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Carboxymethyl Cellulose:Polyvinylamine Complex Hydrogel Swelling

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ABSTRACT: The swelling behavior of the polyelectrolyte complex films made from polyvinylamine (PVAm) or poly(vinylformamide-*co*-vinylamine) copolymers and carboxymethyl cellulose (CMC) was studied as a function of polymer composition, pH, and salt concentration. Swelling is determined by the balance between ionic cross-link density, opposing swelling, with solvation and Donnan effects promoting swelling. Films containing excess ammonium groups gave the greatest swelling at low pH, whereas excess carboxyl groups enhanced swelling at high pH. Films with balanced charge stoichiometry (CMC:PVAm 3:1 w:w) gave the minimum swelling. High concentrations of sodium chloride increased swelling due to the decomposition (screening) of ionic cross-links, whereas calcium ion decreased swelling possibly because of calcium dicarboxylate cross-links. A simple swelling model based on the ionization behavior of dilute polymers and ionic cross-linking predicted the major swelling behaviors, including the effects of pH and polymer composition.

Introduction

Polyelectrolyte complexes form as a result of strong electrostatic interactions between oppositely charged polyelectrolytes in water.[1−3] Polymeric complexes can be prepared as colloidal dispersions, layer-by-layer assemblies on surfaces, and macroscopic films and fibers. The potential applications of polyelectrolyte complexes are as diverse as the range of physical forms. For example, colloidally dispersed polyelectrolyte complexes are used as surgical adhesives,[4] paper strengthening additives,[5,6] and matrices for targeted delivery and controlled release of drugs and proteins.[7−9] Polyelectrolyte complex films are used as ultrafiltration membranes,[10,11] and fibers of polyelectrolyte complexes are used as controlled release of bioactive agents.[12] For many of these applications, the polyelectrolyte complexes are employed as water-swollen hydrogels,[4] and both the mechanical and chemical properties of the complexes are sensitive to the degree of swelling. In this paper we describe models that predict the swelling properties of homogeneous polyelectrolyte complex macroscopic films prepared from mixtures of polyvinylamine and carboxymethyl cellulose, both of which are weak polyelectrolytes. The experimental results include the correlation of complex film swelling and wet tensile properties. The relevant literature is now summarized in an effort to put our new work in context.

Hydrogel swelling is controlled by the balance of the elastic forces due to cross-linking, which oppose swelling, and polymer/water interaction and Donnan pressure, which promote swelling.[13] Mathematically, this is described by the following equation

$$\Pi = \Pi_{mix} + \Pi_{el} + \Pi_{don} \tag{1}$$

where Π_{mix} is the contribution of solvent/polymer interaction to swelling pressure, Π_{el} is the elastic contribution, and Π_{don} is the Donnan contribution. At equilibrium the total pressure, Π, is zero.[14−16] In the case of polyelectrolyte complexes, the cross-links are usually due to the electrostatic association of oppositely charged polymer segments. If the polyelectrolytes are based on weak acid groups, such as carboxyls, and/or weak bases, such as amine groups, the polymer charge density, and therefore the cross-link density, will be functions of pH. For example, the chitosan/pectin complex[17] and chitosan/cashew nut gum complex[18] both display minimum swelling at pH 3.5 and pH 5, respectively, reflecting the pH sensitivity of cross-linking.

The swelling behavior of most hydrogels is sensitive to ionic strength. For charged gels with covalent cross-links, swelling usually decreases with increasing ionic strength because of the attenuation of Donnan and other electrostatic-driven phenomena.[19−21] With polyelectrolyte complex hydrogels, ionic strength effects are complicated by the fact that ionic cross-links dissociate at high ionic strengths.[22] In such cases, polyelectrolyte complex swelling may increase with increasing ionic strength.[18]

There are a few publications describing both the swelling and mechanical properties of polyelectrolyte complex materials. For the poly(styrenesulfonate)/poly(diallyldimethyl ammonium chloride) complex films, Vogel et al.[4] observed a linear decrease of tensile strength with water content from 30 to 90%, corresponding to swelling ratios (wet mass/dry mass) from 1.4 to 10. Kalyuzhnaya et al.[23] reported modulus and water content as a function of polymer ratio for the poly(acrylic acid) and poly(ethylenepiperazine) complex films. They observed that modulus values increased with decreasing water contents. Yin et al.[24] investigated water content and tensile strength as a function of chitosan content for the chitosan/gelatin complex films. The water content decreases with increasing chitosan content, and tensile strength increases with increasing chitosan content.

Herein we present the swelling properties of polyelectrolyte complexes based on mixtures of polyvinylamine (PVAm) and carboxymethyl cellulose (CMC) (see Figure 1 for structures). PVAm has recently become commercially available[25] and includes a range of copolymers with poly(*N*-vinylformamide) (PNVF); see Figure 1 for structures. Both PVAm and its complexes with anionic polymers have shown promise as strength enhancing additives for wet and dry paper.[26,27] The overall goal of this research is to link PVAm/CMC complex film wet and dry mechanical properties to composition, pH, and ionic strength with a view to understanding the factors influenc-

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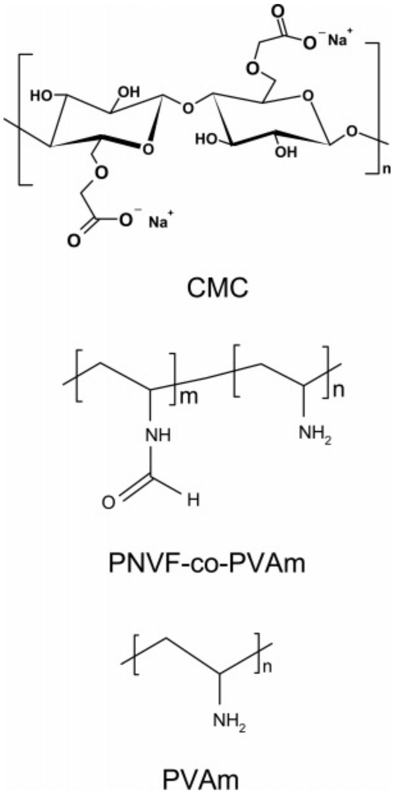

Figure 1. Structures of polymers used in this work.

ing the wet adhesive properties of the corresponding colloidal complexes.

In the first paper in this series we described the preparation and characterization of homogeneous, transparent, macroscopic polyelectrolyte complex films based on PVAm/CMC and PVAm-*co*-PNVF/CMC mixtures cast from formic acid. We also reported the dry mechanical properties of complexes as functions of polymer ratio, polymer composition, and relative humidity.[28] We found that in dry, or nearly dry, PVAm/CMC complex films hydrogen bonding was the main intermolecular interaction, whereas in water, ionic cross-linking dominates. In this paper, we report the swelling behavior and wet mechanical properties of PVAm/CMC and PVAm-*co*-PNVF/CMC complex films as functions of pH, ionic strength, and complex composition. Thus, this paper serves to characterize the cohesive properties of wet polyelectrolyte complexes. The adhesive interactions between PVAm/CMC complexes and wet cellulose will be discussed in a future publication.

Experimental Section

Materials. Poly(vinylformamide-*co*-vinylamine) (PNVF-*co*-PVAm) samples with 60% and 82 mol % vinylamine were supplied by BASF. The polymers were obtained from the partial hydrolysis of poly(*N*-vinylformamide) (PNVF) with a molecular weight of 340 kDa. A sample of the PNVF-*co*-PVAm copolymers was further hydrolyzed to give polyvinylamine (PVAm) homopolymer in the presence of 5% NaOH at 75 °C for 48 h under nitrogen purge.[29] PVAm and copolymers were dialyzed against water and freeze-dried. The degree of hydrolysis was determined by ^{1}H NMR, and the equivalent weights of the freeze-dried polymers were measured by conductometric titration (92 g/mol of N in PVAm and 311 g/mol of carboxyl in CMC).

Three samples of sodium carboxymethyl cellulose (CMC) were purchased from Aldrich and used as received. Most results involved a CMC with a molecular weight of 90 kDa and a degree of carboxymethyl substitution (DS) of 0.7; this is the number of substituents per sugar ring. The carboxymethyl substitutions have been reported to randomly occur at the C2, C3, and C6 hydroxyls.[30,31]

For most experiments, the pH and ionic strength (0.1 M) were controlled with the following buffer solutions: 0.2 M HCl 6.5 mL + 0.2 M NaCl 43.5 mL, diluted to 100 mL giving pH 2; 0.2 M acetic acid 41 mL + 0.2 M sodium acetate 9 mL + 0.4797 g NaCl, diluted to 100 mL giving pH 4; 0.2 M acetic acid 14.8 mL + 0.2 M sodium acetate 35.2 mL + 0.1732 g NaCl, diluted to 100 mL giving pH 5; 0.1 M KH_2PO_4 50 mL + 0.1 M NaOH 5.6 mL + 0.2597 g NaCl, diluted to 100 mL for pH 6; 0.1 M KH_2PO_4 50 mL + 0.1 M NaOH 29.1 mL + 0.1223 g NaCl, diluted to 100 mL for pH 7; 0.1 M tris(hydroxymethyl)aminomethane 50 mL + 0.1 M HCl 29.2 mL + 0.4142 g NaCl, diluted to 100 mL for pH 8; 0.1 M tris 50 mL + 0.1 M HCl 5.7 mL + 0.5517 g NaCl, diluted to 100 mL for pH 9; and, 0.025 M sodium borate 50 mL + 0.1 M NaOH 18.3 mL + 0.2586 g NaCl, diluted to 100 mL at pH 10. The reagents used for preparation of buffers and other solutions were obtained from Aldrich and were of 99% purity. Milli-Q water was used throughout the work.

Film Formation. 1% PVAm in 50% formic acid aqueous solution was mixed with 1% CMC in 50% formic acid with weight ratios of CMC to PVAm ranging from 1 to 5. The mixtures were stirred for 24 h at room temperature and then cast in polystyrene Petri dishes. After drying and film formation in the fume hood for 24 h, the resulting complex films were washed by soaking in ethanol. Finally, the films were dried overnight under vacuum at room temperature. Details of film analysis and purity were reported previously.[28]

Swelling Measurement. The film samples used for swelling tests were cut into blocks of size 1 cm × 1 cm with a thickness of 40 ± 3 μm. After drying overnight under vacuum, each block was weighed and then placed in a Petri dish filled with salt solution or buffer solution for 3 days at room temperature. The block was then taken out and weighed after the water on the surface was carefully and quickly wiped with blotting paper. The swelling ratio was calculated as the wet mass divided by the dry film mass. The reported swelling results are the average of three measurements.

Tensile Strength Measurement. The washed and freeze-dried polyelectrolyte complex films were conditioned at 23 ± 1 °C and 50 ± 2% relative humidity for 24 h and then cut into 5 cm × 1.5 cm strips. The thickness of each strip was measured using a digital micrometer (Testing Machines Inc., Point Claire, Québec) and was recorded as the average of five measurements. The tensile strength measurement was performed on an Instron 4411 universal testing system (Instron Corp., Norwood, MA), fitted with a 50 N load cell, with the film immersed in a 0.01 M NaCl solution at pH 7. The film was clamped on the instrument. After 10 min of swelling, the gauge length was adjusted and measured, and the test performed at a crosshead rate of 25 mm/min, following the ASTM D882-02 procedure for thin plastic films. The stress at break was recorded as the tensile strength of the complex films. Every recorded value was the average of three samples. More details and photographs of the tensile experiments are available in a thesis.[32]

Results

Uniform, transparent CMC/PVAm films were cast from formic acid and cleaned; details of the methodology and film purity and uniformity were described previously.[28] The effect of pH on the swelling of the complex films with various CMC:PVAm dry mass ratios is shown in Figure 2. Swelling is expressed as the ratio of the weight of the film at equilibrium swelling to that of dry film. The lines show modeling results which will be discussed later. Two main observations from this figure are (i) at constant composition the minimum swelling (corresponding to maximum cross-linking) occurs at pH 4−7 depending on composition and (ii) at neutral pH the minimum swelling corresponds to the CMC:PVAm film with an intermediate dry mass ratio of 3:1. Note that the complex films dissolved at pH < 2 and at pH > 12.

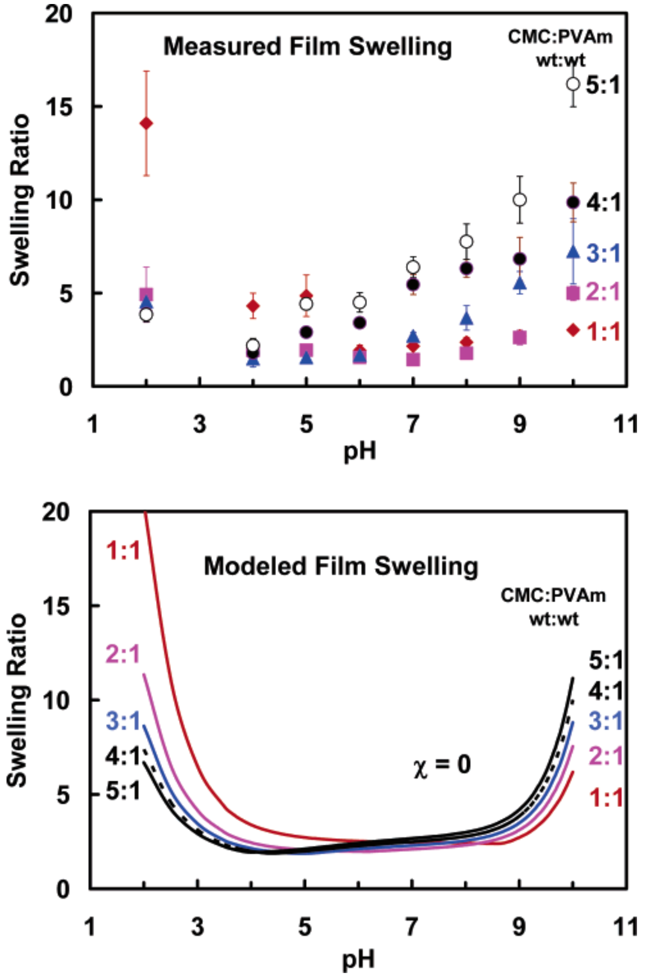

Figure 2. Influence of pH on the swelling of CMC (90 kDa, DS 0.7): PVAm (340 kDa) complex films. The labels give the CMC:PVAm mass ratio. The pH was controlled by buffers with an ionic strength of 0.1 M. The points are experimental data, and the curves are simulation results. The error bars represent standard deviations based on three measurements.

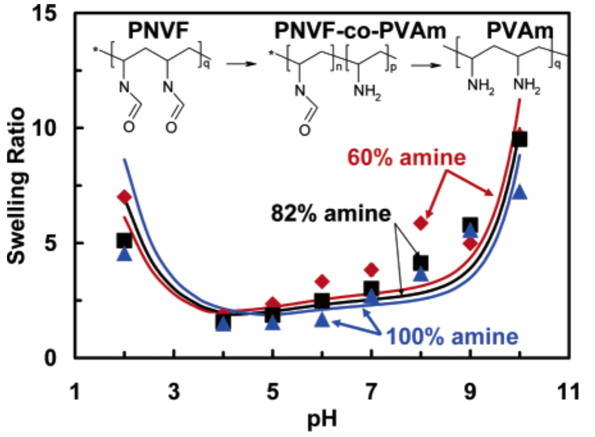

Figure 3. Influence of the degree of PNVF hydrolysis on the swelling behavior of complex films made from 3:1 CMC (90 kDa, DS 0.7): PNVF-*co*-PVAm (340 kDa). The pH was controlled by buffers and the ionic strength was 0.1 M. The curves were calculated with eq 16 assuming $\chi = 0$. The degree of hydrolysis influences the equivalent weight, EW_p in eq 4 of the model.

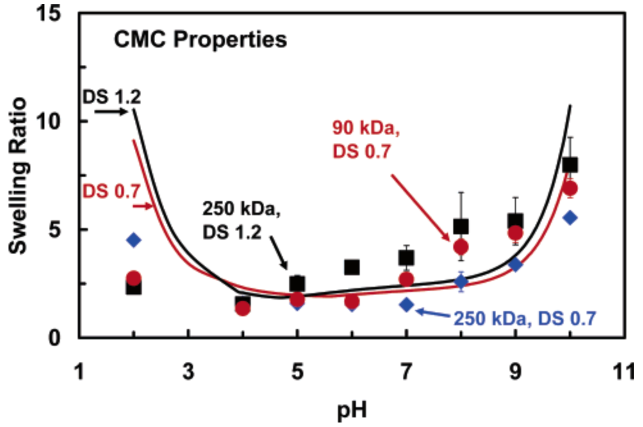

Figure 4. Influence of CMC MW and DS on the swelling behavior of PVAm:CMC = 3:1 complex films in buffers with ionic strength of 0.1 M. The PVAm molecular weight was 150 kDa, and the curves were calculated with eq 16 with $\chi = 0$.

Polyvinylamine is prepared by the hydrolysis of poly(*N*-vinylformamide) (PNVF); partial hydrolysis yields a range of potential PNVF-*co*-PVAm copolymers (see Figure 1 for structures) between PNVF and PVAm homopolymers. The effect of PNVF-*co*-PVAm composition on swelling is illustrated in Figure 3, where the copolymer composition is expressed as the mole percent formamide groups hydrolyzed to amines. At a given pH, the swelling decreased with increasing amine content in the copolymer. The films based on mixtures of nonionic PNVF homopolymer and CMC completely dissolved when placed in water because ionic cross-links could not form.

CMC structure is determined by two parameters: the molecular weight and the degree of substitution (DS), which is the average number of carboxymethyl moieties per sugar ring. Figure 4 shows the influence of CMC molecular weight and carboxyl content. At a constant mass ratio of CMC:PVAm = 3:1, the swelling increased with increasing DS, but was not dependent on CMC molecular weight.

The CMC/PVAm films persist in water because of ionic cross-links. Both the Donnan swelling pressure and the ionic cross-links can be sensitive to electrolyte concentration. In their 1989 review article, Philip et al. explain that electrolyte can induce a “salting-out” driving phase separation of a gel or electrolyte can “shield” electrostatic interactions which decrease cross-link density. Complexes based on anionic polyacrylamide and polyethylenimine dissolved in concentrated sodium chloride, indicating a loss of cross-linking, whereas complexes based on mixtures of cationic and anionic polyacrylamides aggregated to give a shrunken gel indicating salting-out.[3] More recently, Dubas and Schlenoff have shown that polyelectrolyte multilayers, prepared by layer-by-layer assembly, may swell more or less with salt addition depending upon the nature of the polymers strength.[33] Relatively hydrophobic chains will salt out with electrolyte addition giving less swelling, whereas hydrophilic chains will swell more reflecting a loss in electrostatic cross-links. Figure 5 shows the effect of NaCl and $CaCl_2$ on the swelling of our complex films formed with three types of PVAm-*co*-PNVF. To avoid the interference of buffer with the salt effect, the tests here were performed in the absence of buffer. In sodium chloride swelling decreased with increasing salt concentration. The PVAm-*co*-PNVF samples with the lower degrees of hydrolysis gave the highest swellings because at 3:1 CMC:PVAm-*co*-PNVF were furthest from stoichiometric balance. In $CaCl_2$, there was an extreme decrease in swelling at the lowest calcium ion concentration. Higher levels of calcium did not further influence swelling significantly. We propose that in the films made with 60 and 82% hydrolyzed PNVF the excess carboxyl groups are cross-linked with calcium ions. The ability of calcium to bridge carboxyl groups is well documented.[34−36]

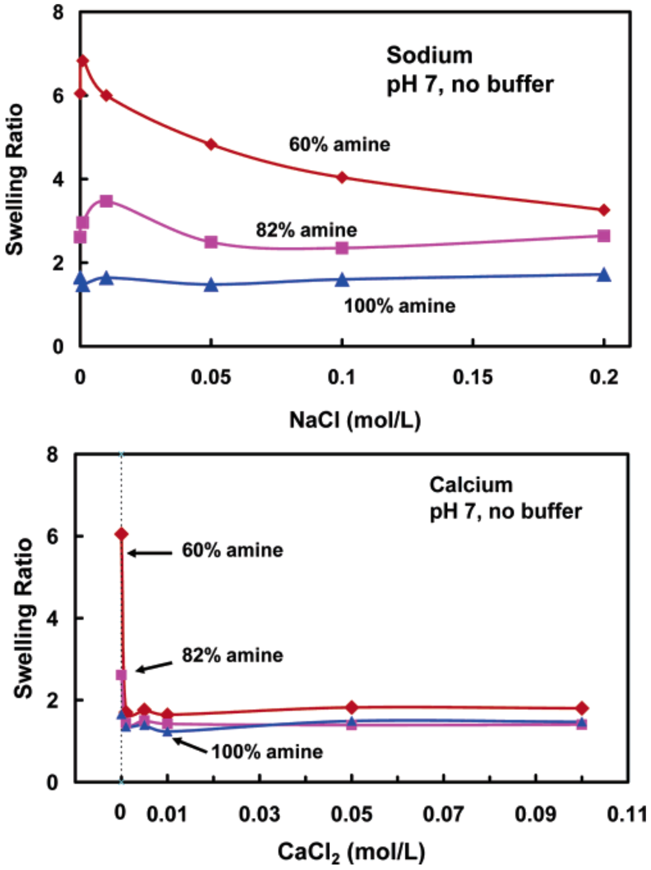

Figure 5. Effect of salt on the swelling behavior of 3:1CMC (90 kDa, DS 0.7):PVAm (340 kDa) and CMC (90 kDa, DS 0.7):PNVF-*co*-PVAm (340 kDa) complex films at pH 7 in the absence of buffer.

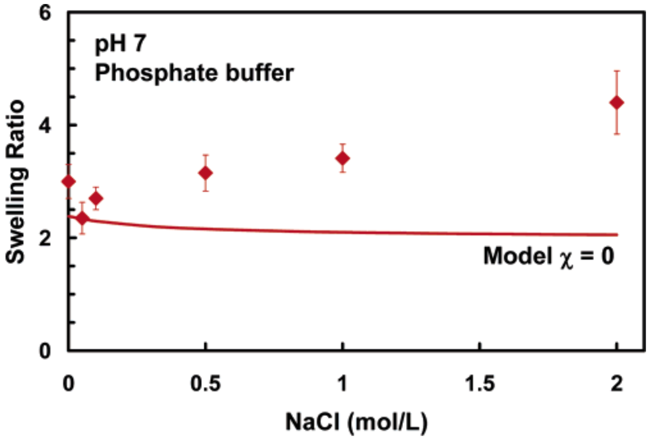

Figure 6. Effect of ionic strength on the swelling of 3:1 CMC (90 kDa, DS 0.7):PVAm (340 kDa) complex film in pH 7 phosphate buffer. Curves represent simulation results from eq 16 with $\chi = 0$.

The swelling behavior of the CMC:PVAm complex films over a wider range of salt concentration in buffer is given in Figure 6. Like the buffer-free results in Figure 5, salt addition initially produces a decrease in swelling. However, swelling increased at much higher salt concentrations, perhaps because of a decrease in electrostatic cross-linking in the highly screened environment.

We measured the tensile strength for the films submerged in buffer, and the results are plotted against the swelling ratio in Figure 7. The slope of the log−log plot is −1.65, which is lower than −3.09, the value reported for chitosan/gelatin complexes.[24] The implication of this result is that when polyelectrolyte complexes are used as wet adhesives, the compositions giving the lowest swelling should give the highest cohesive strength. Factors influencing wet adhesion of the complexes to other materials will be discussed in a future publication.

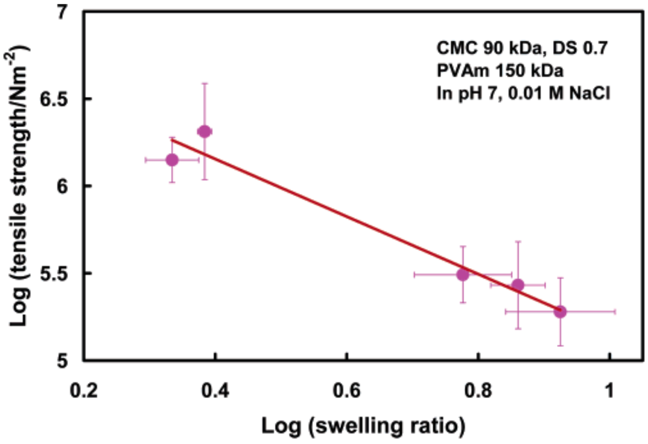

Figure 7. Log−log relationship between tensile strength and swelling ratio in 0.01 M NaCl for the PVAm:CMC complex films. The slope of fitted curve is −1.65, and the preexponential term is $1 \times 10^{6.81}$ N/m^2.

Discussion

In this section we describe the application of existing gel swelling models to our swelling data. In addition to the models themselves, the following assumptions were made: (1) The cross-link density was controlled by the binding equilibrium of positively charged amines and negatively charged carboxyls. (2) The degrees of ionization of PVAm and CMC in the complexes were equal to values measured for the isolated polymer in solution. It should be easier to ionize groups in a complex than in the isolated polymer so this assumption will underestimate ionization and thus cross-link density.

Equation 1 (see Introduction) divides swelling into three contributions: Π_{mix}, Π_{el}, and Π_{don}. Expressions for these terms are now presented. The contribution of polymer/solvent mixing to the osmotic pressure was modeled by Flory's classic theory.[14]

$$\Pi_{\text{mix}} = \frac{-RT}{V_{\text{w}}}[\phi + \ln(1 - \phi) + \chi\phi^2] \qquad (2)$$

where ϕ is the volume fraction of the polymer blend, χ is the Flory−Huggins interaction parameter, R is the gas constant, T is temperature, and V_{w} is the molar volume of water.

The contribution of elastic free energy to the swelling is given by

$$\Pi_{\text{el}} = \frac{RT\phi_0}{V_{\text{w}}N_{\text{x}}}\left[\frac{1}{2}\frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \qquad (3)$$

where ϕ_0 is the volume fraction of the polymer in a reference state (herein we assume $\phi_0 = 1$) and N_{x} is the average number of monomer units between cross-links.[14] The value of N_{x} can be calculated as follows. Assuming r is the mass ratio of dry CMC to PVAm, EW$_{\text{p}}$ is the equivalent weight of PVAm or PNVF-*co*-PVAm, and EW$_{\text{c}}$ is the equivalent weight of CMC, the concentrations (mol/L gel) of charged amine groups, C_{p}, and charged carboxyl groups, C_{c}, in the swollen film are

$$C_{\text{p}} = \frac{\rho\alpha_{\text{p}}\phi}{\text{EW}_{\text{p}}(1 + r)} \qquad (4)$$

$$C_c = \frac{\rho r \alpha_c \phi}{\mathrm{EW}_c(1+r)} \tag{5}$$

$$\rho = \frac{1+r}{\dfrac{1}{\rho_p} + \dfrac{r}{\rho_c}} \tag{6}$$

where ρ, ρ_p, and ρ_c are the densities of polyelectrolyte complex, PVAm, and CMC in the dry state, respectively, and α_p and α_c are the degrees of ionization of PVAm and CMC. In previous work we have shown that the ionization of behavior of polyvinylamine is reasonably modeled by the Katchalsky equations,[37] whereas the behavior of CMC can be fitted to the extended Henderson−Hasselbalch model.[38] The ionization equations are given in our previous paper,[38] and Figure 8 shows the calculated degree of ionization as a function of pH for both polymers in 0.01 M NaCl.

The corresponding total molar concentration of charged polymer segments per unit volume of gel is

$$C_T = \frac{\rho\phi}{\mathrm{EW}_p(1+r)} + \frac{\rho r \phi}{\mathrm{EW}_c(1+r)} \tag{7}$$

We assume that cross-links are formed by the association of oppositely charged polymer segments and that this process is governed by the equilibrium constant. Thus, the number of cross-links per unit volume (X_T) is given by

$$K = \frac{X_T}{(C_p - X_T)(C_c - X_T)} \tag{8}$$

where K is the binding constant (we assumed $K = 10^5$ L/mol in the calculation). Finally, the average number of segments between cross-links (N_x) is given by

$$N_x = \frac{C_T}{X_T} \tag{9}$$

The contribution of Donnan potential to the swelling pressure in the presence of univalent salt is given by

$$\Pi_{\mathrm{don}} = RT[(C_+^i + C_-^i) - (C_+^e + C_-^e)] \tag{10}$$

where C_+^i,C_-^i, C_+^e, and C_-^e are concentrations of positive and negative mobile ions inside (i) and exterior (e) to the gel. Thus, the following relationships hold:

$$C_+^i C_-^i = C_+^e C_-^e \qquad \text{Donnan equilibrium} \tag{11}$$

$$C_+^i = C_-^i + C_c - C_p \qquad \text{electroneutrality for negatively charged gel} \tag{12}$$

$$C_-^i = C_+^i + C_p - C_c \qquad \text{electroneutrality for positively charged gel} \tag{13}$$

$$C_+^e = C_-^e \qquad \text{electroneutrality for external solution} \tag{14}$$

Substituting eqs 11−14 into eq 10 gives

$$\Pi_{\mathrm{don}} = RT\{[(C_p - C_c)^2 + 4(C_+^e)^2]^{1/2} - 2C_+^e\} \tag{15}$$

The total osmotic pressure is the sum of three contributions:

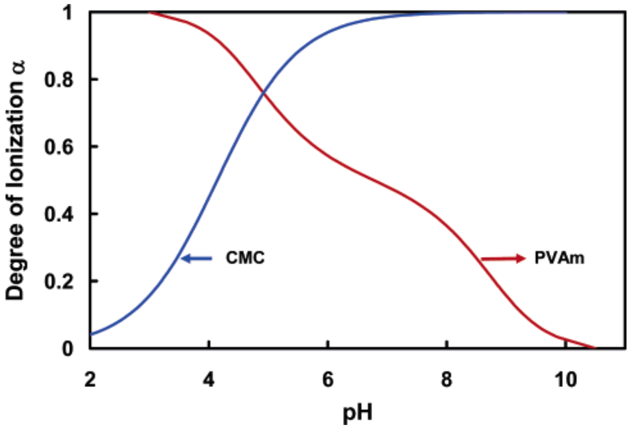

Figure 8. Calculated degrees of ionization for PVAm and of CMC as functions of pH in 0.01 M NaCl. Curves are calculated from the modified Katchalsky and extended Henderson−Hasselbalch equations. (Details are given elsewhere.[38])

$$\Pi = \frac{-RT}{V_w}[\phi + \ln(1-\phi) + \chi\phi^2] + \frac{RT\phi_0}{V_w N_x}\left[\frac{1}{2}\frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] + RT\{[(C_p - C_c)^2 + 4(C_+^e)^2]^{1/2} - 2C_+^e\} \tag{16}$$

MathCAD was used to obtain the volume fraction ϕ_e at which there is no net pressure, i.e., $\Pi = 0$, to give the equilibrium swelling, $1/\phi_e$. A sample calculation is available as Supporting Information.

Figure 9 shows the relative contribution from each interaction to the total swelling at various pH values. The dominant terms are those for polymer/solvent mixing and elastic contributions.

The swelling model (eq 16) has two unknown (adjustable) parameters: the Flory−Huggins interaction parameter (χ) and the binding constant between cationic PVAm segments and anionic CMC segments (K defined in eq 8). For K, we assumed a large constant value of 10^5 L/mol.

Experimental swelling data are compared with the model predictions in Figures 2−4 and 6, where χ was assumed to be 0. Figure 2 shows that the model predicts the overall swelling vs pH behavior, including the relative positions of the films of various compositions. The same results are shown in Figure 10 as a plot of predicted vs measured swelling. The best agreement is at low swelling, corresponding to neutral pH values.

The model also predicts the relative changes in swelling with the degree of PNVF hydrolysis (Figure 3) and CMC degree of substitution (Figure 4). On the other hand, the model did not predict the increase in swelling at high pH (Figure 6) which we attribute to the loss of ionic cross-links due to screening. Ionic strength effects could be incorporated into the cross-link formation in eq 8.

A significant weakness of the swelling model is the use of a single parameter, χ, to describe the interaction of both charged and uncharged segments of PVAm and CMC with water. Figure 11 shows the sum of squares of the deviation divided by the number of data points, L^2, of the predicted swelling from the experimental swelling for the data in Figure 2 as functions of film composition for three values of χ. The lower the L^2 value, the better the model. Clearly, no individual χ value gives the best fit over the range of compositions. When PVAm is in excess (low CMC:PVAm ratio), the highest value of χ gave the best prediction, whereas low χ gave a better fit when CMC was in excess. The use of separate χ values for each polymer and some kind of a mixing rule such as the Scott−Flory−Huggins formula for a binary mixture of a random copolymer could handle this, albeit with an increase in the number of model parameters.[39,40]

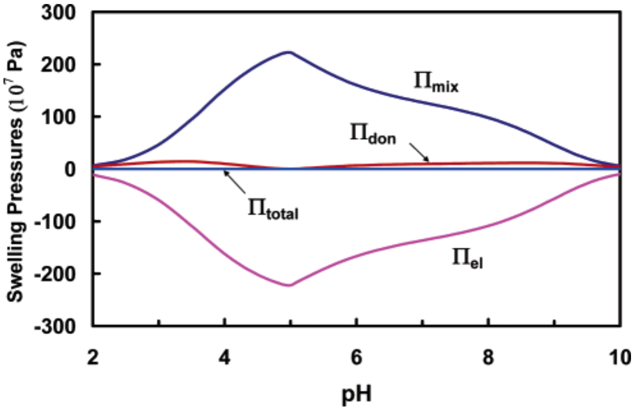

Figure 9. Relative contribution of each component to the total swelling for 3:1 CMC (90 kDa, DS 0.7):PVAm (340 kDa) complex films in buffers of ionic strength of 0.1 and $\chi = 0$.

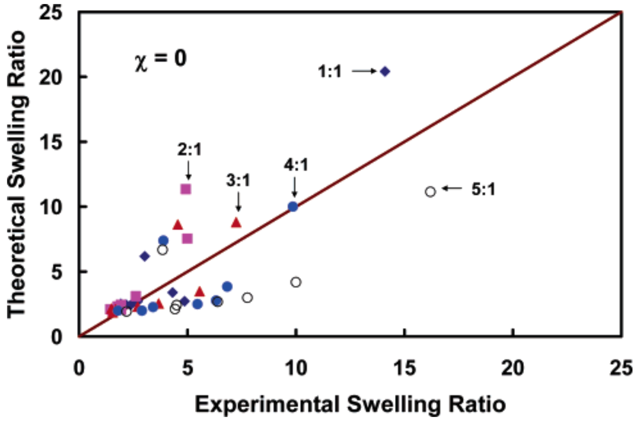

Figure 10. Comparison of theoretical swelling ratio with experimental swelling ratio for complex films with various CMC:PVAm mass ratio (data from Figure 2).

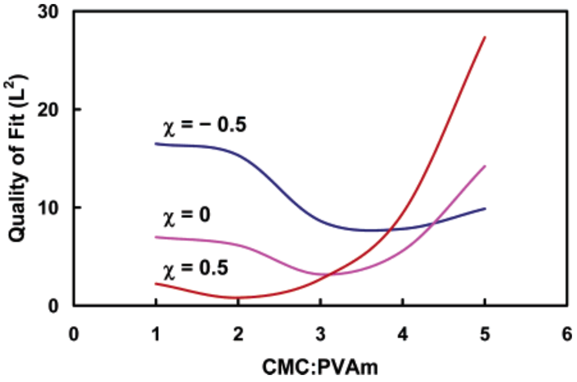

Figure 11. Influence of Flory−Huggins χ on the quality of the swelling model fit to the data in Figure 2. L^2 is the sum of the squares of the deviations of the equivalence line from the experimental points divided by the number of experimental points.

In summary, the simple model expressed as eq 16 with only two adjustable parameters simulates the effects of pH and polymer composition, underscoring the importance of ionic cross-links in film swelling.

Conclusions

1. The swelling behavior of polyelectrolyte complex films, based on mixtures of CMC and PVAm, is determined by the balance between ionic cross-links with solvation and Donnan effects. Thus, ionic cross-links decrease swelling and excess polyions in the film increase swelling.

2. Films containing excess ammonium groups gave the greatest swelling at low pH, whereas excess carboxyl groups enhanced swelling at high pH. Films with balanced charge stoichiometry (CMC:PVAm 3:1) gave the minimum swelling.

3. High concentrations of sodium chloride increased swelling due to the decomposition (screening) of ionic cross-links, whereas calcium ions decreased swelling possibly because of calcium dicarboxylate cross-links.

4. A simple swelling model based on the ionization behavior of dilute polymers and ionic cross-linking, predicted the major swelling behaviors, including the effects of pH and polymer composition.

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Supporting Information Available: An example MathCad printout for a swelling calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

List of Symbols

C_c = concentration of charged amine groups in the swollen gel (mol/L)
C_p = concentration of charged carboxyl groups in the swollen gel (mol/L)
C_T = total concentration of polymer bound charged groups in the swollen gel (mol/L)
C_+^e = concentration of positive mobile ions exterior to the gel (mol/L)
C_+^i = concentration of positive mobile ions in the gel (mol/L)
C_-^e = concentration of negative mobile ions exterior to the gel (mol/L)
C_-^i = concentration of negative mobile ions in the gel (mol/L)
I = ionic strength
K = binding constant of polyvinylamine with carboxymethyl cellulose (L/mol)
N_x = average number of monomer units between cross-links
r = weight ratio of carboxymethyl cellulose to polyvinylamine
R = gas constant (8.3145 J/(mol K))
T = temperature (K)
V_w = molar volume of solvent (m^3/mol)
X_T = number of cross-links per unit volume of gel (mol/L)
EW_c = equivalent weight of carboxymethyl cellulose (kg/mol)
EW_p = equivalent weight of PVAm or PNVF-*co*-PVAm (kg/mol)
α_c = degree of ionization of carboxymethyl cellulose
α_p = degree of ionization of polyvinylamine
Π_{don} = pressure due to Donnan equilibrium effects (Pa)
Π_{el} = pressure due to network elasticity (Pa)
Π_{mix} = pressure due to solvent/polymer mixing (Pa)
ρ = density of dry polymer blend (kg/m^3)
ρ_c = density of dry carboxymethyl cellulose (kg/m^3)
ρ_p = density of dry polyvinylamine (kg/m^3)
ϕ = volume fraction of polymer in the gel
ϕ_0 = volume fraction of the polymer in a reference state
χ = Flory−Huggins polymer−solvent interaction parameter

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