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Swelling Equilibria for Heterogeneous Polyacrylamide Gels

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SWELLING EQUILIBRIA FOR HETEROGENEOUS POLYACRYLAMIDE GELS

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ABSTRACT

To correlate swelling equilibria for heterogeneous polyacrylamide gels in water to the monomer concentration at preparation, it is necessary to modify the classic Flory-Rehner theory. The necessary modification concerns the relation which links the number of segments between junction points to the monomer concentration at preparation. Modified theory is compared to experimental swelling equilibria for polyacrylamide gels synthesized in water by free-radical copolymerization of acrylamide (AAm) and $N,N'$-methylenebis(acrylamide) (BIS) at various monomer concentrations. Synthesis conditions studied are: 1) different AAm-to-BIS ratios with fixed total monomer concentrations, 2) different total monomer concentrations with fixed AAm-to-BIS ratios, and 3) different AAm-to-BIS ratios with a fixed number of BIS molecules. Modified theory and experiment show good agreement.

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INTRODUCTION

Experimental elastic\textsuperscript{1-5} and swelling\textsuperscript{5-9} studies on polyacrylamide gels have shown that polyacrylamide gels are inherently heterogeneous. Structure inhomogeneities in polyacrylamide gels have also been observed by electron microscopy\textsuperscript{10} and by various scattering experiments\textsuperscript{11-16}.

These studies indicate that in polyacrylamide gels, polymer segments and junction points are not uniformly distributed. However, Flory-Rehner-type theories of gel swelling are derived for homogeneous gels. We present here a simple semi-empirical modification of Flory-Rehner theory\textsuperscript{17-21} to take into account gel heterogeneity.

Using standard molecular-thermodynamic models to describe swelling equilibria for polyacrylamide gels in water, Hooper \textit{et al.}\textsuperscript{9} and Baker \textit{et al.}\textsuperscript{5} attempted to correlate the swelling properties of polyacrylamide gels to the monomer concentration at preparation. Theory and experiment, however, showed only semiquantitative agreement, probably because the elastic contribution to the Helmholtz energy of mixing was given by an expression for a perfect network characterized by the monomer concentration at preparation. Our proposed modification in the elastic contribution dramatically improves agreement with experiment.

THEORETICAL BACKGROUND

Chemical Potential. Consider a binary mixture containing solvent (component 1) and a crosslinked polymer molecule (component 2). Following Flory and Rehner, the change in chemical potential of component 1 consists of a mixing contribution and an elastic contribution:

\[
\Delta \mu_1 = \Delta \mu_1^{\text{mix}} + \Delta \mu_1^{\text{elas}} = \mu_1 (\text{in the gel}) - \mu_1 (\text{pure}) .
\]  

(1)

When the swollen gel is in equilibrium with the surrounding solvent, \(\Delta \mu_1 = 0\).
We use Flory-Huggins theory\textsuperscript{17} for $\Delta \mu_{1}^{\text{mix}}$:

$$\frac{\Delta \mu_{1}^{\text{mix}}}{k_{B}T} = \ln(1 - \phi_{2}) + \phi_{2} + \chi \phi_{2}^{2}$$ \hspace{1cm} (2)

where $k_{B}$ is the Boltzmann constant, $T$ is the absolute temperature, $\phi_{2}$ is the volume fraction of polymer, and $\chi$ is the Flory interaction parameter.

We also use the Flory-Rehner theory\textsuperscript{17-21} to calculate $\Delta \mu_{1}^{\text{elas}}$:

$$\frac{\Delta \mu_{1}^{\text{elas}}}{k_{B}T} = \alpha^{2} \frac{\phi_{2}}{N} - \left(1 - \frac{\xi}{\nu} \right) \frac{\phi_{2}}{N}$$ \hspace{1cm} (3)

where $\alpha$ is the expansion factor, $N$ the number of segments between junction points, $\xi$ the cycle rank, and $\nu$ the number of total chains. For a perfect network,

$$\frac{\xi}{\nu} = 1 - \frac{2}{f}$$ \hspace{1cm} (4)

where $f$ is the functionality of a network.

**Expansion Factor.** We use the affine model\textsuperscript{17-21} to calculate the expansion factor. The affine model assumes that the network chains deform affinely with the volume of a gel:\textsuperscript{17-21}

$$\alpha = \left(\frac{\phi_{0}}{\phi_{2}}\right)^{1/3}$$ \hspace{1cm} (5)

where $\phi_{0}$ is the volume fraction of polymer in the reference state where the conformation of network chains is closest to that of unperturbed Gaussian chains\textsuperscript{22}. The reference
state, however, cannot be chosen exactly\(^2\). In this work, we approximate \(\phi_0\) as the volume fraction of polyacrylamide gels at preparation.

For comparison, we also use the blob model by Painter and Shenoy\(^{23,24}\) to calculate the expansion factor. The blob model\(^{23,24}\) represents a polymer gel by a collection of swollen network chains exhibiting the excluded volume effect. Packing factor \(P\) is used to specify the packing condition of network chains.

In the blob model, the volume fraction of polymer \(\phi_2\) is the average volume fraction of polymer inside a swollen network chain. We define packing factor \(P\) such that the overall volume fraction of polymer is equal to \(P\phi_2\). Painter and Shenoy\(^{24}\) give an approximate relationship between \(P\) and \(f\):

\[
P = \frac{f}{8}\ .
\]

The packing factor may also be preset to 0.637, the filling factor for a random close packing of spheres\(^{24}\). In the blob model, the expansion factor is given by\(^{24}\)

\[
\alpha = \left(\frac{1}{\phi_2 N^{1/2}}\right)^{1/3} .
\]

As a measure of the swelling capacity of a gel, we define swelling factor \(Q\) by

\[
Q \equiv \frac{1}{P\phi_e}
\]

where \(\phi_e\) is the equilibrium volume fraction of polymer. For the affine model, \(P=1\). The equation of phase equilibrium is obtained from combining Eqs. (1), (2), and (3):

\[
\frac{\Delta \mu}{k_B T} = \ln(1 - \phi_e) + \phi_e + x\phi_e^2 + \alpha^2 \phi_e N - \left(1 - \frac{\phi_e}{v/N}\right) = 0 .
\]
HETEROGENEOUS GEL: RESULTS AND DISCUSSION

1. Ideal Network

To illustrate the difference between the swelling behavior of an ideal network and that of a heterogeneous polyacrylamide gel, we first review the swelling equilibria for (nearly) ideal gels in a good solvent. Figure 1a shows the swelling factor for polystyrene gels ($f=3$) in benzene$^{25}$ as a function of $M$, the molecular weight of network chains.

Theoretical curves were calculated with $\chi=0.475$, $\phi_0=1$, and $N$ given by

$$N = \frac{DP}{C_\infty}$$

where $DP$ is the degree of polymerization of the network chain and $C_\infty$ is a proportionality constant which was adjusted such that theory agrees with experiment at $M=30300$. The Flory interaction parameter was obtained by linearly extrapolating to $\phi_2=0$ the measured interaction parameters for the system non-crosslinked polystyrene/benzene in the range $\phi_2=0.3$ to $0.8$ reported by Noda et al.$^{26}$

Experimental data in Figure 1a lie almost on a straight line. The blob model and experiment show good agreement. Theoretical curves for the blob model depend only slightly on the packing factor.

2. Polyacrylamide Gels

We next consider swelling equilibria for polyacrylamide gels synthesized in water by free-radical copolymerization of acrylamide and $N,N'$-methylenebis(acrylamide). Literature data are expressed in terms of two monomer concentrations at preparation defined by$^{5,9}$

$$\%C \equiv \frac{\text{moles of cross-link monomer in feed solution}}{\text{total moles of monomer in feed solution}} \times 100$$

(11)
\[
\%T = \frac{\text{mass of all monomers (g)}}{\text{volume of water (mL)}} \times 100.
\] (12)

The number of segments between junction points \(N\) is related to \(\phi_0\) by

\[
\phi_0 = \frac{\nu N v_p}{V_0}
\] (13)

where \(v_p\) is the segment volume and \(V_0\) is the volume of a gel at preparation. For a perfect network, where one cross-link monomer forms one junction point, the number of total chains is given by

\[
\nu = \frac{N_c}{2}
\] (14)

where \(N_c\) is the number of total cross-link monomers in a feed solution. For a perfect network, Eqs. (13) and (14) give

\[
N \sim \frac{\phi_0}{N_c}.
\] (15)

**Effect of \(\%C\) at Fixed \(\%T\).** Consider swelling equilibria for a series of gels having a fixed \(%T\) (i.e., constant \(\phi_0\)) prepared at various \(%C\). From Eq. (15), for a perfect network,

\[
N \sim \frac{1}{N_c}.
\] (16)

Further, the weight fraction of cross-link monomers is essentially proportional to \(%C\) when \(%C\) is small. Therefore,
\[ N \sim \frac{1}{\%C} \tag{17} \]

Figure 1b shows the swelling factor as a function of \%C for polyacrylamide gels synthesized at fixed \%T^{4,9,12}. Theoretical curves are for 5\% T gels with \( \chi = 0.4668 \), \( f = 4 \), and \( N \) given by

\[ N = \frac{N_0}{\%C} \tag{18} \]

where \( N_0 \) is a proportionality constant adjusted such that theory agrees with experiment at \( \%C = 0.1 \). Similar to the results shown in Figure 1a, the affine model underestimates the slope of the swelling factor. In addition, agreement between the blob model and experiment is not as good as that in Figure 1a. Agreement of theory and experiment does not improve by adjusting \( f \).

Poor agreement of theory with experiment is most likely caused by the incorrect limit of Eq. (15), viz. \( N \to \infty \) as \( N_c \to 0 \), which implies \( Q \to \infty \) as \( \%C \to 0 \). On synthesizing polyacrylamide gels, however, a permanent network cannot be formed below a certain minimum value of \%C or \%T that corresponds to the sol-gel transition point where a gel swells to a very large extent.

To represent swelling equilibria for polyacrylamide gels as a function of \%C, we assume a reasonable relationship between \( N \) and \%C:

\[ N = \frac{N_0}{\%C - \%C^*} \tag{19} \]

where \( \%C^* \) is a constant that depends only on \( \phi_0 \) and is independent of \%C. Parameter \( \%C^* \) crudely represents the cross-link monomer concentration at the sol-gel transition point for polyacrylamide gels prepared at fixed \%T. Figure 2a compares
experiment and theory with $N$ given by Eq. (19). The modified affine model shows better agreement with experiment than the modified blob model. For 5%T gels, however, theory and experiment are only in fair agreement, probably because of clustering of cross-link monomers at high %C; such clustering prevents cross-link monomers from forming junction points. Using the modified affine model, Figure 2b shows the swelling factor for 5%T gels. The dash-dot curve is a fit to the data between %C=0.4 and 2 where theory and experiment show good agreement. In the following calculations, we use only the modified affine model with $f=4$.

**Effect of %T at Fixed %C.** For a perfect network synthesized at fixed %C, $N_c$ is proportional to $\phi_0$ which depends on %T. In that event, Eq. (15) shows that $N$ is independent of $\phi_0$. Because $\Delta \mu_1^{\text{elas}}$ for the blob model is independent of $\phi_0$, the blob model predicts that the swelling factor is independent of $\phi_0$. In the affine model, the swelling factor slightly depends on $\phi_0$ because the expansion factor depends on $\phi_0$ as given by Eq. (5).

Experimental data, however, show a strong dependence of the swelling factor on $\phi_0$. Figure 3a shows the swelling factor for polyacrylamide gels having %C=0.61. Theory and experiment show good agreement by using the modified affine model with $N$ given by

$$N = \frac{N_0}{\phi_0 - \phi_0^*}$$  \hspace{1cm} (20)

where $\phi_0^*$ is a constant that depends on %C but is independent of $\phi_0$. Similar to %C* in Eq. (19), parameter $\phi_0^*$ crudely represents the total monomer concentration at the sol-gel transition point for polyacrylamide gels prepared at fixed %C.
Effect of %T at Fixed $N_c$. Finally, we consider a series of gels synthesized by varying %T (i.e., $\phi_0$) at fixed $N_c$. For a perfect network, $N$ is proportional to $\phi_0$ and a gel swells more as $\phi_0$ rises. Experimental data by Hu et al.\textsuperscript{4}, however, show that the swelling factor decreases as $\phi_0$ increases.

Figure 3b shows the swelling factor for a series of polyacrylamide gels synthesized with a fixed amount of cross-link monomers in a feed solution\textsuperscript{4}. The curve is a fit using the modified affine model with $N$ given by

$$N = \frac{N_0 \phi_0^*}{\phi_0 - \phi_0^*}$$

(21)

where $\phi_0^*$ is a constant that depends on $N_c$ but is independent of $\phi_0$. Parameter $\phi_0$ represents the total monomer concentration at the sol-gel transition point for polyacrylamide gels prepared at fixed $N_c$. For a series of polyacrylamide gels in Figure 3b, the swelling factor decreases with $\phi_0$, probably because significant clustering of cross-link monomers occurs at small $\phi_0$.

CONCLUSIONS

Swelling equilibria for heterogeneous polyacrylamide gels were correlated by using an extended affine model for the elastic contribution to the Helmholtz energy of mixing. Semiempirical parameters were introduced into the equation for a perfect network that relates the number of segments between junction points to the monomer concentration at preparation. These parameters provide a reasonable representation of the sol-gel transition concentrations of polyacrylamide gels which may be obtained from kinetic models of network formation\textsuperscript{27}. Modified theory and experiment show good agreement.
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FIGURE CAPTIONS

Figure 1. (a) Swelling factor for ideal polystyrene gels \((f=3)\) in benzene\(^{25}\): (---) blob model with \(P=0.375\) and \(C_\infty=4.30\), (- - -) blob model with \(P=0.637\) and \(C_\infty=1.69\), (---) affine model with \(C_\infty=0.0544\). (b) Swelling factor for heterogeneous polyacrylamide gels\(^9\): (---) blob model with \(P=0.5\) and \(N_0=48.6\), (- - -) blob model with \(P=0.637\) and \(N_0=70.0\), (---) affine model with \(N_0=428\).

Figure 2. (a) Swelling factor for polyacrylamide gels at fixed \%T. Points are experimental data\(^4,9,12\). For the modified affine model, parameters for Eq. (19) are: (●)\(^4\) \%T=15, \(N_0=224\), \%C\(^*\)=0.0460, (●)\(^12\) \%T=8.6, \(N_0=322\). \%C\(^*\)=0.0373, (●)\(^9\) \%T=5, \(N_0=977\), \%C\(^*\)=0.0454. For the modified blob model (15\%T gels), parameters for Eq. (19) are \(P=0.5\), \(N_0=48.7\). and \%C\(^*\)=0.000227. (b) Swelling factor for 5\%T gels\(^9\): (---) modified affine model with parameters used in Figure 2a, (- - -) fit to the data between \%C=0.4 and 2 by the modified affine model with Eq. (19): \(N_0=877\) and \%C\(^*\)=0.106.

Figure 3. (a) Swelling factor for polyacrylamide gels at fixed \%C=0.6\(^1^1\). Parameters for the modified affine model with Eq. (20) are \(N_0=31.9\) and \(\phi_0^* =0.0186\). (b) Swelling factor for polyacrylamide gels having a fixed number of cross-link monomers\(^4\). Parameters for the modified affine model with Eq. (21) are \(N_0=446\) and \(\phi_0^* =0.0169\).
Figure 1

a

$Q$ vs. $M^{-1}$

- Affine
- Blob $(P=0.375)$
- Blob $(P=0.637)$

Data from Belkebir-Mrani et al. (1977)

b

$Q$ vs. $%C$

- Affine
- Blob $(P=0.5)$
- Blob $(P=0.637)$

Data from Hooper et al. (1990)
Figure 2

Part a: Data from Hu et al. (1993), Mallam et al. (1989), Hooper et al. (1990).

Part b: Modified Affine, Modified Blob (P=0.5).

Legend:
- □ %T=5 Data from Hu et al. (1993)
- • %T=8.6 Data from Mallam et al. (1989)
- • %T=15 Data from Hooper et al. (1990)

---

Fit to all data
- Fit to data between %C=0.4 and %C=2

□ %T=5 Data from Hu et al. (1993)