Thermodynamics of hydrogel swelling
Applications of hydrogels in bioengineering

Last Day: Structure of hydrogels

Today: bioengineering applications of hydrogels
Thermodynamics of hydrogel swelling

Reading:


Announcements:
hydrogels
Thermodynamics of hydrogel swelling

Move to a new, larger aqueous bath

V_r

polymerize

swelling

V_s
Thermodynamics of hydrogel swelling

Competing driving forces determine total swelling:

$V_r$  

$V_s$  

swelling
Description of cross-linked network

Cross-linking (relaxed) $V_r$

Expansion factor: $\alpha$

$$\alpha_x \alpha_y \alpha_z = \alpha^3 = \frac{V_s}{V_r} = \frac{V_2 + n_1 v_{m,1}}{V_r}$$

swelling

$$\phi_{2,s} = \frac{V_2}{V_2 + n_1 v_{m,1}}$$
volume fraction of polymer in swollen gel

$$\phi_{2,r} = \frac{V_2}{V_r}$$
volume fraction of polymer in relaxed gel
Free energy of mixing in the network:

Starting point: thermodynamic description of simple polymer-solvent mixing:
Seek to derive an expression for the free energy of mixing:
Free energy of mixing in the network:

Lattice model description of polymers: (Flory/Huggins)

ENTHALPY OF MIXING:

Energy of contacts:

\[ \Delta \omega_{12} \]
Free energy of mixing in the network:

Lattice model description of polymers: (Flory/Huggins)

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ENTROPY OF MIXING:

Image removed due to copyright reasons. Please see: Figure 110 in Flory, P. J. *Principles of Polymer Chemistry*. Ithaca, NY: Cornell University Press, 1953.
Free energy of mixing in the network:

Lattice model description of polymers: (Flory/Huggins)
Description of cross-linked network

Assume cross-links are randomly placed; on average, all are equidistant:

\( \nu = \text{number of subchains in cross-linked network} \)
\( \nu_e = \text{number of ‘effective’ subchains: tethered at both ends} \)

\( M = \text{MW of original chains} \)
\( M_c = \text{MW of subchains = MW between cross-links} \)

Example: assume polymer chains have a molecular weight \( M = 4A \) and each ‘subchain’ has molecular weight \( A \):

Two useful relationships:

\( \nu = \frac{V_2}{\nu_{sp,2} M_c} \)
\( \nu_e = \nu (1 - 2(M_c/M)) \)
Elastic contribution to hydrogel free energy: $\Delta G_{el}$

- Account for entropic retraction force that restrains swelling: $\Delta G_{el} > 0$
Elastic contribution to hydrogel free energy: $\Delta G_{el}$
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Complete expression for the free energy of the gel:
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Complete expression for the free energy of the gel:
Predictions of Flory/Peppas theory

Varying $\phi_{2,r}$:

- Volume fraction polymer in swollen state
- $S = V_s/V_{dry}$

Graphs showing the relationship between $M_c$ (g/mole) and $\phi$ for different values of $S$.
Predictions of Flory/Peppas theory

Varying $\chi$: 

![Graph showing hydrogel swelling vs. solvent quality](image)

- Volume fraction polymer in swollen state vs. Mc (g/mole)
- S vs. Mc (g/mole)
Model parameters

- \( \mu_1^{bath} \): chemical potential of water in external bath \( (\mu_1^0) \)
- \( \mu_1 \): chemical potential of water in the hydrogel
- \( \mu_1^0 \): chemical potential of pure water in standard state
- \( \Delta w_{12} \): pair contact interaction energy for polymer with water
- \( z \): model lattice coordination number
- \( x \): number of segments per polymer molecule
- \( M \): Molecular weight of polymer chains before cross-linking
- \( M_c \): Molecular weight of cross-linked subchains
- \( n_1 \): number of water molecules in swollen gel
- \( \chi \): polymer-solvent interaction parameter
- \( k_B \): Boltzmann constant
- \( T \): absolute temperature (Kelvin)
- \( v_{m,1} \): molar volume of solvent (water)
- \( v_{m,2} \): molar volume of polymer
- \( v_{sp,1} \): specific volume of solvent (water)
- \( v_{sp,2} \): specific volume of polymer
- \( V_2 \): total volume of polymer
- \( V_s \): total volume of swollen hydrogel
- \( V_r \): total volume of relaxed hydrogel
- \( \nu \): number of subchains in network
- \( \nu_e \): number of ‘effective’ subchains in network
- \( \phi_1 \): volume fraction of water in swollen gel
- \( \phi_{2,s} \): volume fraction of polymer in swollen gel
- \( \phi_{2,r} \): volume fraction of polymer in relaxed gel
Key properties of hydrogels for bioengineering applications:
Further Reading