

Swelling of Hydrogels

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May 11, 2016

Abstract

Hydrogels are widely studied for their ability to swell when dialyzed in water. We review briefly the Flory-Huggins theory of the swelling of hydrogels. We compare experimental data to the predictions of the model, and find very good agreement.

Hydrogels are networks of polymers that are joined by cross-links. The ability of hydrogels to expand and contract in response to changes in the relative strengths of different monomer-monomer and monomer-solvent interactions has been studied extensively. Hydrogels are of particular technological interest, not least because of their ability to expand up to hundreds or thousands of times their initial weight in response to external stimuli [3], such as pH or temperature. This property has been utilized as far back as the 1950s for applications in energy storage [10], sensing applications [19, 8, 12], biotechnology [2, 21, 18], and medicine [14, 13, 27, 11].

In addition, hydrogels have been studied extensively for their ability to undergo volumetric phase transitions in response to ionic strength, pH, solvent, electric field, and other stimuli [25, 23, 22, 20, 7, 26, 15]. These phase transitions are observed in gels with many different kinds of interactions, including ionic gels, non-ionic gels, and gels with hydrogen bonding [9, 24, 5, 6].

In this paper, I review briefly the standard theory of gel swelling, and then compare the predictions of that theory to experiment.

1 Flory-Huggins Theory

The swelling of hydrogels is described most commonly by the Flory-Huggins equation of state [4]. Within Flory-Huggins theory, the change in the free energy upon mixing the polymer with the solvent is

$$\Delta F = \Delta F_M + \Delta F_{el}. \quad (1)$$

The free energy associated with mixing the polymer with the solvent, ΔF_M , is given by

$$\Delta F_M = \Delta H_M - T\Delta S_M. \quad (2)$$

Denoting by v_1 and v_2 the volume fractions of solvent and solute, and by n_1 and n_2 the number of solvent and solute molecules, we have

$$T\Delta S_M = k_B T (n_1 \ln(v_1) + n_2 \ln(v_2)). \quad (3)$$

The enthalpy of mixing is determined as follows. The probability, in a θ -solvent, that the position adjacent to a solvent molecule is occupied by a polymer is roughly the volume fraction v_2 of the solvent. Thus, the total heat of formation is proportional to $n_1 v_2$. We thus allow the following equation to define χ_1 :

$$\Delta H_M = k_B T \chi_1 n_1 v_2. \quad (4)$$

Setting $n_2 = 0$, due to the absence of monomers in the structure, it follows that

$$\Delta F_M = k_B T (n_1 \log(v_1) + \chi_1 n_1 v_2). \quad (5)$$

The change in the elastic free energy is given by the familiar equation for the freely jointed chain:

$$\Delta F_{el} = (3k_B T \nu_e / 2) \alpha_s^2, \quad (6)$$

where ν_e is the total number of polymer chains and α_s is the linear swelling factor. Note that in evaluating ν_e , a chain is considered to be any segment of polymer running between two cross-links, and is thus equivalent to the number of cross-links, to a good approximation.

The condition for equilibrium is that the chemical potential of the solvent in the gel must equal the chemical potential of the pure solvent. An equation for the chemical potential can be obtained by differentiating the free energy with respect to n_1 , the number of solvent molecules,

$$\mu_1 - \mu_1^0 = n_A \left(\frac{\partial \Delta F_M}{\partial n_1} \right)_{T,P} + n_A \left(\frac{\partial \Delta F_{el}}{\partial \alpha_s} \right)_{T,P} \left(\frac{\partial \alpha_s}{\partial n_1} \right)_{T,P}, \quad (7)$$

and using the following expression for the swelling ratio,

$$\alpha_s^3 = (V_0 + n_1 \mathbf{v}_1 / n_A) / V_0, \quad (8)$$

where \mathbf{v}_1 is the molar volume of the solvent, and n_A is Avagadro's number. Setting $\mu_1 = \mu_1^0$, we solve equation (7) for v_2 . We find

$$\frac{\mathbf{v}_1 \nu_e}{V_0} v_2^{1/3} = - [\ln(1 - v_2) + v_2 + \chi_1 v_2^2]. \quad (9)$$

Since $v_2 \ll 1$, we can expand the logarithm to first order. Denoting the swelling ratio by $q = 1/v_2$, we obtain

$$q^{5/3} = \frac{V_0}{\mathbf{v}_1} \frac{1/2 - \chi_1}{\nu_e}. \quad (10)$$

The quality of the solvent is expressed by χ_1 , and the cross-linking density is expressed by ν_e , for constant V_0 .

For the case of an ionic gel, the solution above must be modified to include the electrostatic pressure of the gel. The number of fixed charges in the swollen gel per unit volume is denoted by $C_- v_2$. If the concentration of ions outside of the gel is very small compared to the concentration inside the gel, we can obtain

$$q^{5/3} = \frac{V_0}{\nu_e \mathbf{v}_1} ((1/2 - \chi_1) + C_- q). \quad (11)$$

Although this is not as readily solvable, if the contribution to swelling due to charge outweighs the contribution to swelling due to solvent effects, we have

$$q^{2/3} = C_- \frac{V_0}{\nu_e}, \quad (12)$$

where, as before, ν_e accounts for the number of cross-links in the gel (at constant volume).

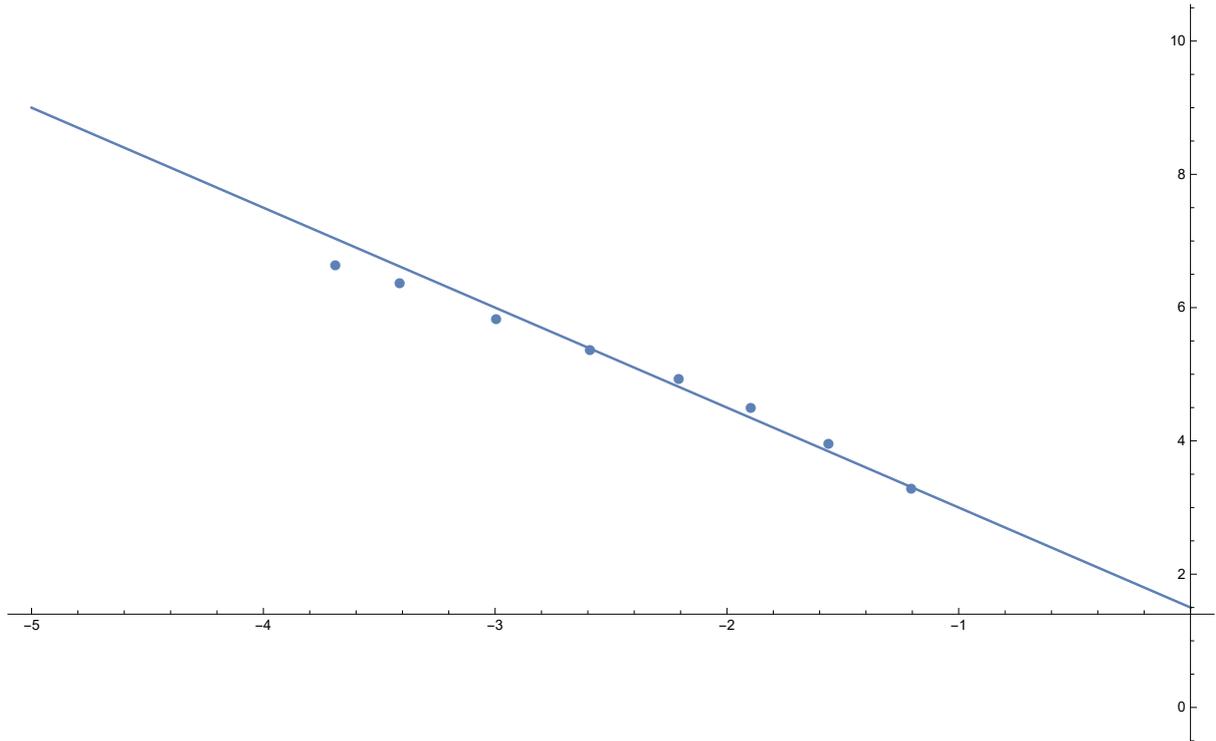


Figure 1: Swelling factor as a function of crosslinker density. The log volumetric swelling factor is on the Y axis. The log crosslinker density (w/w) is on the x axis. $y = -3/2x$ is plotted as a guide to the eye.

2 Comparison of theory to experiment

The most easily testable prediction of the previous section is that, for a non-ionic gel, the swelling factor upon dialysis in water should go like the $-3/5$ power of the cross-linking density, while for an ionic gel, the swelling factor should go like the $-3/2$ power of cross-linking density. To test the latter prediction, I obtained data from [2]. In [2], poly(acrylamide)-copoly(acrylate) gels were formed via free radical polymerization with a variable concentration of N,N'-methylenebisacrylamide as a cross-linker. The data I used, presented in that paper as Figure S5, is shown in Figure 1 with the line $y = -3/2x$. The agreement is very good in the region for which I had data.

To study the swelling of non-ionic hydrogels, I intended to repeat the above experiment for pure acrylamide gels with varying amounts of cross-linker. To do so, I intended to cast gels with 10% (w/w) acrylamide in 1x PBS with 2 molar NaCl and N,N'-methylenebisacrylamide concentrations between 0.025% (w/w) to 0.3% (w/w), by adding 0.2% ammonium persulfate and 0.2% tetramethylethylenediamine and incubating at 37 degrees C for 2 hours. I then intended to dialyze the gels in water before measuring the final swell factors. Unfortunately, however, I was unable to conduct the experiment before the end of the semester.

Instead, a review of the literature revealed only a few studies into the swelling of nonionic gels as a function of the crosslinker density [16, 1], mostly concerning the behavior of crosslinked gels in the limit of very high crosslinker concentration[17]. One study did provide some data that appeared usable, for gels of N-isopropylacrylamide [28]. In that study, the authors cast 5% PNIPAAm gels cross-linked with bisacrylamide at levels varying from 0.05% to 0.6% (w/w), and swelled the gels by cooling them to room temperature. Once again, the agreement with

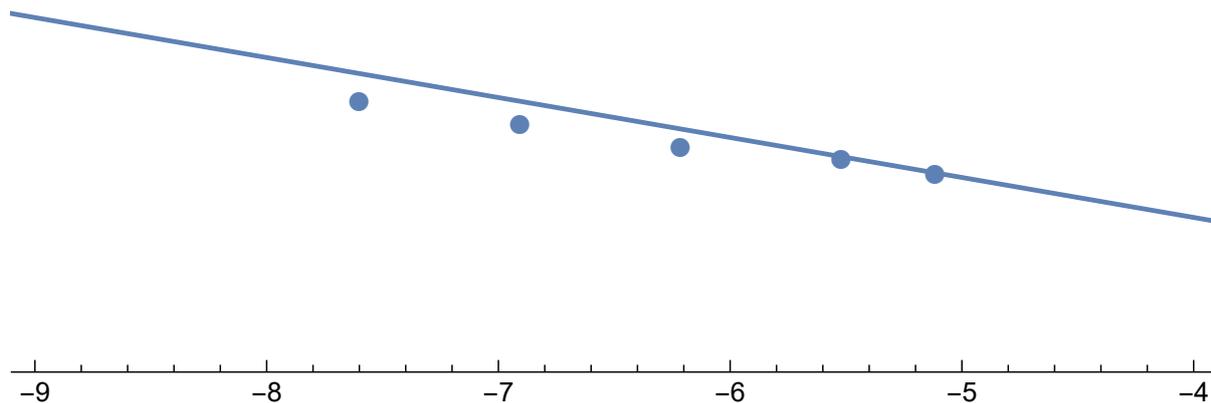


Figure 2: Swelling factor as a function of crosslinker density for nonionic gels. The log volumetric swelling factor is on the Y axis (arbitrary units). The log crosslinker density (w/w) is on the x axis. $y = -3/5x$ is plotted as a guide to the eye.

theory is very good (qualitatively).

The agreement in the scaling between theory and experiment is remarkable, considering that in the two cases presented, two different polymers were used and two different mechanisms were used to expand the gel. In order to obtain a quantitative measure of the agreement with theory, more data and closer analysis would be needed. However, it is clear that the Flory-Huggins theory suffices to explain at least the qualitative behavior of swelling in ionic and nonionic gels.

The agreement of Flory-Huggins theory with experiment is also remarkable, considering the numerous approximations used in formulating the model. For example, that the elastic free energy associated with stretching a polymer is linear in the polymer extension, which is only correct in the Gaussian approximation, and which should thus break down at very large swelling factors. More work is necessary to test the extremes of the theory, with even lower cross-linking density and even higher swelling factors, to find the point at which the theory breaks down.

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