Collapse of Acrylamide-Based Polyampholyte Hydrogels in Water

Saadet Dogu, Melek Kilic, Oguz Okay

Department of Chemistry, Istanbul Technical University, Istanbul, Turkey

ABSTRACT: The swelling behavior of balanced acrylamide (AAm)-based polyampholyte hydrogels in water and in aqueous salt (NaCl) solutions was investigated. Equimolar ratio of the ionic comonomers 4-vinylpyridine (cationic monomer) and acrylic acid (anionic monomer) were used together with the nonionic monomer AAm in the hydrogel preparation. The variations of the hydrogel volume in response to changes in pH were measured. It was found that the hydrogels are in a collapsed state not only at the pH of the isoelectric point pH_{IEP} but also over a wide range of pH including pH_{IEP}. The width of the collapsed plateau increased and the hydrogels assumed a more compact state as the ionic group content is increased. The antipolyelectrolyte behavior was observed along the collapsed plateau region, where the gel occupies a larger volume in salt solution. The experimental swelling data were compared with the predictions of the Flory-Rehner theory of swelling equilibrium including the ideal Donnan equilibria. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1375–1382, 2009

Key words: polyampholyte gels; 4-vinylpyridine; acrylic acid; swelling; phase transition

INTRODUCTION

Polyampholytes are materials containing both positively and negatively charged functional groups. Since the first studies on synthetic polyampholytes in 1950s,[1,2] these materials have received much attention due to the fact that they form model systems for more complicated biological systems such as proteins. Theories qualitatively predict the behavior of polyampholyte chains as a function of net charge and salt concentration.[3–6] When the net charge is very small, the conformation of the molecule is collapsed at very low ionic strength because of the strong attractive interactions between monomers.

Polyampholyte hydrogels have been the subject of relatively few experimental studies.[7–13] Such materials are usually prepared by cross-linking copolymerization of two ionic comonomers having oppositely charged functional groups. The net charge in a polyampholyte hydrogel can be adjusted by changing the comonomer feed composition or, in case of weak electrolyte functional groups, by changing pH of the swelling medium. If the net charge is large, the hydrogel behaves like a conventional polyelectrolyte

in which the osmotic pressure of the counter ions plays a major role. In a balanced polyampholyte hydrogel, that is, if the hydrogel contains equal numbers of positive and negative monomer units, the net electrostatic forces are attractive so that, in water, the network chains have a tendency to collapse into a compact globule. Addition of salt screens these attractive interactions and induces a gel swelling. Therefore, unlike polyelectrolytes, balanced polyampholyte hydrogels have the unique capacity to swell in aqueous solutions of high ionic strengths. This so-called antipolyelectrolyte property has a number of important implications for their technological use. Prausnitz and coworkers[7,8] investigated the swelling behavior of polyampholyte hydrogels based on [(Methacrylamido)propyl]trimethylammonium chloride (MAPTAC) and sodium styrene sulfonate (SSS) comonomers. They showed that the ideal Donnan theory describes qualitatively the swelling behavior of the hydrogels in water and in NaCl solutions. Nisato et al.[14] reported that the degree of charge imbalance of the gel network determines the properties of polyampholyte hydrogels. Takeoka et al.[15] observed first-order phase transitions in MAPTAC/SSS hydrogels immersed in water-organic solvent mixtures. English et al.[16] showed that the collapse transitions in polyampholyte hydrogels at low and intermediate salt concentrations could be predicted by the equilibrium theory of swelling including the Donnan equilibria. Annaka and Tanaka[9] investigated the swelling behavior of hydrogels consisting of MAPTAC and

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acrylic acid (AAc) units. They observed the existence of several gel phases in equilibrium with water. Later, it was shown that the phases mainly appear due to the nonequilibrium between the mobile ions inside the gel with those in the external solution.[10]

In contrast to polyampholyte solutions where the polymer chains collapse at the isoelectric point (IEP), weak electrolyte polyampholyte gels generally exhibit a wide collapsed plateau around the IEP. Theoretical calculations show that this unique feature is due to the fact that the pH inside the gel differs from that of the external solution in the collapse region. Recently, we have investigated the behavior of AAm/MAPTAC/AAc hydrogels containing 70 mol % AAm and 30 mol % ionic comonomer with various proportions of MAPTAC and AAc units.[17] It was shown that the collapsed plateau around the IEP becomes shorter as the MAPTAC content of the hydrogels decreases and, at 1 mol % MAPTAC, it becomes a point at the IEP, as usually observed in polyampholyte solutions.

In this work, we investigated the behavior of balanced polyampholyte hydrogels as a function of their ionic group content. Here, we report results of the equilibrium swelling properties of hydrogels containing acrylamide (AAm, nonionic monomer), 4-vinylpyridine (VP, cationic monomer), and AAc (anionic monomer). Both VP and AAc are weakly dissociating electrolytes and the degree of dissociation depends on pH of the solution. Thus, varying pH of the solution can simply monitor the net charge of the hydrogels. In our experiments, equimolar ratio of VP and AAc was used in the hydrogel preparation, while the mole fraction of the ionic monomers in the monomer mixture was varied between 0.04 and 0.60. The behavior of the hydrogels in the collapsed regime was investigated as a function of the composition of the network chains. The variations of the gel volume in water or in $1M$ NaCl solution in response to changes in pH were measured. The experimental results were interpreted within the framework of the equilibrium theory of swelling of ionic hydrogels including the ideal Donnan equilibria.

EXPERIMENTAL

Materials

AAc (Fluka) and VP (Aldrich) were distilled under reduced pressure. AAm (Merck), N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and N,N,N',N'-tetramethylethylenediamine (TEMED, Merck) were used as received. APS and TEMED stock solutions were prepared by dissolving 0.160 g APS and 0.250 mL TEMED separately in 10 mL of water. BAAm and

AAc stock solutions were prepared by dissolving 0.123 g BAAm and 0.656 mL AAc separately in 10 mL of water. Stock solution of VP was prepared by dissolving 1.03 mL VP in 10 mL methanol.

Synthesis of hydrogels

Hydrogels were prepared by free-radical cross-linking copolymerization of AAm, VP, and AAc monomers with a small amount of BAAm cross-linker in aqueous solution at 24°C. The total concentration of the monomers AAm, VP, and AAc was fixed at 5 w/v %. Equimolar ratio of the ionic comonomers was used while the total amount of the ionic monomer was varied. APS and TEMED were used as the redox initiator system. Except the gel samples prepared with 30 mol % AAc and 30 mol % VP (30/30-gel), all the hydrogels were prepared in the presence of 7.02 mM APS and 0.25 v/v % TEMED. The cross-linker ratio (mole ratio of the cross-linker BAAm to the monomers) was also fixed at 1/80.

To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 15 mol % VP and 15 mol % AAc in the comonomer feed composition, designated as 15/15-gel: AAm (0.318 g) was dissolved in 5 mL of distilled water and, stock solutions of VP (1.00 mL), AAc (1.00 mL), BAAm (1.00 mL), and TEMED (1.00 mL) were added. After bubbling nitrogen, 1 mL of APS stock solution was added and the solution was poured into several plastic syringes of 4 mm internal diameter. The polymerization was conducted for 1 day at 24°C. After the reaction, the hydrogels were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water for 1 day to remove the unreacted species. Extraction tests conducted at room temperature showed that the conversion of the monomers to the cross-linked polymer was complete after the copolymerization.

It should be noted that 30/30-gels were too weak to withstand the swelling tests. Therefore, these gels were prepared at a cross-linker ratio of 1/50 and in the presence of 14 mM APS and 0.50 v/v TEMED redox initiator system. Under this experimental condition, 30/30-gels formed exhibited the same moduli of elasticity (500 ± 100 Pa) as the other sets of gels, indicating that their effective cross-link densities are identical.

Swelling measurements

Swelling measurements were carried out at 24 ± 0.5°C in water and in $1M$ NaCl solution of varying pH between 1 and 11. To obtain various pH between 1 and 11, dilute HCl or NaOH solutions were added into the distilled water or into $1M$ NaCl. pH of the solutions was measured using the pH meter inoLab

(WTW, Germany) with pH electrodes calibrated using three buffer solutions of varying pH. The hydrogels after preparation in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at 24 ± 0.5°C. To reach swelling equilibrium, the hydrogels were immersed in water for at least 1 week replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The normalized volume of the equilibrium swollen hydrogels V_{eq} (volume of equilibrium swollen gel/volume of the gel just after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). V_{eq} was calculated as

$$V_{eq} = (D/D_0)^3 \qquad (1)$$

where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. The hydrogels equilibrium swollen in water were then transferred into solutions of various pH and the swelling measurements were conducted as described above. To prevent nonequilibrium states in gels,[9] the gel samples were always transferred from neutral (water) to acidic or to basic solutions in steps of less than pH = 0.5.

Mechanical measurements

Uniaxial compression measurements were performed on gels just after their preparation. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5°C. The stress–strain isotherms were measured by using an apparatus previously described.[18] The elastic modulus G_o was determined from the slope of linear dependence:

$$F = G_0(\lambda - \lambda^{-2}) \qquad (2)$$

where F is the force acting per unit cross-sectional area of the undeformed gel specimen, and λ is the deformation ratio (deformed length/initial length). For a homogeneous phantom network of Gaussian chains with tetrafunctional cross-links, the elastic modulus of gels G_o is related to the network cross-link density v_e by:[19,20]

$$G_0 = 0.5 v_e \, RT \, v_2^0 \qquad (3)$$

where v_2^0 is the volume fraction of cross-linked polymer after preparation, R and T are in their usual meaning.

RESULTS AND DISCUSSION

Polyampholyte hydrogels were prepared at fixed initial monomer (AAm + VP + AAc) concentration. The molar ratio of the ionic comonomers VP and AAc was also fixed at 1/1 while their mole fraction in the monomer mixture was varied. In the following, the hydrogels were designated as X/Y-gels, where X and Y denote the mole percent of VP and AAc units in the network chains. Four sets of gels designated by 30/30-, 15/15-, 5/5-, and 2/2-gels were prepared and subjected to swelling tests in water as well as in $1M$ NaCl solution of various pH. Because $X = Y$, the IEP of all hydrogels immersed in water should occur if the dissociation degree α of AAc becomes equal to the dissociation degree β of VP. Further, since the dissociation degree of weak electrolytes relates to pH or pOH by:

$$pH = pK_a + \log\left(\frac{\alpha}{1-\alpha}\right) \qquad (4a)$$

$$pOH = pK_b + \log\left(\frac{\beta}{1-\beta}\right) \qquad (4b)$$

one may calculate the pH (pH_{IEP}), at which the gel is in its IEP as:

$$pH = 7 - \frac{pK_b - pK_a}{2} \qquad (5)$$

Using $pK_a = 4.25$ and $pK_b = 8.77$ reported for poly(acrylic acid) gels[21] and poly(4-vinylpyridine),[22] pH_{IEP} was calculated as 4.74 for all the polyampholyte hydrogels, irrespective their compositions.

In Figure 1, the equilibrium volume V_{eq} of 30/30-gel is plotted against pH of the external solution. The two data sets shown by circles and triangles are results of measurements using gel samples prepared twice. An excellent reproducibility was obtained from the swelling tests. The vertical dotted line in the figure points out $pH_{IEP} = 4.74$, at which the dissociation degrees of both AAc and VP units are equal, i.e., the gel is in its IEP. It is seen that 30/30-gel is in a collapsed state not only at pH_{IEP} but in the range of pH between 3.2 and 6.9. Thus, a three orders of magnitude variation of the hydrogen ion concentration in the external solution does not induce swelling of the collapsed 30/30-gel. This behavior is completely different from polyampholyte solutions where the chains are in a collapsed state only at pH_{IEP}. Figure 1 also shows that the gel undergoes rapid swelling transitions as pH is changed outside of the collapsed plateau region. For example, at pH = 6.88, the gel sample exhibited a 27-fold smaller volume than at pH = 7.04, clearly demonstrates the occurrence of a first-order volume phase transition in the gel at pH = 6.95 ± 0.10.
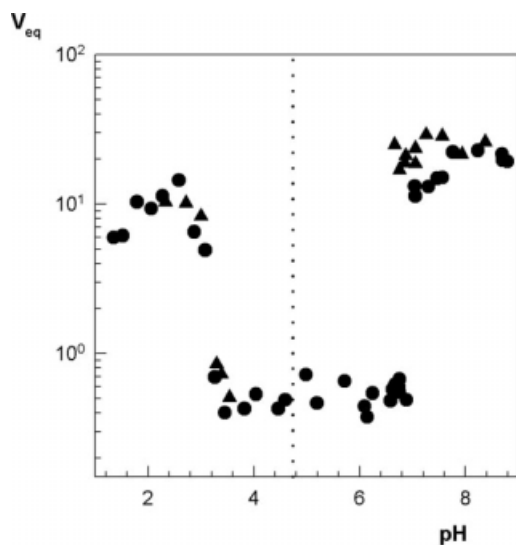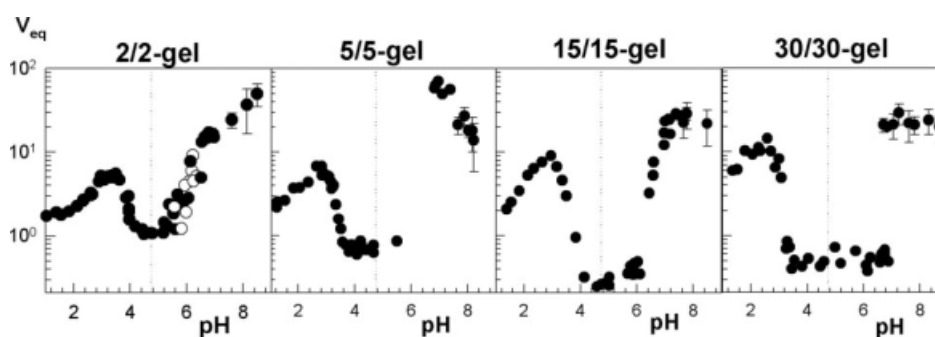
Figure 1 The equilibrium volume V_{eq} of 30/30-gel plotted against pH of the external solution. The vertical dotted line indicates $pH_{IEP} = 4.74$. The two data sets shown by circles and triangles are results of measurements using gel samples prepared twice.

Another first-order volume phase transition was observed at pH = 3.15 ± 0.15. Thus, infinitesimal change in pH at both ends of the plateau regime induces conformation transition in the network chains.

Filled symbols in Figure 2 shows the equilibrium volume V_{eq} of the hydrogels with various ionic monomer content plotted against pH of the external solution. The vertical dotted lines in the figures indicate $pH_{IEP} = 4.74$ of the hydrogels. All the hydrogels assume a compact conformation over a wide range of pH including pH_{IEP}. The general trend shown in Figure 2 is that, as pH increases from 1, V_{eq} first increases and reaches a maximum value around pH = 3. Then, it decreases again with a further increase in pH and attains a minimum gel volume around

the IEP. The volume of the collapsed gel remains constant over a certain range of pH. After passing this collapsed plateau region, the gel reswells again up to pH = 7. The results of measurements above pH > 7.5 were not reproducible, probably due to the hydrolysis of AAm units into AAc units.[23,24] Open symbols in the swelling curve of 2/2-gel represent results of the measurements in distilled water as the swelling medium. Note that the distilled water was slightly acidic (pH = 5.8–6.0) after a few weeks of swelling time of the gel samples, probably due to the CO_2 absorption from the air. We observed that the gel immersed in distilled water changed from swollen to collapsed state with increasing swelling time due to the simultaneous decrease in pH because of the CO_2 absorption of water. For example, the gel sample in distilled water at pH = 6.2 exhibited a relative volume of 6.0 while after a few days, if pH attained the value 5.8, it occupied a volume of only 1.2. Thus, the deswelling transition in the gel occurs at pH = 5.9 ± 0.1.

Although the shape of the swelling curves shown in Figure 2 is similar for all the gel samples, distinct differences depending on the gel composition are observable. First, the collapsed plateau becomes longer as the ionic comonomer content increases. This behavior is also illustrated in Figure 3(A) where the pH range for the collapsed gel state is plotted against VP or AAc mol %. Second, increasing amount of the ionic monomer decreases the volume of the collapsed gels (V_{min}), i.e., the gel assumes a more compact state at high ionic monomer contents. Another point is that the larger the amount of ionic monomer, the larger is the gel volume in acidic solutions ($V_{max,1}$). These features are shown in Figure 3(B) as the dependences of the minimum gel volume V_{min}, and the maximum gel volume in acidic solution $V_{max,1}$ on VP or AAc mol %. As the ionic monomer content is increased from 2 to 30 mol %, the collapsed gel volume decreases from 1 to 0.3 while the maximum gel volume in acidic solution

Figure 2 The equilibrium volume V_{eq} of the hydrogels with four different molar ratios of ionic/nonionic comonomers shown as a function of pH of the external solution. Results of measurements in distilled water are shown by the open symbols. The vertical dotted lines indicate $pH_{IEP} = 4.74$.
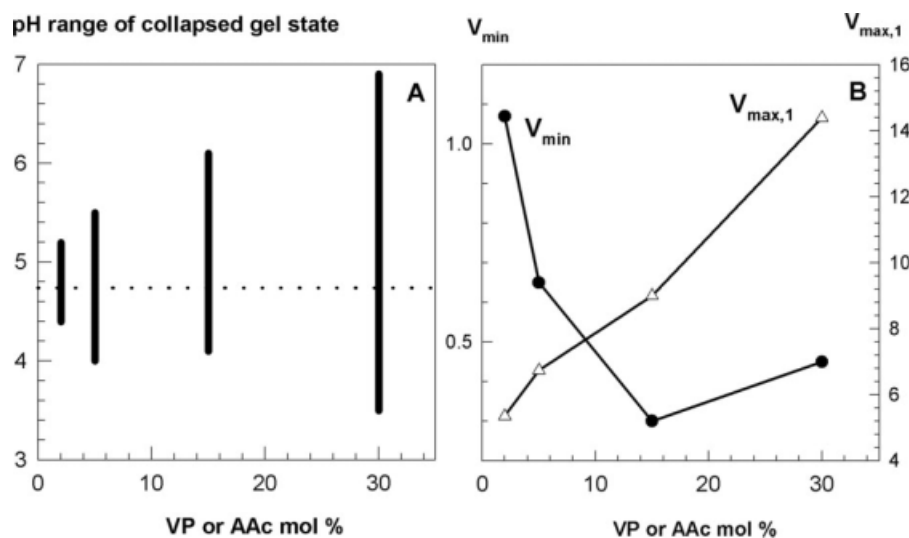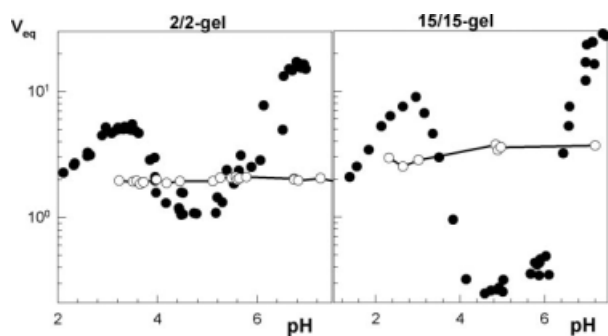
Figure 3 (A) The pH range, over which the collapsed gel state is stable shown as a function of the ionic comonomer content of the hydrogels. (B) The gel volume in the collapsed state V_{min}, and the maximum gel volume in acidic solution $V_{max,1}$ shown as a function of the ionic comonomer content.

increases from 5 to 14. Thus, it is seen that the gels having the same IEP behave differently when subjected to swelling tests in water.

Open symbols in Figure 4 shows the volume V_{eq} of 2/2- and 15/15- hydrogels plotted against pH of $1M$ NaCl solution. For comparison, data obtained in water are also shown by the filled symbols. In contrast to the nonmonotonic swelling behavior of gels in water, the gel volume in $1M$ NaCl does not change much as a function of pH due to the fact that all the electrostatic interactions are screened at such a high salt concentration. Further, at a given pH, the hydrogel outside of the collapsed plateau region is less swollen in $1M$ NaCl than in water, due to the screening of electrostatic interactions. This is a characteristic of polyelectrolyte hydrogels. The anti-polyelectrolyte effect is observable around the pla-

teau region, where the gel occupies a larger volume in $1M$ NaCl than in water due to the screening of the opposite charges in the gel by the mobile ions and unfolding of the compact conformation. Comparison of the volumes of gels in water with those in $1M$ NaCl shows that, although 15/15-gel at the IEP is in a much more compact state than 2/2-gel, in concentrated NaCl solutions, both gels exhibit the same gel volumes.

To interpret the results of experiments, the swelling behavior of the hydrogels was analyzed within the framework of the Flory-Rehner theory of swelling equilibrium including the ideal Donnan equilibria. According to the Flory-Rehner theory, the osmotic pressure π of a gel is the sum of three contributions:[25,26]

$$\pi = \pi_{mix} + \pi_{el} + \pi_{ion} \qquad (6)$$

where π_{mix}, π_{el}, and π_{ion} are the osmotic pressures due to polymer–solvent mixing (mix), due to deformation of network chains to a more elongated state (el), and due to the nonuniform distribution of mobile counterions between the gel and the solution (ion), respectively. According to the Flory-Huggins theory, π_{mix} is given by:[19]

$$\pi_{mix} = -\frac{RT}{\overline{V}_1}\left(\ln(1 - v_2) + v_2 + \chi v_2^2\right) \qquad (7)$$

where v_2 is the volume fraction of cross-linked polymer at the state of the equilibrium swelling, which is related to the experimentally determined gel volume by $v_2 = v_2^0/V_{eq}$, χ is the polymer-solvent interaction parameter, and $\overline{V}_1$ is the molar volume of solvent (18 mL/g). To describe the elastic contribution π_{el},

Figure 4 The equilibrium volume V_{eq} of 2/2- and 15/15-gels shown as a function of pH of the external solution. Filled symbols are the results of measurements in water while open symbols are those measured in $1M$ NaCl solutions.

we will use here the simplest phantom network model to describe the behavior of our gels:[19]

$$\pi_{el} = -0.5 \, \nu_e \, RT(\nu_2)^{1/3} \left(\nu_2^0\right)^{2/3} \qquad (8)$$

Ionic contribution π_{ion} to the swelling pressure is caused by the concentration difference of counterions between the gel and the outer solution:[19]

$$\pi_{ion} = RT \sum_i \left(C_i^g - C_i^s\right) \qquad (9)$$

where C_i is the mobile ion concentration of species i, the superscripts g and s denote the gel and solution phases, respectively.

To evaluate π_{ion}, we consider a gel, consisting of nonionic AAm, and weak electrolyte VP and AAc units, immersed in an infinite volume of an aqueous solution of HCl. Thus, the mobile counterions existing in this system are H^+, and Cl^- ions. Further, we define the concentrations of the AAc and VP units in the gel by C_A and C_B, respectively. Because of the local electroneutrality condition in the gel phase, the net charge of the network chains given by ($\alpha C_A - \beta C_B$) is balanced by the mobile counterions in the gel, which gives the following equality:

$$\alpha C_A - \beta C_B = C_{H^+}^g - C_{Cl^-}^g \qquad (10)$$

Moreover, the ideal Donnan equilibria for univalent salts require the equality:

$$C_{H^+}^g \, C_{Cl^-}^g = C_{H^+}^s \, C_{Cl^-}^s = \left(C_{H^+}^s\right)^2 \qquad (11)$$

Solution of eqs. (10), (11) for the mobile ion concentrations both in the gel and in the solution phases and substituting these concentrations into eq. (9) lead to:

$$\pi_{ion} = RT\sqrt{(\alpha C_A - \beta C_B)^2 + \left(2C_{H^+}^s\right)^2} - 2 \, RTC_{H^+}^s \qquad (12)$$

At the swelling equilibrium, the total osmotic pressure π becomes equal to zero. Thus, using eqs. (7), (8), and (12), the equilibrium swelling condition of polyampholyte gels is given by:

$$\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2 + 0.5 \, \nu_e \overline{V}_1(\nu_2)^{1/3}\left(\nu_2^0\right)^{2/3}$$
$$- \overline{V}_1 \sqrt{(\alpha C_A - \beta C_B)^2 + \left(2C_H^s\right)^2} + 2\overline{V}_1 C_{H^+}^s = 0 \qquad (13)$$

The dissociation degrees α and β of AAc and VP units, respectively, are related to their dissociation constants by:

$$\alpha = \frac{K_a}{K_a + C_{H^+}^g} \qquad (14a)$$

$$\beta = \frac{K_b}{K_b + K_w/C_{H^+}^g} \qquad (14b)$$

where K_a and K_b are the dissociation constants of AAc and VP groups, respectively, and K_w is the dissociation constant of water. Thus, solution of eq. (13) requires the degrees α and β of the ionic groups, which in turn require the concentration of H^+ ions in the gel phase $C_{H^+}^g$, i.e., the pH inside the gel solution. Substitutions of eqs. (14a), (14b), and (11) into eq. (10), we obtained a fourth order polynomial equation for calculation of $C_{H^+}^g$:

$$C_{H^+}^g{}^4 + (K_1 + C_B)C_{H^+}^g{}^3 + \left[K_2 + K_a(C_B - C_A) - C_{H^+}^s{}^2\right]$$
$$\times C_{H^+}^g{}^2 - \left(K_2 C_A + K_1 C_{H^+}^s{}^2\right) C_{H^+}^g - K_2 \, C_{H^+}^s{}^2 = 0 \qquad (15)$$

where $K_1 = K_a + K_w/K_b$ and $K_2 = K_a K_w/K_b$. Note that the calculations as described above, but in the presence of NaOH instead of HCl lead to the same equation except that $C_{H^+}^s$ has to be redefined as the concentration of NaOH in the external solution. eq. (15) contains the ionic comonomer concentrations C_A and C_B in the gel phase. Defining f_- and f_+ as the mole fractions of AAc and VP units in the network, they are given by:

$$C_A = f_- \frac{\nu_2}{\overline{V}_r} \times 10^3 \qquad (16a)$$

$$C_B = f_+ \frac{\nu_2}{\overline{V}_r} \times 10^3 \qquad (16b)$$

where $\overline{V}_r$ is the molar volume of polymer units. In the following, eqs. (13)–(16) were solved numerically with the bisection method for both H^+ concentrations in the gel ($C_{H^+}^g$) and the polymer concentration ν_2. For calculations, $C_{H^+}^s$, i.e., pH of the external solution was taken as the independent parameter, which was varied in our experiments. The solution of the equations requires the values of the parameters ν_e, $\overline{V}_r$, ν_2^0, and χ, characterizing the network and the extent of the network-solvent interactions. Using the molecular weight of AAm, AAc, and VP units (71, 72, and 105 g/mol, respectively) together with the polymer density (1.35 g/mL[27]), $\overline{V}_r$ was calculated as $\overline{V}_r = 36.8 + 77.8f_+ + 53.3f_-$ (mL/mol). From the modulus of elasticity of the hydrogels $G_o = 500 \pm 100$ Pa, ν_e was calculated using eq. (3) as 11 mol/m³. The volume fraction of cross-linked polymer after preparation, ν_2^0, was calculated from the initial monomer concentration (5 w/v %) together with the polymer density, as 0.037. The χ parameter value
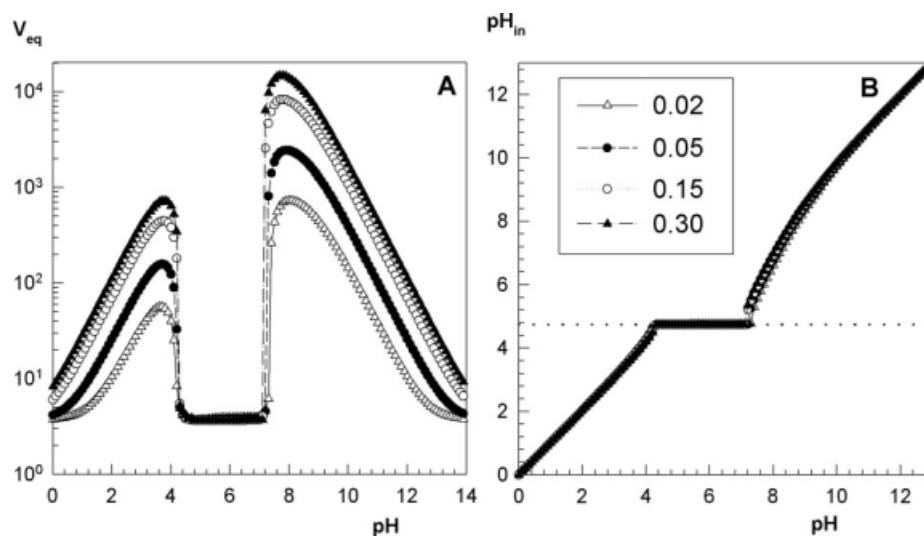
Figure 5 Theoretical curves showing the equilibrium gel volume V_{eq} (A) and the pH in the gel solution (pH$_{in}$, B) as a function of pH of the external solution. Calculations were using eqs. (13) and (15). The mole fractions of VP or AAc are indicated.

was taken as 0.48. This value of χ provided a good fit to the experimental swelling data of AAm-based anionic, cationic, and polyampholyte hydrogels of various compositions.[28]

Simulation results for the gels immersed in water of various pH are shown in Figure 5. Here, the gel volume V_{eq} and the pH in the gel phase pH$_{in}$ $(10^- C_{H^+}^g)$ are plotted against pH of the external solution. Comparison of the theoretical swelling curves with the experimental data given in Figure 2 shows that the theory qualitatively predicts the experimental behavior of gels. The collapsed plateau was also predicted by the theory. In agreement with the experiments, the maxima in the curves shift toward larger volumes as the ionic monomer content of the hydrogels is increased. At a low pH, the gel network exists as a cationic polyelectrolyte because of suppression of its AAc groups. However, the gel remains collapsed at a low pH due to the high H$^+$ concentration in the solution $C_{H^+}^g$, which totally screens the VP groups. As pH increases, the gel swells due to the decrease of hydrogen ion concentration in the gel phase $C_{H^+}^g$. However, at $C_{H^+}^g = 1.8 \times 10^{-5}M$ corresponding to pH$_{IEP} = 4.74$, the gel rapidly deswells as the network is electroneutral and adopts a compact conformation. In this range of pH, since the hydrogen ion concentration in the gel is very low compared to the concentrations of the dissociated AAc and VP units, the local electroneutrality in the gel phase is provided by the intraionic VP–AAc attractions. As seen from Figure 5(B), along the collapsed region of gel, pH$_{in}$ remains constant at pH$_{IEP} = 4.74$. At pH = 7.2, the osmotic pressure due to the concentration difference of H$^+$ ions between the gel and outer solution exceeds the negative osmotic pressure due to the gel rubber-like elasticity

holding the gel in a collapsed state. As a result, the gel undergoes a first-order swelling transition, during which the gel network transforms from electroneutral to anionic one. Moreover, as the VP or AAc content is increased, the charge density of the ionic gel at both low and high pH also increases so that the maxima observed in acidic and basic solutions increases [Fig. 5(A)].

It should be noted that the theory does not predict the variation of the width of the collapsed plateau as well as the volume of the collapsed gel (V_{min}) depending on VP or AAc %. Thus, in contrast to the experimental results given in Figure 3, the theory predicts the same behavior for all the hydrogels. Experimental results also show a much more compact state for the balanced hydrogels compared to the theory's prediction. This is due to the neglect of electrostatic interaction between oppositely charged sections of the chains.[29] Moreover, gel heterogeneities as well as inhomogeneous distribution of the ionic comonomer units along the network chains also contribute to the observed discrepancies.[30] The attraction between charge density fluctuations due to the gel inhomogeneities may lead to a chain collapse and form a much dense globule than predicted by the theory. Furthermore, the use of a single dissociation constant for the ionic units is also questionable.[31] The simple swelling model presented here qualitatively describes the equilibrium swelling behavior of polyampholyte hydrogels under various experimental conditions.

CONCLUSIONS

The swelling behavior of AAm-based polyampholyte hydrogels in water and in 1M NaCl solution was

investigated. Equimolar ratio of the ionic monomers VP and AAc were used while the total number of ionic monomers in the feed was varied between 4 and 60 mol %. The variations of the hydrogel volume in response to changes in pH were measured. It was found that the hydrogels are in a collapsed state not only at the pH of the isoelectric point pH_{IEP}, but over a wide range of pH including pH_{IEP}. The width of the collapsed plateau increased and the hydrogels assumed a more compact state as the ionic group content is increased. The antipolyelectrolyte behavior was observed along the collapsed plateau region, where the gel occupies a larger volume in $1M$ NaCl solution. The experimental swelling data were compared with the predictions of the Flory-Rehner theory of swelling equilibrium including the ideal Donnan equilibria.

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