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

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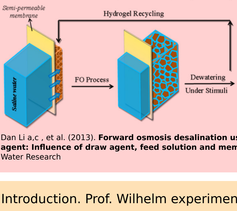
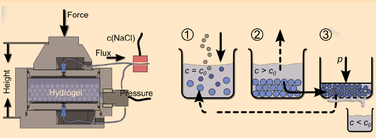
Introduction.

- Hydrogels for desalination
- Forward osmosis
- Various stimuli: thermo-, pH-, electric-, magnetic-, light-indused gel collapse



Dan Li a,c , et al. (2013). **Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance**. Water Research

Introduction. Prof. Wilhelm experiment.



Fengler, C., et al (2020). **Desalination of Seawater Using Cationic Poly(acrylamide) Hydrogels and Mechanical Forces for Separation.** Macromolecular Materials and Engineering

Mean field analythical model.

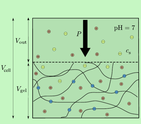


Figure 1: The hydrogel in equilibrium with a bath of aqueous solution

- 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

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

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

Mean field analythical model. Donnan potential.

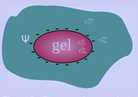


Figure 2: Electrostatic potentioal of the particle surface is a driving force of ion partitioning

- Donnan electrostatic potential, ψ

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

- Local electroneutrality condition

$$\alpha c_p + c_{Cl^-}^{in} + c_{OH^-}^{in} = c_{Na^+}^{in} + c_{H^+}^{in}$$

$$\xi(c_p, c_s) = \sqrt{1+\left(\frac{\alpha c_p}{2c_s}\right)^2} \pm \frac{\alpha c_p}{2c_s}$$

pH sensitive hydrogel.

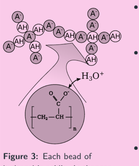


Figure 3: Each bead of hydrogel is acidic. It changes its charge depending on pH.

- ionization reaction

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

- ionization equilibrium

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

$$\frac{\alpha}{1-\alpha} = 10^{pK-pH}\left(\sqrt{1+\left(\frac{\alpha c_p}{2c_s}\right)^2} \mp \frac{\alpha c_p}{2c_s}\right)$$

- Free energy ionization term

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

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