln \frac{V^N}{N!} + \mu N$$

The change of free energy associated with a sngle particle exchange is

$$\boxed{\Delta\Omega = k_B T \ln \left(V^\xi \frac{N!}{(N+\xi)!} \right) + \xi\mu + \Delta E}$$

`accept if` $\mathcal{R}^\xi < e^{\Delta\Omega / k_B T}$

Grand-reaction ensemble.



Reaction ensemble

The reaction of an acidic unit

$$\mathrm{HA} \overset{K}{\leftrightarrows} \mathrm{A}^- + \mathrm{H}^+$$

$$\Omega = E - TS + \sum_i \left(\mu_i - \mu_i^{\ominus}\right) N_i$$

Then the change of system free energy during a single reaction step

$$\Delta\Omega = k_B T \ln\left(\prod_i V^{\nu_i \xi} \frac{N_i!}{(N_i + \nu_i \xi)!}\right) + \xi\left(\sum_i \nu_i \mu_i - \sum_i \nu_i \mu_i^{\ominus}\right) + \Delta E$$

`accept if` $\mathcal{R}^{\xi} < e^{\Delta\Omega / k_B T}$

Grand-reaction ensemble.

$$\boxed{\Delta\Omega = k_B T \ln\left(K^{\xi}\prod_i V^{\nu_i\xi}\frac{N_i!}{(N_i+\nu_i\xi)!}\right)+\Delta E}$$

$$\boxed{K = e^{-\sum_i \nu_i \mu_i^{\ominus}}}$$

$$\mathrm{HA} \overset{K}{\leftrightarrows} \mathrm{A}^- + \mathrm{H}^+$$

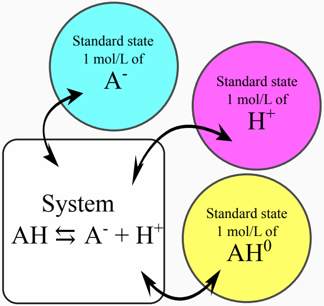
$$K = \mu^{\ominus}_{\mathrm{H}^+} + \mu^{\ominus}_{\mathrm{A}^-} - \mu^{\ominus}_{\mathrm{HA}}$$

$$\emptyset \leftrightarrows \mathrm{Na}^+ + \mathrm{Cl}^-$$

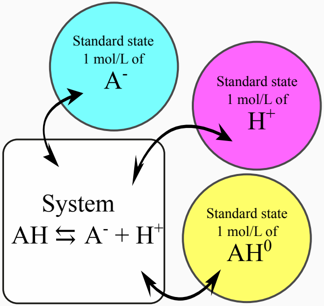
$$K = \mu_{\mathrm{Na}^+} + \mu_{\mathrm{Cl}^-}$$

$$\emptyset \leftrightarrows \mathrm{Ca}^{2+} + 2\mathrm{Cl}^-$$

$$K = 2\mu_{\mathrm{Ca}^{2+}} + \mu_{\mathrm{Cl}^-}$$



Grand-reaction ensemble.



Moderate pH conditions

The reaction of an acidic unit

$$\mathrm{HA} \overset{K}{\leftrightarrows} \mathrm{A}^- + \mathrm{H}^+$$

Is happening only simultaneously with one of these two

$$\begin{aligned} \mathrm{H}^+ &\leftrightarrows \mathrm{Na}^+ \\ 2\mathrm{H}^+ &\leftrightarrows \mathrm{Ca}^{2+} \end{aligned}$$

$$\mathrm{HA} \overset{K'}{\leftrightarrows} \mathrm{A}^- + \mathrm{Na}^+, \quad K' = K \exp(\mu_{\mathrm{H}^+} - \mu_{\mathrm{Na}^+})$$

$$2\mathrm{HA} \overset{K''}{\leftrightarrows} 2\mathrm{A}^- + \mathrm{Ca}^{2+}, \quad K'' = K \exp(2\mu_{\mathrm{H}^+} - \mu_{\mathrm{Ca}^{2+}})$$

Simulation protocol.

1. Choose randomly: LMD, RE, or EX.

2. Simulate the chosen, collecting 50 samples of:

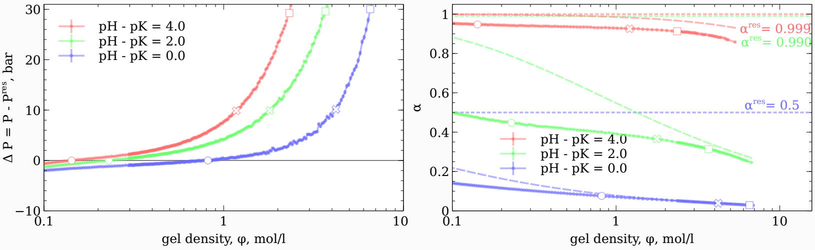
LMD: pressure, P, and $\{R_e\}$	RE: number of ionized segments, N_{A^-}	EX: number of salt ions, N_{Na^+} and N_{Cl^-}

   Check the autocorrelation of each samples array.
   Pearson coefficient must be < 0.2.

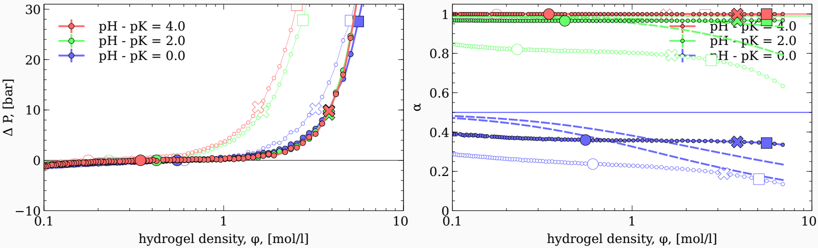
3. Repeat collecting at least 200 averages from each process.

Results

Monovalent salt. Compression.



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



(b) high salinity, $c_s = 0.209$ mol/l

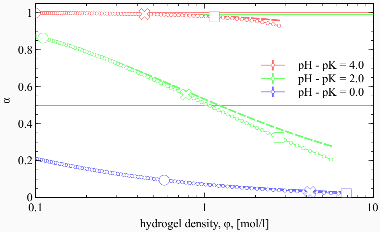
Monovalent salt. “No electrostatics” vs “Mean field theory”.

$$\frac{\alpha}{1-\alpha}10^{\mathrm{p}K-\mathrm{pH}} = \sqrt{1+\left(\frac{\alpha c_{\mathrm{p}}}{2c_{\mathrm{s}}}\right)^2} - \frac{\alpha c_{\mathrm{p}}}{2c_{\mathrm{s}}}$$

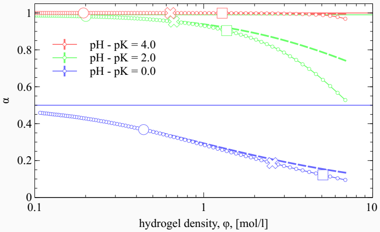
Together with electroneutrality condition it translates to

$$-\frac{\alpha^3 c_{\mathrm{p}}}{c_{\mathrm{s}}} + \alpha^2\left(\frac{c_{\mathrm{p}}}{c_{\mathrm{s}}} + \Theta - \frac{1}{\Theta}\right) + \frac{2\alpha}{\Theta} - \frac{1}{\Theta} = 0$$

where $\Theta = 10^{\mathrm{p}K-\mathrm{pH}}$.



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



(d) high salinity, $c_s = 0.209$ mol/l

Monovalent salt. Desalination effect.

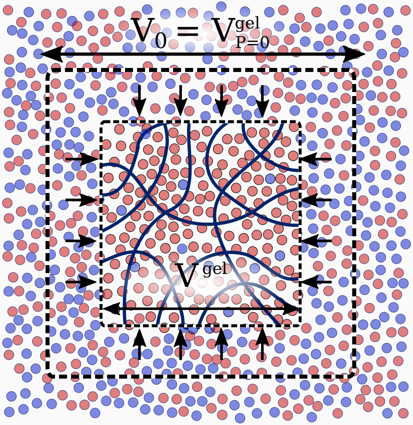
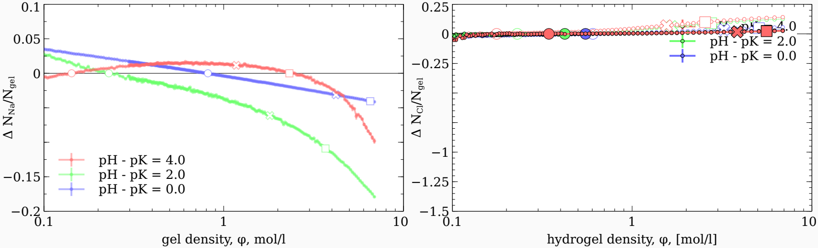
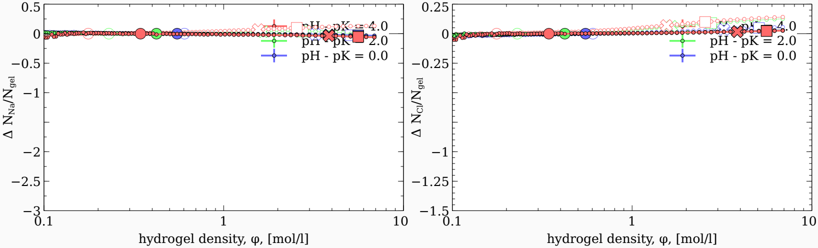


Figure 3: Schematic illustration of the hydrogel being compressed isotropically by pressure ΔP from the initial volume at free swelling equilibrium, V_0 to a volume V^{gel}. Simultaneously, the gel exchanges small ions with a reservoir solution of salinity c_{s}.

Monovalent salt. Desalination effect.

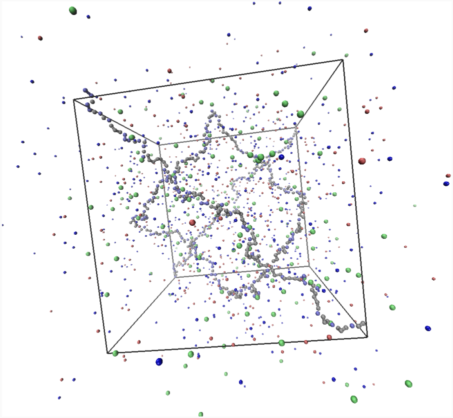


(a) low salinity, $c_s = 0.007$ mol/l



(b) high salinity, $c_s = 0.209$ mol/l

Divalent salt.



Seawater model:

$$c_{\mathrm{Cl}^-} = 0.54 \text{ mol/l}$$
of negative ions

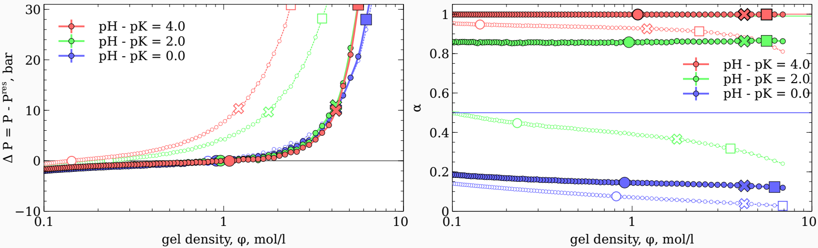
$$c_{\mathrm{Na}^+} = 0.47 \text{ mol/l}$$
of positive ions

$$c_{\mathrm{Ca}^{2+}} = 0.063 \text{ mol/l}$$
of positive divalent ions

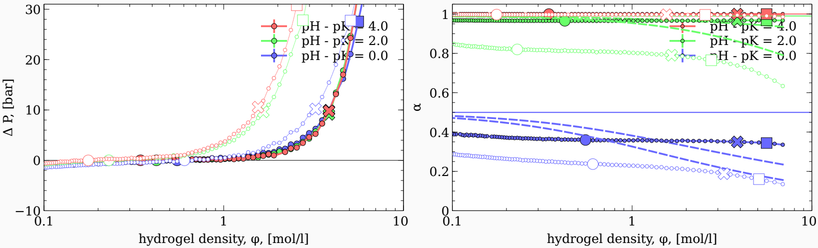
$$c_{\mathrm{Na}^+} \simeq 0.87 \cdot c_{\mathrm{Cl}^-}$$
$$c_{\mathrm{Ca}^{2+}} \simeq 0.117 \cdot c_{\mathrm{Cl}^-}$$

$$\mu_{\mathrm{Na}^+} = \mu_{\mathrm{Cl}^-} - 0.139kT$$
$$\mu_{\mathrm{Ca}^{2+}} = \mu_{\mathrm{Cl}^-} - 2.03kT$$

Divalent salt. Compression.



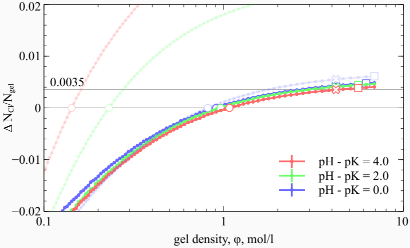
(c) low salinity, $c_s = 0.007$ mol/l

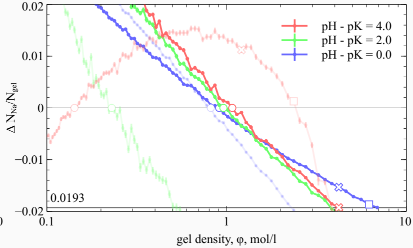


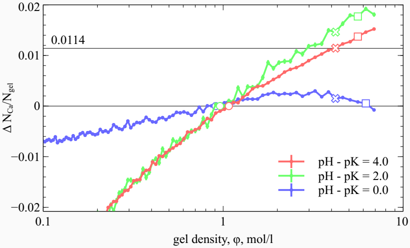
(d) high salinity, $c_s = 0.209$ mol/l

Divalent salt. Desalination or ion exchange.

Low salinity $c_{\mathrm{Cl}^-} = 0.007$

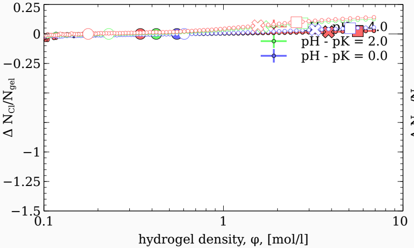


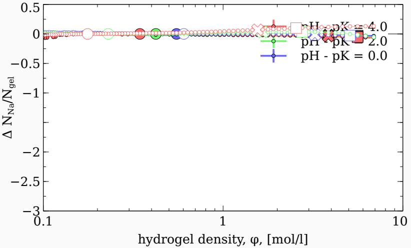


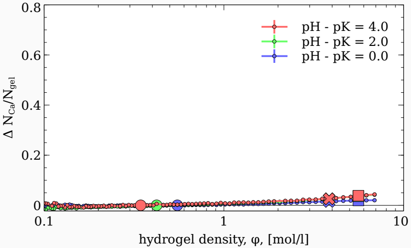


Divalent salt. Desalination or ion exchange.

High salinity $c_{\mathrm{Cl}^-} = 0.263$







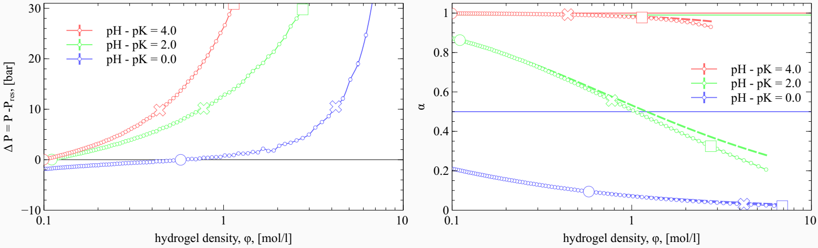
Conclusion

Summary

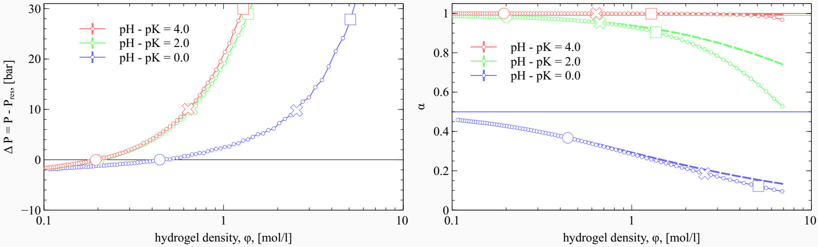
1. monovalent ions
    1.1 ionization of the hydrogel is suppressed as compared to predictions for monomeric acid, due
        - to the Donnan partitioning of H + ions;
        - to the electrostatic repulsion between charges of the gel.
    1.2 the decrease of ionisation degree is much less significant than previously estimated using mean-feld models.
    1.3 decreasing the ionization of the gel upon compression may completely reverse the desalination effect forcing the gel to release counterions upon compression instead of absorbing them.
2. with divalent ions
    2.1 the electrostatics is almost completelly screened
    2.2 alpha does not change versus compression
    2.3 The compression of gel in presence of divalent ions works as ion exchanger of Ca ion by Na

Questions?

Monovalent salt. “No electrostatics” vs “Mean field theory”.



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



(l) high salinity, $c_s = 0.209$ mol/l