Phase transition in hydrophobic weak polyelectrolyte gel. A computer simulation study.

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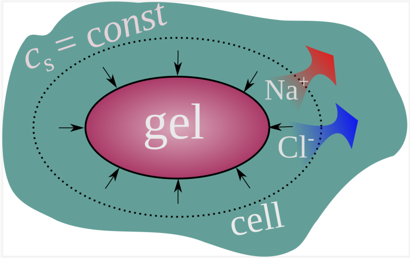
Intro

Introduction



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

1. 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
2. Yu, C., Wang, Y., Lang, X., Fan, S. (2016). **A Method for Seawater Desalination via Squeezing Ionic Hydrogels.** Environmental Science and Technology

The model of a polyelectrolyte gel.

Mean field thory.

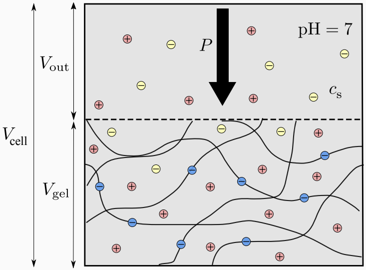


Figure 1: The hydrogel in equilibrium with a bath of aqueous solution

- Free energy of a hydrogel chain

$$F = F_{conf} + F_{int} + F_{ion}$$

- Conformational entropy

$$F_{\text{conf}} = \frac{3}{2}\frac{R^2/(b^2N)-1}{1-R^2/(b^2N^2)} - \frac{3}{2}\ln\left(\frac{R^2}{b^2N}\right)$$

- Steric interactions

$$F_{\text{int}} = \frac{N}{c_{\text{p}}}\left[(1-c_{\text{p}})\ln(1-c_{\text{p}}) - \chi c_{\text{p}}^2\right]$$

$$F_{ion} = \frac{N}{c_{\text{p}}}\sum_i \left(c_i^{in}\ln\frac{c_i^{in}}{c_i^{out}} + c_i^{out} - c_i^{in}\right)$$

Mean field thory. Donnan potential.

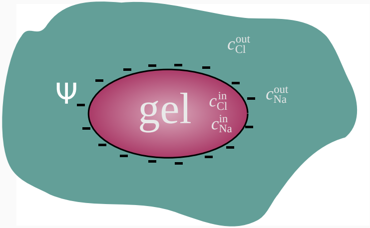


Figure 2: Electrostatic potentioal of the particle surface is a driving force of ion partitioning

- Donnan electrostatic potential, ψ

$$e^{\psi} = \xi = \frac{c^{out}_{\mathrm{H}^+}}{c^{in}_{\mathrm{H}^+}} = \frac{c^{out}_{\mathrm{Na}^+}}{c^{in}_{\mathrm{Na}^+}} = \frac{c^{in}_{\mathrm{Cl}^-}}{c^{out}_{\mathrm{Cl}^-}} = \frac{c^{in}_{\mathrm{OH}^-}}{c^{out}_{\mathrm{OH}^-}}$$

- Local electroneutrality condition

$$\alpha c_p + c^{in}_{\mathrm{Cl}^-} + c^{in}_{\mathrm{OH}^-} = c^{in}_{\mathrm{Na}^+} + c^{in}_{\mathrm{H}^+}$$

$$\boxed{\xi(c_{\mathrm{p}}, c_{\mathrm{s}}) = \sqrt{1 + \left(\frac{\alpha c_{\mathrm{p}}}{2c_{\mathrm{s}}}\right)^2} \pm \frac{\alpha c_{\mathrm{p}}}{2c_{\mathrm{s}}}}$$

pH-sensitive hydrogel

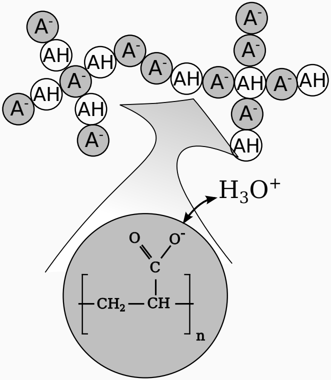


Figure 3: Each bead of hydrogel is acidic. It changes its charge depending on pH.

- ionization reaction

$$\mathrm{pAH} \overset{K}{\rightleftharpoons} \mathrm{pA^-} + \mathrm{H^+}$$

- ionization equilibrium

$$\frac{\alpha}{1-\alpha} = \frac{c^{in}_{\mathrm{H^+}}}{K} = \frac{c^{out}_{\mathrm{H^+}}}{K}\frac{c^{in}_{\mathrm{H^+}}}{c^{out}_{\mathrm{H^+}}} = 10^{pK-pH}\xi^{-1}$$

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

- Free energy ionization term

$$F_\alpha = \alpha N\left(\ln\alpha + \ln(1-\alpha) + \ln c^{in}_{\mathrm{H^+}} - \ln K\right)$$

Equation of state

$$F(c_\mathrm{p}, c_\mathrm{s}) = F_{conf}(c_\mathrm{p}) + F_{int}(c_\mathrm{p}, \chi) + F_{ion}(c_\mathrm{p}, c_\mathrm{s}) + F_\alpha(c_\mathrm{p}, c_\mathrm{s}, pK)$$

pK and χ are the parameters of the model

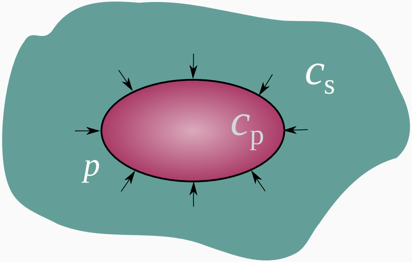
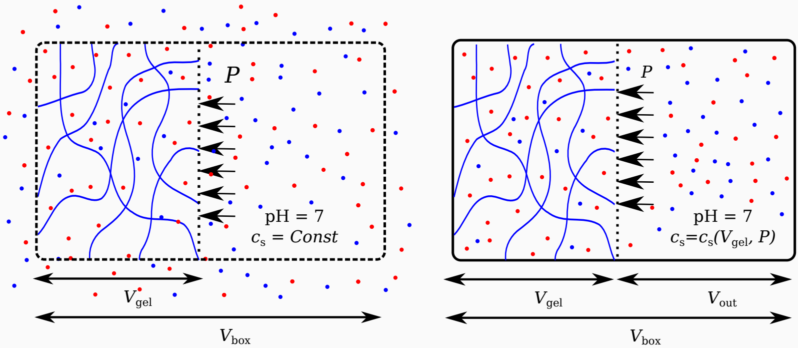


Figure 4: Gel particle under compression in equilibrium with aqueous solution of salinity c_s

Partial pressure of the gel network

$$\boxed{\left(\frac{\partial F}{\partial V}\right)_{c_\mathrm{s}} = -p}$$

Two ways of hydrogel compression



Open system: Compression under constant salinity c_s

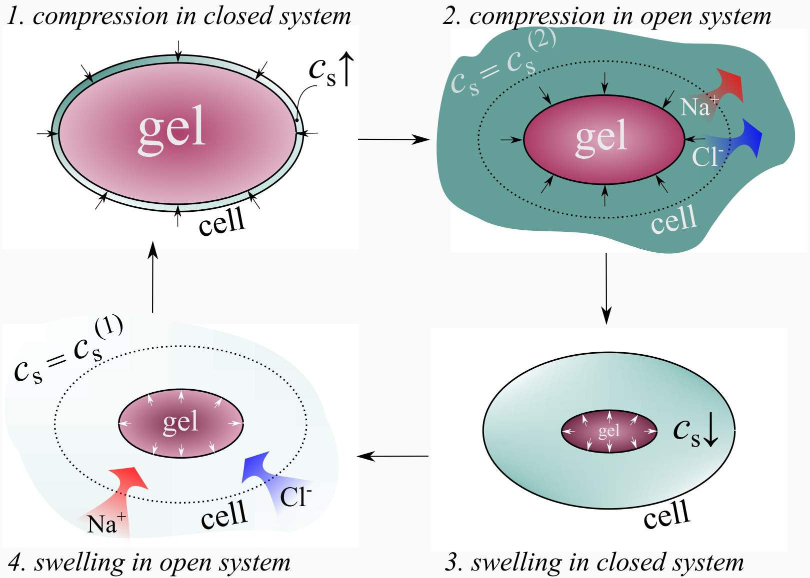
$$p = p(c_p, c_s)$$

Closed system: constant number of ions N_{Na^+} and N_{Cl^-}

$$p = p(c_p, c_s)$$

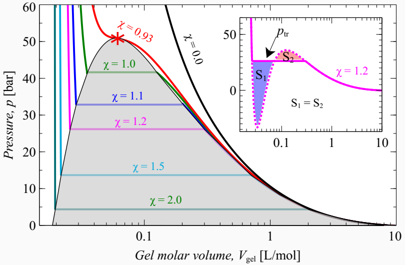
$$N_{Na^+} = Const, \; N_{Cl^-} = Const$$

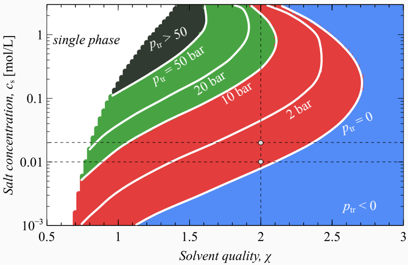
Desalination cycle



Results

Compression of hydrogel.





Maxwell construction: Definition of p_{tr}

Phase diagramm: transition pressure versus c_s and χ

Comparison of desalination cycles (P — V coordinates).

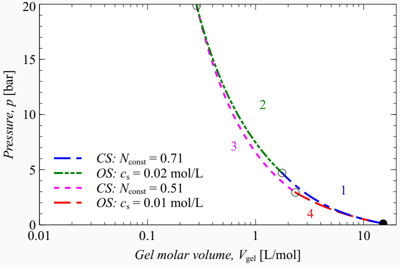


Figure 5: hydrophilic gel

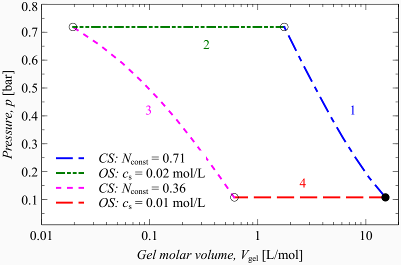


Figure 6: hydrophobic gel

Comparison of desalination cycles (c_s — N coordinates).

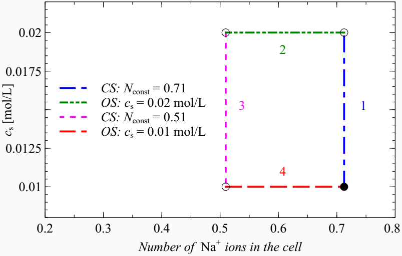


Figure 7: hydrophilic gel

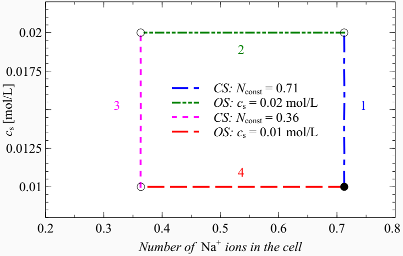


Figure 8: hydrophobic gel

Conclusion

Summary

1. Compression of a weak polyelecyrolyte and hydrophobic gel initiates first order phase transition, which happens at certain p_{tr} and separates two states of a gel
2. The transition hapens due to an interplay between electrostatic and hydrophobic interactions
3. The transition separates two states:
   - swollen and significantly charged gel
   - collapsed and almost fully discharged gel
4. The value of transition pressure depends on c_s and χ (and pH-pK)
5. Employing the phase transition halps to significantly decrease the pressure used in desalination cycle and to limit it within 0 and 1 bar

Prokacheva, V. M., Rud, O. V., Uhlík, F., Borisov, O. V. (2021). Phase transition in hydrophobic weak polyelectrolyte gel utilized for water desalination. **Desalination**, 511, 115092. https://doi.org/10.1016/j.desal.2021.115092

Questions?

Comparison of desalination cycles (α — V coordinates).

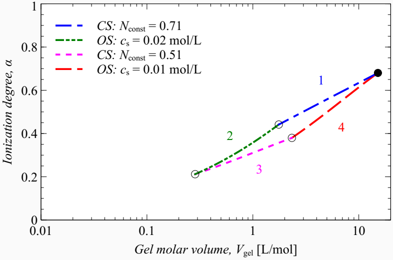


Figure 9: hydrophilic gel

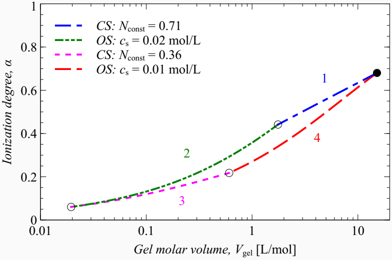


Figure 10: hydrophobic gel

Cubic equation for α.

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

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