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Structural analysis of charged polymeric networks

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Summary

A new model was developed to accurately describe the swelling behavior of charged polymeric networks. The model incorporates elastic, mixing and ionic contributions to the chemical potential. Changes in the equilibrium degree of swelling as a function of pH can be predicted.

Introduction

Swollen networks of charged macromolecular chains are widely used in the biomedical, pharmaceutical and related fields (1). As discussed by Peppas and Barr-Howell (2), the crosslinked structure of such systems defines their "mesh size" and, therefore, their diffusive characteristics.

One of many methods to determine the number average molecular weight between crosslinks, $\bar{M}_c$, is by equilibrium swelling experiments. Many theories have been presented which analyze the equilibrium swelling behavior of polymeric networks; the earliest one was developed by Flory and Rehner (3).

From their swelling expression, the molecular weight between crosslinks, $\bar{M}_c$, can be expressed by equation (1).

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2]}{[v_{2,s}^{1/3} - \frac{v_{2,s}}{2}]} \tag{1}$$

The parameters used here and throughout this manuscript are: the number average molecular weight of the polymer chains before crosslinking, $\bar{M}_n$; the specific volume of the polymer, $\bar{v}$; the molar volume of the swelling agent, V_1; the polymer volume fraction in the equilibrium-swollen gel, $v_{2,s}$; and the Flory polymer-solvent interaction parameter, χ_1. Equation (1) is applicable for networks without ionic interactions which were prepared by crosslinking in the solid state.

A similar equation which is applicable to systems where solvent was present during the crosslinking process of the macromolecular chains was presented by Peppas and Merrill (4). In equation (2) an additional term representing the polymer volume fraction, $v_{2,r}$, in the relaxed state (after crosslinking but before swelling), is used.

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$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\bar{v}/V_1)[\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2]}{v_{2,r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right]} \tag{2}$$

Model for Ionomeric Networks

When an ionomeric network is placed in a swelling agent, there are three contributions to the free energy of the system: mixing, elastic-retractive, and ionic free energies as expressed by ΔG_{mix}, ΔG_{el}, and ΔG_{ion}, respectively.

$$\Delta G = \Delta G_{mix} + \Delta G_{el} + \Delta G_{ion} \tag{3}$$

These free energies may be related to the respective chemical potential contributions as shown in equation (4).

$$(\Delta \mu_1^*)_{ion} - (\Delta \mu_1)_{ion} = (\Delta \mu_1)_{mix} + (\Delta \mu_1)_{el} \tag{4}$$

Thus, the sum of the contributions to the chemical potential of the mixing and elastic forces due to polymer/solvent interactions is equal to the difference between the ionic contributions from the chemical potentials inside and outside the gel.

The mixing contribution in the previous equation may be derived from liquid lattice theory as

$$(\Delta \mu_1)_{mix} = RT\left(\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2\right) \tag{5}$$

The elastic contribution was derived by Peppas and Merrill (4) from the statistical theory of rubber elasticity for the common case of crosslinking in the presence of a solvent:

$$(\Delta \mu_1)_{el} = RT\left(\frac{V_1}{\bar{v}\,\bar{M}_c}\right)\left(1 - \frac{2\bar{M}_c}{\bar{M}_n}\right)v_{2,r}\left(\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right) \tag{6}$$

The models developed here incorporate an ionic contribution term, which may be related to the concentrations of ionic species within the polymer, c_j, and outside the polymer, c_j^*, as given by

$$(\Delta \mu_i^*)_{ion} - (\Delta \mu_1)_{ion} = V_1 RT \sum_j (c_j - c_j^*) \tag{7}$$

Assuming that the swollen polymer network behaves as a dilute solution with activities that may be approximated by corresponding concentrations, one can write for an anionic polymer network:

$$c_+ = \nu_+ c_s \qquad c_- = \nu_- c_s + ic_2/z_- \tag{8}$$

$$c_+^* = \nu_+ c_s^* \qquad c_- = \nu_- c_s^* \tag{9}$$

Here, c_s^* is the internal concentration of the electrolytic charges. Then,

$$\left(\frac{c_s}{c_s^*}\right)^{\nu+} = \left(\frac{c_s^*}{c_s + ic_2/\nu_- z_-}\right)^{\nu-} \tag{10}$$

and the ionic contribution can be estimated as:

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = V_1 RT \left(\frac{ic_2}{z_-} - \nu(c_s^* - c_s)\right) \tag{11}$$

When $c_s^* > ic_2$, and the concentration difference of the mobile electrolyte between the inside and outside of the gel, $c_s^* - c_s$, is comparable in magnitude to the concentration of counterions, ic_2/z, then

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = V_1 RT \left(\frac{i^2 c_2^2}{2z_+ z_- \nu c_s^*}\right) = V_1 RT \left(\frac{i^2 c_2^2}{4I}\right) \tag{12}$$

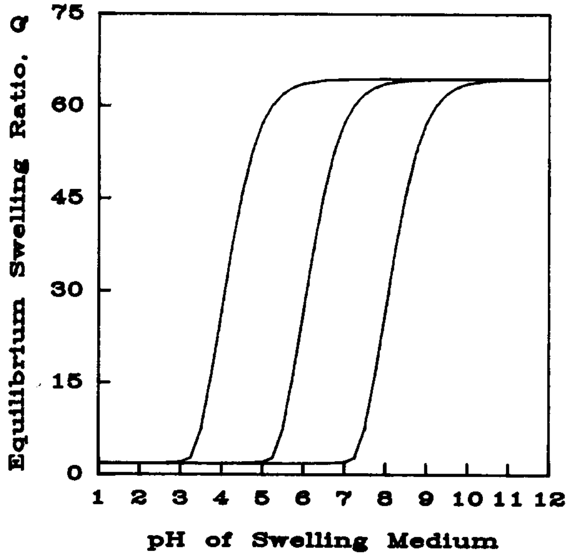

Figure 1. Effect of the pH of the swelling medium on the equilibrium swelling ratio for ionic gels with pK_a of 4,6 and 8 (curves from left to right, respectively).

where I is the ionic strength. By appropriate expression of the degree of ionization, i, in terms of pH and K_a, we obtain

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = \frac{V_1RT}{4I}\left(\frac{v_{2,s}}{\bar{v}}\right)^2\left(\frac{K_a}{10^{-pH}+K_a}\right)^2 \tag{13}$$

Therefore, for polymers crosslinked with solvent present and with a Gaussian chain length distribution, the complete equilibrium expression is

$$\frac{V_1}{4I}\left(\frac{v_{2,s}}{\bar{v}}\right)^2\left(\frac{K_a}{10^{pH}+K_a}\right)^2 = \ln(1-v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2$$

$$+\left(\frac{V_1}{\bar{v}\,\bar{M}_c}\right)\left(1-\frac{2\bar{M}_c}{\bar{M}_n}\right)v_{2,r}\left(\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right) \tag{14}$$

Predictions of Model and Experimental Data

The final equation (14) is one of many equations developed by Brannon (5). It shows the general relation between structural characteristics of the polymer

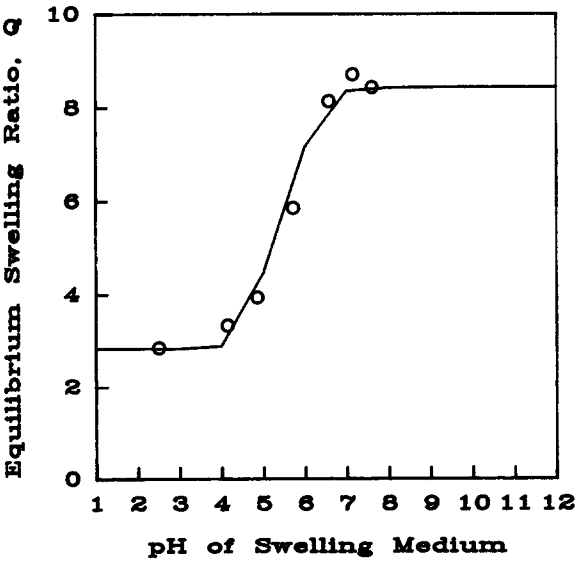

Figure 2. Prediction of the experimental data (o) of Nishi and Kotaka for poly(acrylic acid) gel swelling, using the model of equation (14).

such as the number average molecular weight between crosslinks, $\overline{M}_c$, and the polymer volume fraction, $\upsilon_{2,s}$, ionic characteristics of the gel such as the pK_a, and defining quantities of the surrounding fluid such as the pH and the interaction parameter χ.

One of the most useful functions of this model is to predict the equilibrium swelling ratio, $Q = \upsilon_{2,s}^{-1}$, as a function of the pH of the swelling medium. This prediction is shown in Figure 1 for gels with pK_a values of 4, 6, and 8, when the crosslinking has been set at $\overline{M}_c = 2000$ and the interaction parameter is $\chi_1 = 0.8$. It can be seen that an abrupt change of the swelling ratio is observed at a specific pH value. Thus, one can design novel pH-sensitive hydrogels from knowledge of their structural characteristics.

To show the predictive capabilities of the model, the equilibrium degree of swelling, Q, was plotted as a function of pH for poly(acrylic acid) using the data of Nishi and Kotaka (6). Then, from equation (14) values of $\chi_1 = 0.636$ and $pK_a = 4.75$ were calculated, and the overall pH dependence of the equilibrium swelling was estimated as shown in Figure 2. The data points are very close to the model predictions.

Acknowledgements

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