Poly-Electrolyte Gel [pln66]

In [pln65] we have investigated the swelling equilibrium of a polymer gel and expressed it as the balancing of osmotic pressure acting as an expanding force and gel elasticity acting as a restoring force. For uncharged polymers in a solvent with negligible amounts of ions we have derived the following expression for the osmotic pressure:

$$\pi_{\mathrm{sol}}(\phi) = \frac{k_{\mathrm{B}}T}{v_{\mathrm{c}}}\big[-\ln(1-\phi) - \phi - \chi\phi^2\big].$$

In [pln62] we have investigated the Donnan equilibrium of a poly-electrolyte in contact with a solvent containing mobile ions. We have found that the Donnan equilibrium features an ionic contribution to the osmotic pressure,

$$\pi_{\mathrm{ion}}(n_b, n_s) = k_{\mathrm{B}}T\left[\sqrt{n_b^2 + 4n_s^2} - 2n_s\right],$$

where n_b is the number density of bound charges in ionic groups on the poly-electrolyte molecules and n_s is the number density of mobile ions in pure solvent.

When we investigate the swelling equilibrium of a poly-electrolyte gel we must take into account both contributions to the osmotic pressure. An approximate implementation of this requirement just adds the two contributions. The modified swelling equilibrium then becomes

$$G_0\left(\frac{\phi}{\phi_0}\right)^{1/3} = \pi_{\mathrm{sol}}(\phi) + \pi_{\mathrm{ion}}(\hat{n}_b, n_s),$$

where $\hat{n}_b = n_b(\phi/\phi_1)$ reflects the change in the number density of bound charges due to swelling.

A more accurate implementation would start from the free-energy density with all contributions included and then determine the equilibrium from the extremum condition.

Given the known shape of $\pi_{\mathrm{sol}}(\phi)$ and the weak dependence of $\pi_{\mathrm{ion}}(\hat{n}_b, n_s)$ on ϕ it is readily concluded that the presence of ions has an enhancing effect on the swelling.

[extracted in part from Doi 2013]