Swelling Behavior of Anionic Acrylamide-Based Hydrogels in Aqueous Salt Solutions: Comparison of Experiment with Theory

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ABSTRACT: A series of hydrogels were prepared from acrylamide and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) monomers with 0–80 mol % AMPS and using N,N'-methylenebis(acrylamide) as the crosslinker. The swelling capacities of hydrogels were measured in water and in aqueous NaCl solutions. The volume swelling ratio q_v of hydrogels in water increases sharply when the mole fraction f_c of AMPS increases from 0 to 0.06. At higher values of f_c from 0.06 up to 0.18, no change in the swelling capacities of hydrogels was observed; in this range of f_c, q_v becomes nearly constant at 750. However, as f_c further increases, q_v starts to increase again monotonically over the entire range of f_c. At a fixed value of f_c, the swelling ratio of hydrogels decreases with increasing salt concentration in the external solution. The results of the swelling measurements in aqueous salt solutions were compared with the predictions of the Flory–Rehner theory of swelling equilibrium. It was shown that the theory correctly predicts the swelling behavior of hydrogels up to 80 mol % charge densities. The method of estimation of the network parameters was found to be unimportant in the prediction of the experimental swelling data. The network parameters used in the simulation only correct the deficiency of the swelling theory. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 567–575, 1998

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INTRODUCTION

In recent years, hydrophilic gels called hydrogels have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Hydrogels are mainly prepared by free-radical crosslinking copolymerization of acrylamide (AAm) and a divinyl monomer (crosslinker) in aqueous solutions. To increase the swelling capacity of hydrogels, an ionic monomer is also included in the monomer mixture. The desired property of hydrogels, such as their swelling capacity, is obtained by adjusting the concentration as well as the composition of the initial monomer mixture.

Investigations of the swelling behavior of hydrogels have been reported in the last 4 decades. Most of these studies have been concentrated on hydrogels containing weakly ionizable groups such as the carboxylate groups.[1–7] The swelling properties of these weak polyelectrolyte gels strongly vary depending on the pH of the solution.

However, hydrogels with strong electrolytes dissociate completely in the overall pH range and, therefore, exhibit pH independent swelling behavior. Sulfonic acid containing hydrogels represent a class of strong polyelectrolyte gels with a high degree of ionization. It was shown that the linear polymers with sulfonate groups derived from 2-acrylamido-2-methylpropanesulfonic acid (AMPS) exhibit extensive coil expansion in aqueous solutions;[7] even in 5M NaCl solution, the expansion of polymer coils due to charge repulsion cannot be totally screened.[7] Liu and colleagues[8] investigated the swelling properties of the corresponding hydrogels and observed a similar behavior. Highly concentrated salt solutions were required to screen the charge interactions within the hydrogel derived from AMPS and N,N-dimethylacrylamide (DMAA).

Tong and Liu[9] observed a constant swelling capacity of AMPS/DMAA hydrogels in the whole pH range and concluded that the AMPS content of the hydrogel corresponds to its charge density. Their calculation results showed a large discrepancy between the measured swelling data in water and that predicted by the Flory–Rehner theory of swelling equilibrium. Hooper and colleagues[10] and Baker and colleagues[11,12] investigated the swelling properties of strong polyelectrolyte AAm-based cationic and ampholytic hydrogels in water and in aqueous salt solutions. In contrast to Tong and Liu, they observed a good agreement between the Flory–Rehner theory and experiment. It seems that the approximations of the swelling theory cancel each other, so that it correctly predicts the swelling behavior of their hydrogels with charge densities below 5 mol %.

The scope of the present work was to establish whether it is possible to predict the swelling behavior of highly swollen hydrogels with charge densities up to 80 mol % using the Flory–Rehner theory. It was also of interest to clarify the sensitivity of the theory's predictions to the estimation method of the network parameters. For this purpose, we prepared a series of strong polyelectrolyte AAm-AMPS hydrogels with various ionic group content and measured their swelling capacities in water and in aqueous NaCl solutions ranging in concentration from 10^{-5} to 1M. Instead of DMAA, AAm was used as a comonomer of AMPS to increase the swelling capacity of our hydrogels. The measured swelling data of the hydrogels were compared with that predicted by the Flory–Rehner theory. As will be shown, this simple theory correctly predicts the swelling behavior

of hydrogels with swelling capacities up to 2 L of water per mL of dry hydrogel.

EXPERIMENTAL

Materials

AAm (Merck), N,N'-methylenebis(AAm) (BAAm; Merck), AMPS (AKSA), ammonium persulfate (APS; Merck), N,N,N',N'-tetramethylethylenediamine (TEMED; Merck), and NaCl (Merck) were used as received. Double distilled and deionized water were used in hydrogel preparation and in swelling measurements.

Hydrogel Synthesis

Hydrogels were prepared by free-radical crosslinking copolymerization of AAm and AMPS with a small amount of BAAm as a crosslinker in aqueous solution. APS and TEMED were, respectively, the initiator and accelerator. Reactions were conducted at room temperature (21 ± 2°C). Gels were prepared according to the following scheme.

5 g AAm-AMPS mixture, NaOH (in the amount corresponding to the number of moles of AMPS), 133 mg BAAm, and 40 mg APS were dissolved in double distilled water under cooling to give a total volume of 100 mL. After addition of 0.24 mL of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. Polymerization was conducted for 24 h. Homologous series of anionic hydrogels were prepared in this way, allowing systematic variation of the AMPS concentration between 0 and 80 mol % (with respect to the monovinyl monomers). The total monomer concentration and the crosslinker ratio X (mole ratio of vinyl to divinyl monomers) were fixed at 5 w/v % and 82, respectively. It must be pointed out that, due to the electrostatic repulsion between the AMPS monomer and the growing chains, one may expect a lesser reactivity for AMPS compared with AAm in free-radial crosslinking copolymerization. Therefore, the microstructure concerning the composition of the network chains in the hydrogels may be heterogeneous.

After polymerization, hydrogel samples were cut into specimens of ~ 10 mm in length. The samples (usually 10 pieces) were then immersed in a large excess of distilled water for at least 1 week; during this period, water was replaced every other day to remove the unreacted species. It was found that the sol fraction in the gels is

<0.1% after extraction with water. Half of the gel samples were then subjected to swelling measurements, whereas the remaining samples were dried according to the following procedure: the swollen gel samples were successively washed with solutions whose compositions were changed gradually from water to pure methanol. This solvent exchange process facilitates final drying of the gel samples. The collapsed samples after the treatment with methanol as a final solvent were dried in vacuum at 60°C to constant weight. The weight swelling ratio of hydrogels after preparation, q_F, was calculated as

$$q_F = \frac{\text{mass gel after preparation}}{\text{mass dry gel}} \qquad (1)$$

Swelling Measurements

The swollen hydrogel samples from the same gel (usually five pieces) were immersed in vials (100 mL) filled with water. 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 water at least for 1 week; the swelling equilibrium was tested by weighing the samples. The gels were then weighed in the swollen state and transferred to vials containing the most concentrated aqueous NaCl solution. The concentration of NaCl solutions ranged from $1.0M$ to $10^{-5}M$. Gel samples were allowed to swell in the solution at least for 1 week, during which aqueous NaCl was refreshed to keep the concentration as feeded. After the swelling equilibrium is established, the samples were weighed and then transferred into the next dilute NaCl solution. The swelling measurements in aqueous NaCl were conducted both in direction of decreasing salt concentration from $1M$ to water and in reverse direction from water up to $1M$ NaCl. No systematic variation in the recorded swelling data was observed. The weight swelling ratios of hydrogels in water and in aqueous NaCl, q_w (mass gel after swelling/mass dry gel), were calculated using the equations

$$q_w(\text{H}_2\text{O}) = q_F \frac{\text{mass gel in water}}{\text{mass gel after preparation}} \qquad (2a)$$

$q_w(\text{NaCl}_{aq})$

$$= q_w(\text{H}_2\text{O}) \frac{\text{mass gel in aqueous NaCl}}{\text{mass gel in water}} \qquad (2b)$$

The volume swelling ratio of hydrogels, q_v, was calculated as

$$q_v = 1 + \frac{(q_w - 1)\rho}{d} \qquad (3)$$

where ρ and d are the densities of polymer and solution, respectively. The values ρ and d used were 1.35 g mL^{-1} and 1 g mL^{-1}, respectively. Each swelling ratio reported in this article is an average of at least five separate measurements; standard deviations of the measured swelling ratios were <4% of the mean.

THEORY OF SWELLING EQUILIBRIUM

The state of equilibrium swelling of a polymer network immersed in a solvent is obtained when the solvent inside the network is in thermodynamic equilibrium with that outside. This equilibrium state is described by the equality of the solvent chemical potential μ_1 in both phases. Thus, at swelling equilibrium, we have

$$\Delta\mu_1^g = \Delta\mu_1^s \qquad (4)$$

where the superscripts g and s denote the gel and solution phases, respectively. In terms of the osmotic pressure π, eq. (4) can also be written as

$$\pi = -\frac{\mu_1^g - \mu_1^s}{V_1} = 0 \qquad (5)$$

where V_1 is the molar volume of solvent. Osmotic pressure π of a gel determines whether the gel tends to expand or to shrink. When nonzero, π provides a driving force for gel volume change. Solvent moves into or out of the gel until π is 0 (i.e., until the forces acting on the gel are balanced). During the swelling process, there are at least three forces acting on an ionic gel: those 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*). Within the framework of the Flory–Rehner theory, the osmotic pressure π of a gel is the sum of these three contributions[13,14]:

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

According to the Flory–Huggins theory, π_{mix} is given by[15]

$$\pi_{\text{mix}} = -\frac{RT}{V_1}(\ln(1 - v_2) + v_2 + \chi v_2^2) \qquad (7)$$

where v_2 is the volume fraction of polymer in the hydrogel (i.e., $v_2 = 1/q_v$), χ is the polymer–solvent interaction parameter, R is the gas constant, and T is temperature. To describe the elastic contribution π_{el} to the swelling pressure, several theories are available.[16–22] We will use here the simplest affine network model to describe the behavior of our gels[15]:

$$\pi_{\text{el}} = -\frac{RT}{V_1}N^{-1}(v_2^{1/3}v_2^{02/3} - v_2/2) \qquad (8)$$

where N is the average number of segments in the network chain and v_2^0 is the volume fraction of polymer network after preparation. Ionic contribution π_{ion} to the swelling pressure is caused by the concentration difference of counterions between the gel and the outer solution. To describe this effect completely, one should consider the ion–ion, ion–solvent, and ion–polymer interactions. The ideal Donnan theory ignores these interactions and gives π_{ion} as the pressure difference of mobile ions inside and outside the gel[15]:

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

where C_i is the mobile ion concentration of species i. According to ideal Donnan equilibria, the chemical potential of an ionic species i inside the hydrogel must be equal to that outside. Thus, for aqueous solutions of univalent salts, we have the equality

$$C_+^g C_-^g = C_+^s C_-^s = C_{\text{salt}}^{s\,2} \qquad (10)$$

where C_{salt}^s represents the salt concentration in the external solution. On the other hand, the condition of electroneutrality inside an anionic hydrogel requires

$$C_+^g = C_-^g + C_{\text{fix}} \qquad (11)$$

where C_{fix} is the concentration of fixed charges in the gel.

Using eqs. (4)–(11), we obtain the following system of equations describing equilibrium value of v_2 of hydrogels in aqueous salt solution and the distribution coefficient K of counterions between the gel and solution phases:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1}(v_2^{1/3}v_2^{02/3} - v_2/2)$$
$$- 2(K - 1)V_1 C_{\text{salt}}^s - V_1 C_{\text{fix}} = 0 \quad (12a)$$

$$K(K + C_{\text{fix}}/C_{\text{salt}}^s) - 1 = 0 \qquad (12b)$$

where $K = C_-^g/C_{\text{salt}}^s$. Let f be the mole fraction of charged units in the network and $\bar{V}_r$ the molar volume of a polymer repeat unit, C_{fix} equals to

$$C_{\text{fix}} = \frac{f}{\bar{V}_r}v_2 \qquad (12c)$$

In the case of swelling of hydrogels in water free of ionic species ($C_{\text{salt}}^s = 0$), eq. (12a) reduces to

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1}(v_2^{1/3}v_2^{02/3} - v_2/2)$$
$$- V_1 C_{\text{fix}} = 0 \quad (13)$$

Note that, for $C_{\text{salt}}^s < 10^{-6}M$, the contribution of the salt concentration in the external solution to the swelling equilibrium represented by eqs. (12a) and (12b) becomes negligible; thus, eq. (12a) also reduces to eq. (13) for $C_{\text{salt}}^s < 10^{-6}M$.

Moreover, for highly swollen hydrogels, since $v_2 \ll 1$, eqs. (12a) and (12b) can also be written as

$$-(0.5 - \chi)v_2^2 + N^{-1}v_2^{02/3}v_2^{1/3} - 2V_1 C_{\text{salt}}^s(K - 1)$$
$$- V_1 C_{\text{fix}} = 0 \quad (14)$$

where

$$K = 0.5\left(\sqrt{\left(\frac{C_{\text{fix}}}{C_{\text{salt}}^s}\right)^2 + 4} - \frac{C_{\text{fix}}}{C_{\text{salt}}^s}\right) \qquad (14a)$$

Calculations

The system of eqs. (12a) and (12b), in combination with eq. (12c), was solved numerically to calculate the equilibrium swelling ratio of hydrogels in aqueous salt solutions ($q_v = 1/v_2$) and the distribution coefficient of counterions K. For calculations, the values used were $V_1 = 18$ g mL^{-1}

and $\bar{V}_r = 52.6 + 117 f$ (obtained using the values 71 and 229 g mol^{-1} for the molecular weights of AAm and AMPS units, respectively, and using $\rho = 1.35$ g mL^{-1}). The χ parameter value for polyacrylamide (PAAm)–water system was recently evaluated from the swelling data for uncharged PAAm hydrogels swollen in water.[10] A best-fit value for χ of 0.48 was obtained.[11] This value of the χ parameter provided a good fit to the experimental swelling data of AAm-based anionic, cationic, and ampholytic hydrogels of various compositions.[11,12] In the following calculations, χ was held constant at this value. The volume fraction of polymer network after preparation, v_2^0, was calculated from the experimental q_F values as

$$v_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d} \right]^{-1} \tag{15}$$

The experimental value of v_2^0 increased from 0.038 to 0.070 with increasing AMPS content from 0 to 80 mol %. C_{salt}^s is the independent variable of eqs. (12a) and (12b), which was varied between $10^{-5}M$ and $1.0M$ in our experiments.

To solve eqs. (12a) and (12b) for the two unknowns, $q_v = 1/v_2$ and K, the values of the network parameters f and N characterizing the hydrogels must also be known. The f and N values of hydrogels can be estimated by two different approaches.

Chemically Fixed Crosslink Density of Hydrogels

Because both the crosslinker ratio X (mole ratio of monomer to crosslinker) and the total monomer concentration were fixed in our experiments, whereas only the mole fraction of AMPS varies between the hydrogels, it is reasonable to assume a constant crosslink density for all the hydrogels. Thus, using the swelling ratio of nonionic gel in water $q_v = 40.9$ and using eq. (13) for $C_{\text{fix}} = 0$, we calculated N as 1.2×10^3, which should be valid for all other ionic hydrogels. After calibration of the gels, that is, after finding their crosslink densities in terms of N, f value of the ionic hydrogels obtained at the same chemical crosslink density was calculated from their swelling ratio in water and using eq. (13) for the condition $N = 1.2 \times 10^3$. Note that this method of estimation of the network parameters assumes that the addition of AMPS in the comonomer mixture does not change the network topology.

Chemically Varied Charge Density of Hydrogels

Because AMPS is a strong dissociating electrolyte, the amount of AMPS used in the hydrogel preparation should be equal to its charge density. Thus, f in eq. (12c) is given by

$$f = \frac{\text{AMPS mol \%}}{100} \tag{16}$$

From the equilibrium swelling ratio of hydrogels in water and using eqs. (13) and (16), one may calculate the crosslink densities of hydrogels in terms of N. Note that this method of estimation of network parameters neglects counterion condensation[6,23] and assumes that the ionization degree of AMPS units equals to unity. Also, it is assumed that AMPS completely reacts during the gel formation, and no reactions such as the hydrolysis reaction of AAm units take place during the swelling measurements.

In the following section, we will use both approaches to evaluate the network parameters and to compare the predictions of the theory with the experimental data.

RESULTS AND DISCUSSION

Figure 1 shows the volume swelling ratio q_v of AMPS/AAm hydrogels in water and in aqueous salt solutions plotted as a function of f_c, the mole fraction of AMPS used in the gel preparation. As expected, q_v increases sharply when the mole fraction f_c of AMPS increases from 0 to 0.06. This is due to the fact that, as f_c increases, the mobile ion (Na$^+$) concentration inside the gel also increases to maintain the electroneutrality condition. As a result, the difference between the mobile ion concentration inside and outside the gel increases with increasing f_c, which creates an additional osmotic pressure that expands the gel. Also expected is the decreased swelling ratio of hydrogels with increasing salt concentration in the external solution; this is due to decrease in the concentration difference of counterions inside and outside the hydrogel. In $1.0M$ NaCl solution, the swelling ratio is almost independent on the AMPS content of hydrogels due to screening of charge interactions within the hydrogel.

Interestingly, at higher values of f_c from 0.06 up to 0.18, no change in the swelling capacities of hydrogels was observed; in this range of f_c, q_v becomes nearly constant at 750. This may be a

result of counterion condensation, as was observed previously in carboxylate-containing AAm hydrogels.[6] However, as f_c further increases, q_v starts to increase again monotonically over the entire range of f_c. This swelling behavior of hydrogels with $f_c > 0.2$ may be a result of their high swelling ratios. The network chains in these swollen hydrogels are in 9- to 10-fold expanded configuration with respect to dry state, so that a destruction of the chains may occur during the swelling process. For AMPS/DMAA hydrogels, Tong and Liu also obtained a similar swelling curve as given in Figure 1. However, due to their insufficient data points in the range of $f_c < 0.20$, they interpreted the results as a monotonic increase of q_v over the entire f_c range from 0 to 0.90. However, the present results clearly illustrate the plateau in the swelling curve between $f_c = 0.06$ and 0.18.

Using the equilibrium swelling data q_v of hydrogels in water, we can now evaluate the network parameters f and N, describing the average number of charged units and of segments in a network chain, respectively. First, the value $q_v = 40.9$ found by experiments for nonionic gels in water yields $N = 1.2 \times 10^3$, compared with its chemical value $N_c = 41$ calculated from the crosslinker ratio $X = 82$. Comparison of these two values indicates that >90% of the crosslinker BAAm used in the gel synthesis were consumed in cycles and/or in multiple crosslinks. This is in accord with our previous results.[24,25] Second, to evaluate f and N values of ionic hydrogels, we will use both approaches explained in the previous section.

Chemically Fixed Crosslink Density

Assuming that $N = 1.2 \times 10^3$ is valid for all other hydrogels, eq. (13) can be solved for f using the experimental q_v data of ionic hydrogels. The calculated values of f are shown in Figure 2(A) as filled symbols plotted as a function of mole fraction of AMPS in the gel synthesis f_c. In the figure, the dotted line represents the relation $f/f_c = 1$ (i.e., in this line AMPS content of hydrogels equals to their charge density). It is seen that, in up to 1% AMPS content, all AMPS units act as charged units in the gel swelling. However, as f_c further increases, deviations appear from the straight line dependence, and f approaches a limiting value of 0.25.
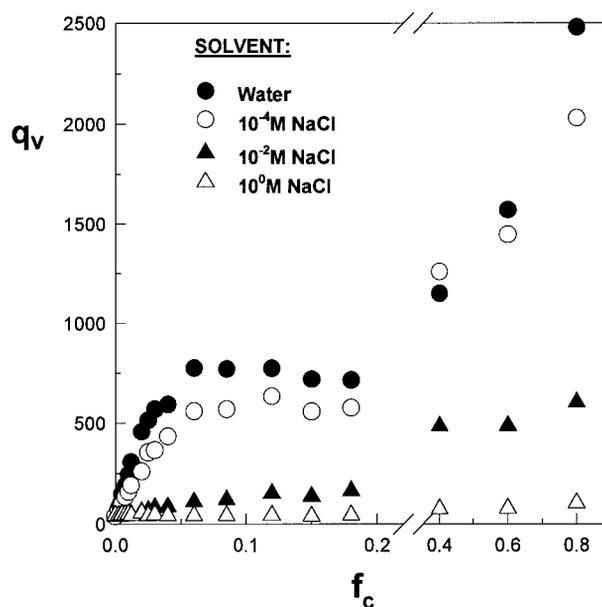

Figure 1   Variation of the volume swelling ratio q_v of AAm/AMPS hydrogels in water and in aqueous NaCl solutions with the mole fraction of AMPS used in the gel preparation f_c.

Chemically Varied Charge Density

Assuming that $f = f_c$, eq. (13) can be solved for N using the experimental q_v data of ionic hydrogels. The calculated values of N are also shown in Figure 2(B) as open symbols plotted as a function of f_c. N strongly decreases on rising f_c and approaches its stochiometric value of $N_c = 41$, shown in Figure 2(B) as the horizontal dashed line.

It is seen that the two approaches used in the estimation of the network parameters f and N yield totally different values. We will use now both approaches to predict the swelling capacities of hydrogels in aqueous NaCl solution. The results are collected in Figures 3 and 4. Herein, the volume swelling ratios q_v of hydrogels are shown as a function of the NaCl concentration. The experimental data are shown as symbols. The solid curves were calculated using eqs. (12a) and (12b) and using f and N values evaluated from the first approach. The dotted curves were calculated in the same way; but we used f and N values evaluated from the second approach. It is seen that both approaches provide good agreement with the experimental data up to 1.5 mol % AMPS (Fig. 3). In this range of AMPS concentration, the first approach (solid curves, N fixed) provides a slightly better agreement with the experimental
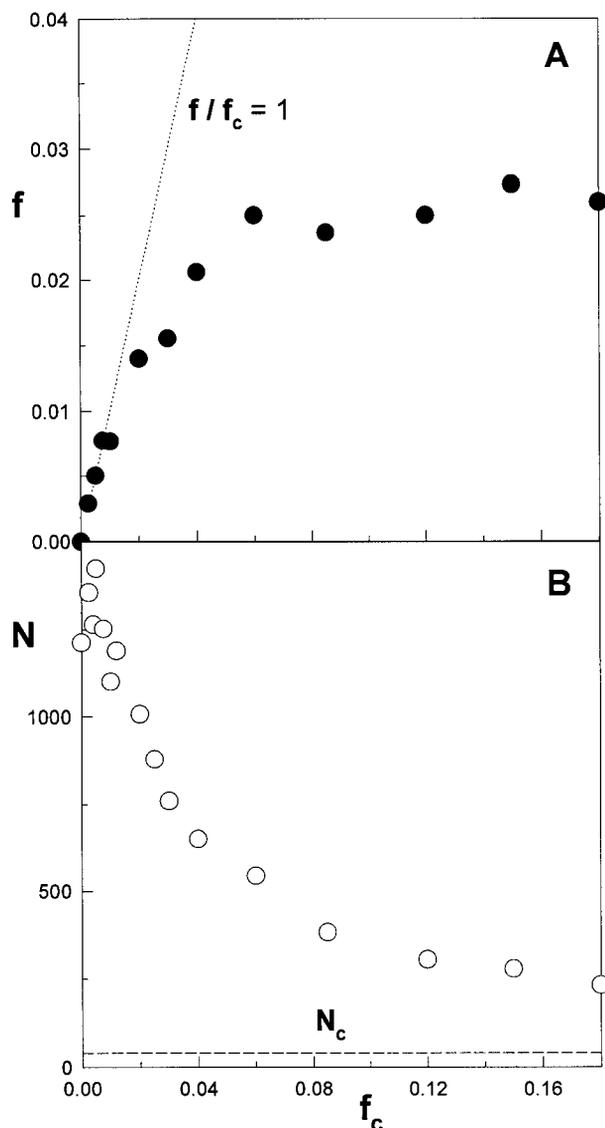
Figure 2 Variation of the network parameters f and N with the AMPS content of hydrogels f_c. In (A), the crosslink density of hydrogels is assumed to be constant (chemically fixed crosslink density), whereas in (B) the charge density of hydrogels is assumed to be equal to their AMPS content (chemically varied charge density). The f and N values were evaluated from the swelling ratio of hydrogels in pure water and using eq. (13).

data. Agreement between theory and experiment becomes qualitative at high AMPS contents ($>18\%$; Fig. 4); Herein, the second approach ($f = f_c$) provides a better fit to the experimental data. We can conclude that both estimation methods of the network parameters can be used to predict the swelling behavior of hydrogels in aqueous salt solutions. In fact, due to the several assumptions and

approximations of the Flory–Rehner and Flory–Huggins theories, no agreement between theory and experiment can be expected, especially in case of highly swollen hydrogels. This is, of course, in the case, where the actual values of f and N were used in the calculations.[9,11] The present results indicate that the deficiency of the theories are compensated by the values of the parameters f and N used in the fit. Thus, it must be pointed out that the values of f and N generated from the experimental swelling data should only be considered as fit parameters.

Another interesting point that is not visible in the magnification of Figures 3 and 4 is illustrated in Figure 5. The equilibrium swelling ratio q_v of hydrogels with <3 mol % AMPS content increases again, when the salt concentration further increases from $0.01M$ to $1.0M$. This interesting feature, not predicted by the theory, was also observed previously by Baker and colleagues[12] in ampholytic and nonionic AAm-based hydrogels. Specific interactions between AAm and mobile ions seem to be responsible for this behavior.

Figure 6 shows the calculated distribution coefficient K of mobile counterions Cl^- between inside and outside the gel phase plotted as a function of the NaCl concentration in the external
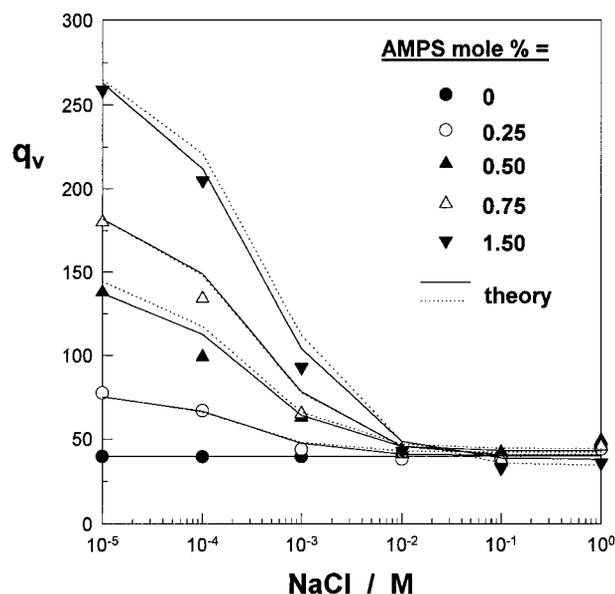

Figure 3 Variation of the volume swelling ratio q_v of hydrogels with the NaCl concentration in the external solution. Experimental data are shown as symbols. Curves were calculated using the swelling theory. Calculations were for fixed N (solid curves) and for $f = f_c$ (dotted curves).
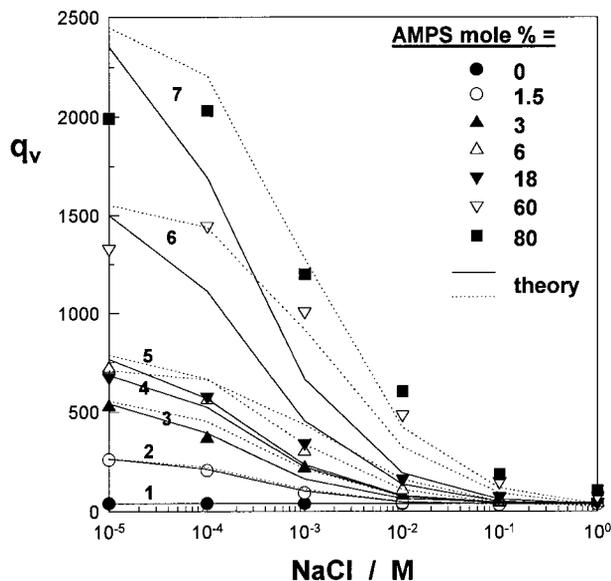
Figure 4   Variation of the volume swelling ratio q_v of hydrogels with the NaCl concentration in the external solution. Experimental data are shown as symbols. Curves were calculated using the swelling theory. Calculations were for fixed N (solid curves) and for $f = f_c$ (dotted curves). AMPS mole % = 0 (1), 1.5 (2), 3 (3), 6 (4), 18 (5), 60 (6), and 80 (7).

solution. Calculations were using the network parameters generated by the first approach and for hydrogels with 0–18 mol % AMPS content. Here, $K = 1$ means that the anion concentration inside the anionic gel is equal to that in the solution, whereas $K = 0$ means that the anionic gel excludes all the anions. Figure 6 indicates that a large amount of Cl^- ions penetrate into the gel if the salt concentration in the outer solution is high. Decreasing salt concentration in the solution decreases the K ratio, and it approaches 0 for NaCl concentrations $<10^{-5}M$. Thus, if the concentration of NaCl in the outer solution is sufficiently low, the Cl^- ion does not penetrate inside the hydrogel.

CONCLUSIONS

A series of hydrogels from AAm and AMPS monomers were prepared by free-radical crosslinking copolymerization using BAAm as the crosslinker. The swelling capacities of the hydrogels were measured in water and in aqueous salt solutions ranging in concentration from 10^{-5} to $1M$. The volume swelling ratio q_v of hydrogels in water increases sharply as the mole fraction f_c of AMPS
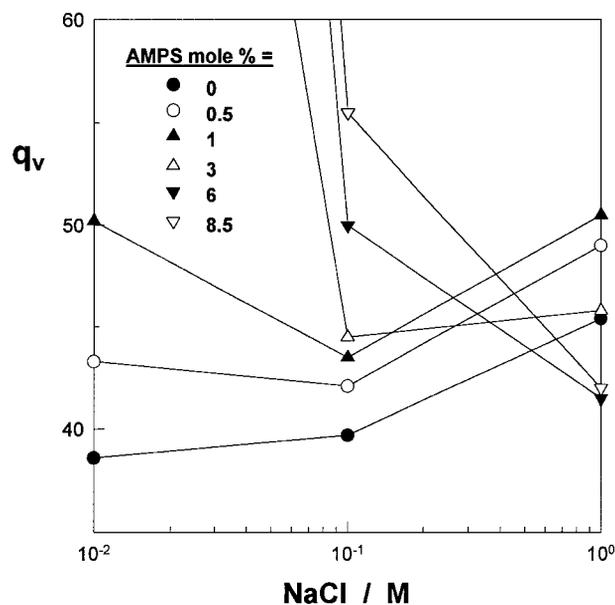

Figure 5   Variation of the volume swelling ratio q_v of hydrogels with the NaCl concentration in the external solution. Experimental data are shown as symbols. Curves only show the trend of data.

increases from 0 to 0.06. At higher values of f_c from 0.06 up to 0.18, no change in the swelling capacities of hydrogels was observed. However, as
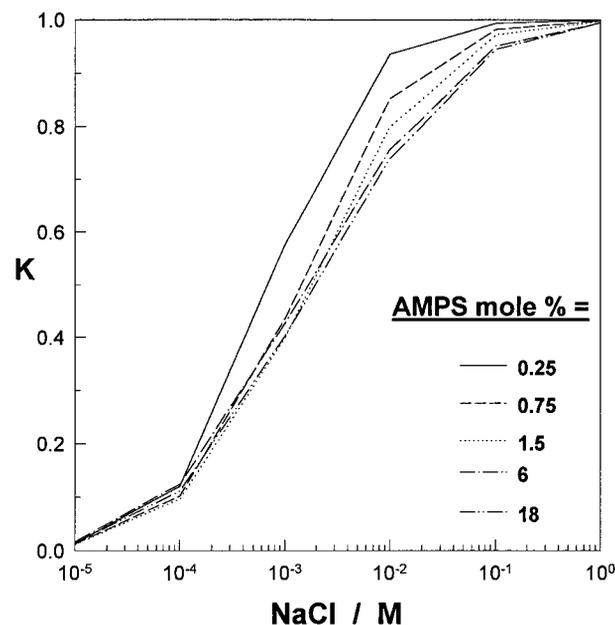

Figure 6   Variation of the calculated distribution coefficient K of Cl^- ions between the gel and solution phases as a function of the NaCl concentration. Calculations were for a fixed crosslink density N.

f_c further increases, q_v starts to increase again monotonically over the entire range of f_c. The results of swelling measurements of hydrogels in aqueous NaCl solutions were compared with the theory of swelling equilibrium. It was shown that the theory correctly predicts the swelling behavior of hydrogels up to 80 mol % charge densities. The method of estimation of the network parameters was found to be insignificant in the simulation of the experimental swelling data. The network parameters only correct the deficiency of the swelling theory.

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