Swelling of Polyacrylamide Gels in Polyacrylamide Solutions

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ABSTRACT: Swelling behavior of polyacrylamide (PAAm) and polyacrylamide-co-polyacrylic acid (PAAm-co-PAAc) gels was investigated in aqueous solutions of monodisperse PAAms with molecular weights ($M_w$) ranging from $1.5 \times 10^3$ to $5 \times 10^6$ g/mol. The volume of the gels decreases as the PAAm concentration in the external solution increases. This decrease becomes more pronounced as the molecular weight of PAAm increases. The classical Flory–Huggins (FH) theory correctly predicts the swelling behavior of nonionic PAAm gels in PAAm solutions. The polymer–polymer interaction parameter $\chi_{23}$ was found to decrease as the molecular weight of PAAm increases. The swelling behavior of PAAm-co-PAAc gels in PAAm solutions deviates from the predictions of the FH theory. This is probably due to the change of the ionization degree of AAc units depending on the polymer concentration in the external solution. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 1313–1320, 1998

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INTRODUCTION

Hydrophilic gels called hydrogels receive considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Investigations of the swelling behavior of hydrogels in low molecular weight solvents have been reported repeatedly in the last 4 decades. However, only a few were concerned with swelling in polymer solutions.1–7 First theoretical studies on such (quasi)ternary systems assumed that the linear macromolecules cannot enter the gel phase.8 Others neglected the energetic interactions between the polymer and network segments.8 Recent experimental results indicate that these assumptions are unrealistic.9,10 Linear polymers can penetrate into the network, depending on the thermodynamic parameters of the system, leading to the contraction of the gel. Because the linear polymer concentration inside the network depends on the size of the macromolecules, the gel excludes high molecular weight polymers. This characteristic of the gels is of pronounced practical interest; for example, polymeric gels can be used as extraction solvents to concentrate aqueous solutions of proteins or other biological systems.11,12 More recently, theoretical calculations using the classical Flory–Huggins theory predicted the possibility of a first-order (discontinuous) phase transition in such systems.13,14 This prediction was proved experimentally with poly(N-isopropylacrylamide) and polyacrylamide (PAAm) gels swollen in aqueous poly(ethylene glycol) solutions.15,16

This article presents the results of observations on PAAm gels immersed in aqueous solutions of monodisperse PAAms with molecular weights ranging from $1.5 \times 10^3$ to $5 \times 10^6$ g/mol. The gels were prepared by free radical crosslinking.
copolymerization of acrylamide and acrylic acid comonomers with a small amount of \(N,N'\)-methylenebis(acrylamide) as the crosslinker in aqueous solutions. The swelling behavior of the gels in PAAm solution was investigated as a function of the concentration and the molecular weight of PAAm in the outer solution. The experimental data were analyzed in terms of the classical Flory–Huggins theory of swelling equilibrium.

**EXPERIMENTAL**

**Materials**

PAAm gels were prepared by free radical crosslinking copolymerization of acrylamide (AAm) with a small amount of \(N,N'\)-methylenebis(acrylamide) (BAAm) in aqueous solution. Acrylic acid (AAc) was used as the ionizable comonomer. Ammonium persulfate (APS) and \(N,N,N',N'\)-tetramethylethylenediamine (TEMED) were, respectively, the initiator and the accelerator. The reactions were carried out at room temperature (21 ± 2°C). The gels were prepared according to the following scheme:

Five grams of the monomer mixture (AAm and AAc), 133 mg BAAm, and 40 mg APS were dissolved in double distilled water to give a total volume of 100 mL. To eliminate oxygen from the polymerization system nitrogen was bubbled through the solution for 10 min. After addition of 0.24 mL of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. The gelation took place within 5 min. After 3 h, the gels 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. It was found that the sol fraction in the gels is less than 0.1% after extraction with water.

Linear PAAm of molecular weight \(5 \times 10^6\) g/mol was purchased from Polyscience Inc. and used without further purifications. Its polydispersity index \((M_w/M_n)\) was reported as 2.3. Other linear PAAm samples were prepared according to two different polymerization methods. Before polymerization, AAm was recrystallized twice from acetone–ethanol mixtures and dried thoroughly in vacuum. To obtain PAAms of molecular weights ranging from \(2.5 \times 10^4\) to \(1 \times 10^5\) g/mol; 7 g AAm, 0.54 g potassium persulfate, 0.316 g \(Na_2S_2O_3\), 0.168 g NaHCO\(_3\), and 16 mL isopropanol were dissolved in 200 mL distilled water. Polymerization was conducted at 40°C for 2 h under nitrogen atmosphere. The conversion to polymer was 95%. The polymer solution was diluted with water to obtain a 0.5 \(M\) solution and PAAm was fractionated into 21 fractions in water–methanol mixture at 30°C by the fractional solution technique. The 2nd, 5th, and 18th fractions with \(10^{-4} M_w = 10, 6, \text{ and } 2.5 \text{ g/mol, respectively, were used as polymer samples in swelling experiments. To obtain lower molecular weight PAAms; 7 g AAm, 0.21 g thioglycolic acid, 0.12 g 2,2'-azobisisobutyronitrile (AIBN) and 20 mL THF were placed in a 50-mL flask. Polymerization was carried out at 60°C for 10 min under nitrogen atmosphere. The resulting polymer was diluted with water and precipitated in methanol. The conversion was 78%. The polymer was then dissolved in PAAm gels were prepared by free radical cross-linking copolymerization of acrylamide (AAm) water to produce a 0.5 \(M\) solution and PAAm was fractionated into 10 fractions, as reported above.

**Swelling Measurements**

Swelling experiments were carried out using aqueous solutions of PAAms of various concentrations and molecular weights. The solution of PAAms of molecular weights higher than \(6 \times 10^4\) g/mol exhibited a pH value of 5.6–5.8. However, pH of low molecular weight PAAm solutions was in the range of 3 to 4.5. Because pH is an important parameter determining the ionization degree of gels, the swelling experiments were conducted at a fixed pH value, namely at pH = 5.6–
5.8, using titration of PAAm solutions with a dilute NaOH solution.

The PAAm gel samples were immersed in vials (100 mL) filled with a PAAm–water solution. The volume of solution in the vial was much larger than the gel volume so that the concentration of the solution was practically unchanged. The vials were set in a temperature-controlled bath at 25 ± 0.1°C. To reach the equilibrium degree of swelling, the gels were immersed in solutions at least for 1 week. The diameter of the gels was measured by a calibrated digital compass and the equilibrium swelling ratio of the gels, \(V/V_0\), where \(V\) and \(V_0\) are the volumes of gel at equilibrium and after preparation, respectively, was calculated as

\[
V/V_0 = (D/D_0)^3
\]  

where \(D\) and \(D_0\) are the diameter of the gels after equilibrium swelling and after preparation, respectively. Each swelling ratio reported in this article is an average of at least two separate measurements; standard deviations of the measured swelling ratios were less than 10% of the mean value.

**THEORY**

The experimental data were analyzed in terms of the classical Flory–Huggins (FH) theory of swelling equilibrium. Swelling of a polymer network is governed by at least three free-energy terms, i.e., the changes in the free energy of mixing \(\Delta G_m\), the free energy of elastic deformation \(\Delta G_d\), and in the free energy of electrostatic interactions \(\Delta G_i\):

\[
\Delta G = \Delta G_m + \Delta G_d + \Delta G_i \tag{3}
\]

According to the Flory–Huggins theory, \(\Delta G_m\) is given by:

\[
\Delta G_m = RT\left(\sum_i n_i \ln \nu_i + \sum_{i<j} n_i n_j \chi_{ij}\right) \tag{4}
\]

where \(n_i\) is the mol of the species \(i\), \(\nu_i\) is its volume fraction, \(\chi_{ij}\) is the interaction parameter between the species \(i\) and \(j\), \(R\) is the gas constant, and \(T\) is temperature. For the present ternary system, the subscript \(i = 1, 2,\) and 3 denotes the solvent (water), the network (PAAm or PAAm-co-PAAc), and the linear polymer (PAAm), respectively. For the free energy of elastic deformation \(\Delta G_d\), several theories are available. However, we will use here the simplest affine network model to describe qualitatively the elasticity of PAAm network:

\[
\Delta G_d = \frac{3}{2}(RT/NV_1)(\nu_2^{2/3} - \nu_2/2) - 1 - \ln(\nu_2^{2/3}) \tag{5}
\]

where \(N\) is the average number of segments in the network chains, \(V_1\) is the molar volume of solvent, \(\nu_2\) and \(\nu_2^0\) are the volume fraction of polymer network in the equilibrium swollen gel and after preparation, respectively. Use of other elastic free energy equations does not affect the results of the present study. The existence of fixed ions on the PAAm-co-PAAc network results in nonequal distribution of mobile counterions between the inside and outside the gel. For such weakly charged ionic gels, this contribution \((\Delta G_i)\) may be written as follows:

\[
\Delta G_i = RT \frac{f}{N} \frac{\nu_2}{\nu_1} n_1 \ln(f\nu_2/N) \tag{6}
\]

where \(f\) is the average number of ionic units in a network chain. Substitution of eqs. (4)–(6) into eq. (3) and differentiating with respect to the number of mol of solvent \(n_1\) and polymer molecules \(n_3\) yield the following set of equations for the excess chemical potentials of the solvent and the polymer in both gel \((\Delta \mu_{\text{sol}}^\text{gel})\) and solution phases \((\Delta \mu_{\text{sol}}^\text{sol})\):

\[
\frac{\Delta \mu_{\text{gel}}^\text{gel}}{RT} = N^{-1}(\nu_2^{2/3} - \nu_2/2) + \ln \nu_1
\]

\[
+ (1 - \nu_1) - \nu_2/y + (\chi_{12}\nu_2 + \chi_{13}\nu_3)
\]

\[
\times (1 - \nu_1) - \chi_{23}\nu_2\nu_3 - \nu_2 f/N \tag{7a}
\]

\[
\frac{\Delta \mu_{\text{sol}}^\text{gel}}{RT} = \ln(1 - \phi) + \phi(1 - 1/y) + \chi_{13}\phi^2 \tag{7b}
\]

\[
\frac{\Delta \mu_{\text{gel}}^\text{sol}}{yRT} = N^{-1}(\nu_2^{2/3} - \nu_2/2) + (1/y)\ln \nu_3
\]

\[
+ (1/y)(1 - \nu_3) - \nu_1 + (\chi_{13}\nu_1 + \chi_{23}\nu_2)
\]

\[
\times (1 - \nu_3) - \chi_{12}\nu_1\nu_2 - \nu_2 f/N \tag{8a}
\]

\[
\frac{\Delta \mu_{\text{sol}}^\text{sol}}{yRT} = (1/y)\ln \phi - (1 - \phi)
\]

\[
+ (1/y)(1 - \phi) + \chi_{13}(1 - \phi)^2 \tag{8b}
\]

where \(y\) is the number of segments in the linear polymer and \(\phi\) is its volume fraction in the solu-
tion phase. The state of equilibrium swelling of a network immersed in a polymer solution is obtained when the solvent and the polymer inside the network are in thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential \( \mu \) of these components in both phases. Thus, at swelling equilibrium, we have:

\[
\Delta \mu_1^{\text{gel}} - \Delta \mu_1^{\text{sol}} = 0 \quad (9a)
\]

\[
\Delta \mu_3^{\text{gel}} - \Delta \mu_3^{\text{sol}} = 0 \quad (9b)
\]

### Calculations

The system of equations represented by eqs. (9a) and (9b) has been solved numerically to calculate the swelling ratio of PAAm gels in aqueous PAAm solutions \( V/V_0 = \nu_2^{\text{sol}}/\nu_2^{\text{gel}} \) and the linear PAAm concentration inside the gel phase \( \nu_3 \). For calculations, the values used were \( \nu_2^{\text{sol}} = 0.035 \) (estimated assuming additivity of the volumes of water and PAAm, \( \rho = 1.42 \text{ g/mL} \)), and \( \chi_{12} = \chi_{13} = 0.48 \). The number of segments in a network chain \( N \) was estimated from the swelling ratio of nonionic gels in pure water and using eq. (7a) for the condition \( f = 0 \), \( \nu_3 = 0 \) and \( \Delta \mu_3^{\text{gel}} = 0 \). The value \( \nu_2^{\text{gel}} = 0.0216 \) found by experiments for the nonionic gels swollen in water yielded \( N = 1490 \). \( N \) was held constant at this value in the calculations described here. After calibration of the gels, that is, after finding their crosslink densities in terms of \( N \), \( f \) value of PAAm-co-PAAc gels obtained at the same chemical crosslink density was calculated from their swelling ratio in water and using eq. (7a) for the condition \( N = 1490 \), \( \nu_3 = 0 \) and \( \Delta \mu_3^{\text{gel}} = 0 \). The value \( \nu_2^{\text{gel}} = 0.0022 \) found by experiments for the PAAm-co-PAAc gels swollen in water yielded \( f = 5.7 \). Note that the calculation assumes that the addition of acrylic acid in the comonomer mixture does not change the network topology. It was also assumed that \( y \) is equal to the degree of polymerization of linear PAAms. The only unknown parameter \( \chi_{23} \) was taken as a model parameter. To find \( \chi_{23} \), we minimized the sum of the squared residuals between the calculated and experimental swelling ratio \( V/V_0 \) values.

### RESULTS AND DISCUSSION

#### Nonionic PAAm Gels

Variation of the equilibrium degree of swelling \( V/V_0 \) of PAAm gels with the volume fraction of linear PAAm in the external solution \( \phi \) is shown in Figure 1(A) and (B). The molecular weights \( M_w \) of linear PAAms were between \( 5 \times 10^6 \)–6 \times 10^4 \text{ g/mol} \) in Figure 1(A) and between 2.5 \times 10^4–1.5 \times 10^5 \text{ g/mol} \) in Figure 1(B). Measurements at higher polymer concentrations could not be carried out for high molecular weight PAAms because they were not dissoluble. Experimental data are shown as symbols. Filled symbols represent the results of measurements with nonionic PAAm gels, whereas the empty symbols for PAAm-co-PAAc (ionic) gels with 11 mol % AAc content (based on dry gel). As the PAAm concentration outside the gel phase increases, the volume of PAAm gels decreases. This decrease becomes more pronounced as the molecular weight of PAAm in the solution increases.

The solid and dashed curves shown in the figures were calculated using the FH theory for nonionic and ionic gels, respectively. For \( M_w = 5 \times 10^6 \text{ g/mol} \), because the experimental data are only available in a narrow range of polymer concentration, calculations were not performed. For all other nonionic PAAm gel samples, calculation results for \( \chi_{23} = 0 \), i.e., assuming athermal interactions between polymer and network segments, led to poor agreement between theory and experiment. For instance, in Figure 2, representing \( V/V_0 \) vs. PAAm concentration \( \phi \) dependence for \( M_w = 2.5 \times 10^4 \text{ g/mol} \), the dotted curve was calculated for \( \chi_{23} = 0 \). The nonionic gel deswells in PAAm solution much more than predicted using the FH theory for athermal interactions. The solid curve in Figure 2 that is a best fit to the experimental data yields \( \chi_{23} = 0.0048 \). Similarly, the solid curves in Figure 1(A) and (B) were calculated using the least-square analysis of the two swelling equations [eqs. (9a) and (9b)] with the swelling ratio data, and yield \( \chi_{23} = 0.0048, \text{ 0.0025, 0.011, 0.034, and 0.1 for } 10^{-4} M_w = 10, 6, 1, 0.5, \text{ and 0.15 g/mol, respectively. It can be seen that, after adjusting } \chi_{23} \text{ parameter for each polymer molecular weight, the FH theory and experiment show good agreement for } M_w \approx 10,000 \text{ g/mol. Previous works also indicate that the FH theory correctly predicts the equilibrium degree of swelling of polymer gels in polymer solutions.}^{5,6} \text{ This is probably, as pointed out in the refs. 8 and 32, due to favorable cancellation between two approximations of the theory. For linear PAAms with } M_w = 1500 \text{ and } 5000 \text{ g/mol, however, theory and experiment are only in fair agreement. This may be due to the high concentration of short linear chains inside the gel phase, which increases the}
POLYACRYLAMIDE GEL SWELLING IN POLYACRYLAMIDE SOLUTIONS

Figure 1. Variation of the swelling ratio \( V/V_0 \) of PAAm gels with the volume fraction of linear PAAm in the outer aqueous solution \( \phi \). Filled symbols represent the results of measurements with nonionic PAAm gels, whereas the empty symbols for PAAm-co-PAAc (ionic) gels with 11 mol % AAc content (based on dry gel). The curves were calculated using eqs. (9a) and (9b) for nonionic (solid curves) and ionic gels (dashed curves). The molecular weights \( M_m \) of linear PAAms are: (A) \( 6 \times 10^4 \) \( \Delta, \Delta, 2 \); and \( 5 \times 10^5 \) g/mol \( \nabla, \nabla \); (B) \( 1.5 \times 10^3 \) \( \bullet, \bigcirc, 1 \); \( 5 \times 10^3 \) \( \Delta, \Delta, 2 \); \( 1 \times 10^4 \) g/mol \( \nabla, \nabla, 3 \); and \( 2.5 \times 10^4 \) g/mol \( \blacksquare, \square, 4 \).

interchain entanglements between the network and polymer chains acting as effective crosslinks.

\( \chi_{23} \) parameter values calculated for each set of experimental data indicate that \( \chi_{23} \) decreases as the molecular weight of PAAm increases. The smaller the molecular weights are, the larger \( \chi_{23} \) is. This trend of \( \chi_{23} \) is similar to that of the second virial coefficient \( A_2 \) in a binary solution, which also decreases with increasing molecular weight.\(^{30}\) The molecular weight dependence of \( \chi_{23} \) was also observed previously in several systems.\(^{10,33,34}\) It must be noted that, if the linear polymer chains are short, the combinatorial entropy of mixing in the FH expression (the first term in the parenthesis of eq. (4)) is incorrect.\(^{35}\) Therefore, the molecular weight dependence of \( \chi_{23} \) may also appear to compensate the inaccuracy in the FH theory for short polymer chains.

In Figure 3, the concentration of linear PAAm inside the gel phase \( \nu_\phi \), calculated using eqs. (9a) and (9b), is shown as a function of the PAAm concentration in the external solution \( \phi \). Calculations were for polymer molecular weights studied in this work and using the \( \chi_{23} \) parameters derived from the swelling curves of PAAm gels. The dotted line in the figure represents the relation \( \nu_\phi/\phi = 1 \), i.e., on this line, the PAAm concentration inside the gel is equal to that in the solution. PAAm concentration in the gel phase is always smaller than in the outer solution, i.e., \( \nu_\phi/\phi \) ratio is smaller than unity. This is due to the fact that the conformational entropy of linear PAAm inside the nonionic gel is much smaller than in the outer solution.\(^{13}\) This concentration difference creates an osmotic pressure compressing the gel. At low polymer concentrations, \( \nu_\phi \) increases with the increase in \( \phi \), and the gel deswells gradually (Figs. 1–2). The smaller the linear PAAm in the external solution, the higher the \( \nu_\phi/\phi \) ratio, and thus, the higher the extent of swelling of the gel in polymer solution. As the molecular weight of linear polymer increases, the effect of the concentration difference becomes more pronounced and, if the molecular weight of PAAm is sufficiently high, the linear polymer does not penetrate inside the nonionic PAAm network. Another feature shown in Figure 3 is that, as the polymer concentration increases, \( \nu_\phi \) becomes, after passing a maximum, a decreasing function of \( \phi \). This is due to the repulsive interactions between network and polymer.
Linear polymer in the external solution increases. The swelling ratio of ionic gels approaches that of nonionic gels at high polymer concentrations. The dashed curves in Figures 1 and 2 were calculated using the FH theory with $\gamma_{23}$ parameters estimated from the swelling curves of nonionic gels. In these calculations, the free-energy term representing the contribution from the translational entropy of counterions [eq. (6)] was also taken into account. It is seen that, in contrast to the experimental results, the theory predicts almost no change in the volume of the ionic gel over the whole concentration and molecular weight ranges of PAAm. The high swelling ratios predicted by the theory for ionic gels are also reflected in the calculated $n_3/\phi$ ratios, which are always close to unity; because, according to theory, ionic gels do not deswell in polymer solutions and linear polymers can enter inside the gel without an essential loss in their conformational entropy. Taking $\gamma_{23}$ as a model parameter to fit the experimental data, the observed swelling behavior of ionic gels cannot be predicted by the FH theory. Calculations showed that, for small values of $\gamma_{23}$, ionic gels remain in the swollen state over the entire range of polymer concentration. If $\gamma_{23}$

![Figure 2. Variation of the swelling ratio $V/V_0$ of non-ionic (●) and ionic PAAm gels (○) with the volume fraction of linear PAAm in the outer aqueous solution $\phi$. The molecular weight ($M_w$) of linear PAAm is $2.5 \times 10^4$ g/mol. The solid and dashed curves were calculated for nonionic and ionic gels, respectively for $\gamma_{23} = 0.0048$. The dotted curve was calculated for the non-ionic gel and for $\gamma_{23} = 0$. The results of measurements for ionic gels carried out at 80°C are shown as open triangles.](image)

segments in the gel, represented by the value of $\gamma_{23}$. These interactions dominate at high polymer concentrations and exceed the osmotic pressure of linear polymers in the outer solution. As a result, the concentration of linear polymers inside the gel drops and simultaneously the magnitude of the deswelling becomes larger, as seen in Figures 1–2. The values of $\phi$ corresponding to the maxima in $n_3-\phi$ curves depend both on the molecular weight of polymer and the value of $\gamma_{23}$. Note that, for $\gamma_{23} = 0$, theory predicts a monotonous increase of $n_3$ on rising $\phi$.

Ionic PAAm Gels

In Figures 1 and 2, the empty symbols represent the swelling volumes of PAAm-co-PAAc (ionic) gels in aqueous PAAm solutions. As expected, $^{21}$ ionic gel swells in water much more than the corresponding neutral gel due to the osmotic pressure of mobile counterions within the gel phase. Moreover, the ionic gel deswells significantly as the concentration or the molecular weight of the linear polymer in the external solution increases. The swelling ratio of ionic gels approaches that of nonionic gels at high polymer concentrations. The dashed curves in Figures 1 and 2 were calculated using the FH theory with $\gamma_{23}$ parameters estimated from the swelling curves of nonionic gels. In these calculations, the free-energy term representing the contribution from the translational entropy of counterions [eq. (6)] was also taken into account. It is seen that, in contrast to the experimental results, the theory predicts almost no change in the volume of the ionic gel over the whole concentration and molecular weight ranges of PAAm. The high swelling ratios predicted by the theory for ionic gels are also reflected in the calculated $n_3/\phi$ ratios, which are always close to unity; because, according to theory, ionic gels do not deswell in polymer solutions and linear polymers can enter inside the gel without an essential loss in their conformational entropy. Taking $\gamma_{23}$ as a model parameter to fit the experimental data, the observed swelling behavior of ionic gels cannot be predicted by the FH theory. Calculations showed that, for small values of $\gamma_{23}$, ionic gels remain in the swollen state over the entire range of polymer concentration. If $\gamma_{23}$

![Figure 3. Linear PAAm concentration inside the gel phase, $n_3$, shown as a function of its concentration in the outer solution $\phi$. The solid curves were calculated using eqs. (9a) and (9b) for nonionic PAAm gels. The molecular weights ($M_w$) of linear PAAm’s are $1.5 \times 10^3$ (1); $5 \times 10^3$ (2); $1 \times 10^4$ (3); $2.5 \times 10^4$ (4); $6 \times 10^4$ (5); and $1 \times 10^5$ g/mol (6). The dotted line represents the relation: $n_3/\phi = 1$.](image)
exceeds a critical value, theory predicts a first-order transition from swollen to collapsed state. At sufficiently large values of $\chi_{23}$ (i.e., $\chi_{23} = 0.4$ for $y = 350$), although the jump-wise transition of the gel volume disappears, the gel deswells significantly in a narrow range of polymer concentration because the network does not mix with the linear polymer. The calculation results are thus totally at variance with the experimental data.

To explain the discrepancy between theory and experiment, one has to consider effects that are not taken into account within the theory. Two effects may explain the observed behavior of ionic gels in polymer solutions: (1) complex formation and (2) ion pair formation. A complex between AAm and AAc units due to hydrogen bonding is known to be much more hydrophobic than the polymer chains taken separately. Increasing PAAm concentration in the solution would increase the polymer content inside the gel, so that the network becomes more hydrophobic and it deswells in water solutions. It was reported that the stability of such complexes lowers sharply with the decrease of the molecular weight of polymer chains or, with the increase of the temperature or the pH of the solution. To check this point, additional swelling experiments were carried out at four different temperatures, namely, in addition to the room temperature experiments, at 50, 70, and 80°C. The results of experiments at 80°C are shown in Figure 2 as open triangles. The volume of the gel phase increased only slightly as the swelling temperature increases. Even at 80°C, the gel volume in polymer solution is much smaller than that predicted by the theory (Fig. 2). Thus, we can conclude that the complexation is not responsible for contraction of ionic gels in PAAm solutions.

A more plausible explanation for the deswelling of ionic gels in polymer solution is a change in the degree of ionization of AAc units on the network chains, depending on the polymer concentration, i.e., an increase in the number of counterions forming ion pairs on rising polymer concentration in the external solution. Recent studies indicate the importance of ion pairing for the collapse behavior of weakly charged polyelectrolytes. Theoretical calculations show that the fraction of ions forming ion pairs in the gel strongly depends on the dielectric constant $\varepsilon$ of the gel phase; decrease in $\varepsilon$ increases the probability of ionpairing and results in the collapse of the gel. Because the dielectric constants $\varepsilon$ of PAAm is about unity compared to the value $\varepsilon = 80$ for water, increasing content of PAAm in the gel phase decreases the effective dielectric constant of the gel. As a result, formation of ion pairs on PAAm-co-PAAc network chains is more pronounced as the PAAm concentration increases, leading to the deswelling of the gel. Indeed, calculations using the FH theory also showed that, if $f$ (number of fixed charges in a network chain) is taken as a fit parameter instead of $\chi_{23}$, theory predicts the swelling data of ionic gels shown in Figures 1–2. The $f$ values needed to fit the experimental data vs. $\phi$ plot gives a single curve, independent of the molecular weight of linear polymers. The value of $f$ decreases from 5.7 to 0.5, i.e., more than 90% of charged groups in the network vanish on rising the polymer concentration $\phi$ from 0 to 0.4.

**CONCLUSIONS**

The volume of PAAm gels in aqueous solutions of linear PAAm decreases as the concentration or the molecular weight of linear polymer in the external solution increases. It is shown that this swelling behavior of nonionic gels is correctly predicted by the classical FH theory. The polymer–polymer interaction parameter $\chi_{23}$ decreases as the molecular weight of PAAm increases. The swelling behavior of ionic PAAm gels in PAAm solutions deviates from the predictions of the FH theory. This is probably due to the change of the ionization degree of AAc units, depending on the polymer concentration in the external solution.

**REFERENCES AND NOTES**