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Swelling of strong polyelectrolyte hydrogels in polymer solutions: effect of ion pair formation on the polymer collapse

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Abstract

A series of strong polyelectrolyte hydrogels based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid sodium salt or [(Methacrylamido)propyl]trimethyl ammonium chloride were prepared by free-radical crosslinking copolymerization. Their swelling behavior was investigated in a good solvent (water), in polymer melt and in aqueous polymer solutions. Poly(ethylene glycol) of various molecular weights was used as the linear polymer in the swelling experiments. The equilibrium volume swelling ratio q_v of the hydrogels in water scales with the network charge density f by the relation $q_v \propto f^{0.66}$. The volume of the hydrogels in the polymer melt decreases as the number of segments, y, on the polymer increases. It was shown, for the non-ionic hydrogels, that this deswelling occurs due to the mixing entropy of the linear polymer in the external solution, whereas, for the ionic gels, due to trapping of counterions caused by the decreased polarity of the medium. The network–polymer interaction parameter χ_{23} was found to vary with y by the relation $\chi_{23} = \text{constant}/y$. The hydrogels also deswell in aqueous polymer solutions as the polymer concentration increases. This deswelling occurs smoothly or jumpwise, as a first-order phase transition, depending on the ionic group content of the hydrogels. The Flory–Huggins theory correctly predicts the swelling and collapsing behavior of the hydrogels in polymer solutions if the variation of the effective charge density depending on the medium polarity is taken into account.

Keywords: Hydrogels; Acrylamide; 2-acrylamido-2-methylpropane sulfonic acid sodium salt

1. 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 often reported in the last four 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 [1]. 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. Since 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 (FH) 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 poly(acrylic acid-*co*-acrylamide) (PAAc–PAAm) hydrogels swollen in aqueous poly(ethylene glycol) (PEG) solutions [15,16]. However, in order to predict the collapse of ionic PAAm gels in polymer solutions using the FH theory, unrealistic large values have to be assigned to the extent of the energetic interactions between the polymer and network segments (χ_{23}) [16]. Thus, an artificial incompatibility between the network and the linear polymer was necessary in order to reproduce the experimental course from the theory. Our recent results of observations on PAAc–PAAm hydrogels immersed in aqueous solutions of monodisperse PAAms indicated that the change in the ionization degree of the acrylic acid (AAc)

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units in the network chains, depending on the polymer concentration, is responsible for the deswelling behavior of the hydrogels [17]. It seems that, instead of the incompatibility between the network and the linear polymer, the increasing extent of ion pair formation in polymer solution is mainly responsible for the collapse of ionic hydrogels in polymer solution.

The present work was carried out in order to justify this point. We investigated the swelling behavior of strong polyelectrolyte PAAm hydrogels in aqueous PEG solutions. The ionic group content of the hydrogels, the concentration and the molecular weight of PEG in the external solution were the independent variables of this study. A series of hydrogels were prepared using 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) or [(Methacrylamido)-propyl]trimethyl ammonium chloride (MAPTAC) as the ionic comonomer of acrylamide AAm by free-radical crosslinking copolymerization. The choice of these hydrogels is motivated by the fact that both AMPS and MAPTAC monomers dissociate completely in the overall pH range, and therefore, the resulting hydrogels exhibit a pH-independent swelling behavior [18–20]. Also, the possibility of a complex formation due to hydrogen bonding is excluded by the choice of these systems [17]. The experimental swelling data of the hydrogels in water, in PEG and in aqueous PEG solutions were analyzed in terms of the FH theory. As will be shown below, this theory correctly predicts the swelling and collapsing behavior of hydrogels in polymer solution if the formation of ion pairs due to the decreased polarity of the medium is taken into account.

2. Experimental

2.1. Materials

Acrylamide (AAm, Merck) was crystallized from an acetone/ethanol mixture (70/30 by volume) below 30°C. 2-acrylamido-2-methylpropane sulfonic acid (AMPS-H^+, Merck) was crystallized from boiling methanol. The purity of the monomers was checked by IR, NMR and elemental microanalysis. AMPS stock solution was prepared by dissolving 20 g of AMPS-H^+ in about 40 ml of distilled water and adding to this solution 10 ml of a 30% NaOH solution under cooling. Then, the solution was titrated with 1 M NaOH to $pH = 7.00$ and finally, the volume of the solution was made up to 100 ml with distilled water. 1 ml of AMPS stock solution thus prepared contained 0.966 mmol AMPS. A 50% solution of MAPTAC in water was purchased from Aldrich and used as received. N,N'-methylenebis(acrylamide) (BAAm, Merck) and potassium persulfate (KPS, Merck) were used as received. KPS stock solution was prepared by dissolving 0.040 g of KPS in 10 ml of distilled water. Distilled and deionized water was used for the swelling experiments. For the preparation of the stock solutions and for the hydrogel synthesis, distilled and deionized water was distilled again prior to use and cooled under nitrogen bubbling. Reagent-grade PEGs were purchased from Fluka (PEG 200, 300, 400 and 600, where the number indicates its molecular weight), and used without further purification.

2.2. Synthesis of hydrogels

PAAm gels were prepared by free-radical crosslinking copolymerization of AAm with a small amount of BAAm in aqueous solution at 40°C in the presence of 0.474 mM KPS as the initiator. AMPS and MAPTAC were used as the ionic comonomers. Both the crosslinker ratio (mole ratio of the crosslinker BAAm to the monomers AAAm + AMPS or MAPTAC) and the total monomer concentration were fixed at 1/82 and 0.700 M, respectively, whereas the ionic comonomer (AMPS or MAPTAC) content of the monomer mixture was varied from 0 to 10 mol%. To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with 1 mol% AMPS in the comonomer feed composition.

AAm (0.492 g), AMPS stock solution (0.072 ml), BAAm (0.0131 g) and KPS stock solution (0.32 ml) were dissolved in 10 ml of distilled water. After bubbling nitrogen for 20 min, the solution was poured into several glass tubes of 4.5–5 mm internal diameters and about 100 mm long. The glass tubes were sealed, immersed in a thermostated water bath at 40°C and the polymerization was conducted for 1 day. For the preparation of AAm/MAPTAC gels, the reaction time was set to 2 days. Temperature measurements during the experiments showed a temperature rise of less than 1°C inside the reaction solution, indicating that the dilute reaction condition provides a nearly isothermal condition. 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.

A homologous series of hydrogels were prepared in this way, allowing for systematic variation of the ionic monomer content of the monomer mixture. The ionic comonomer content in the feed was represented by x_i, which is defined as:

$$x_i = \frac{\text{mol of AMPS or MAPTAC in feed solution}}{\text{total mol of monomer in feed solution}} \tag{1}$$

Our previous work showed that under the reaction condition given above, both the gel fraction and the fractional monomer conversion are larger than 0.98 in the AAm/AMPS crosslinking copolymerization [21]. Therefore, the x_i of AAm/AMPS networks also corresponds to the real mole fraction of the ionic unit in the network. However, since no kinetic data are available for AAm/MAPTAC copolymerization, the x_i values of these hydrogels may differ from the actual composition of the network chains.

2.3. Swelling measurements

Swelling experiments were carried out at room temperature (24 ± 1°C) using water or aqueous solutions of PEGs of various concentrations and molecular weights. The hydrogel samples were immersed in vials (100 ml) filled with a PEG–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. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions for at least 1 week, during which the solutions were replaced twice. After the swelling equilibrium is established, the diameter of the gels was measured by a calibrated digital compass.

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

$$V/V_0 = (D/D_0)^3 \tag{2}$$

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

The concentration of aqueous PEG-300 solution used in the swelling experiments ranged from 0 to 100% by volume. In order to prevent formation of kinetically frozen structures within the gel samples [22], the swelling measurements in aqueous PEG-300 were conducted in the direction of increasing PEG concentration.

The equilibrium volume swelling ratio of the hydrogels q_v (volume of swollen gel/volume of dry gel) and the volume fraction of the network in the swollen gel v_2 was calculated as

$$q_v = \frac{1}{v_2} = \frac{(V/V_0)}{v_2^0} \tag{3}$$

where v_2^0 is the volume fraction of the network after the gel preparation, which was calculated from the mole fraction of the ionic unit in the network x_i, the molecular weights of AMPS, MAPTAC and AAm (229, 220.5 and 71 g/mol, respectively), and the polymer density ρ as:

$$v_2^0 = C_0\bar{V}_r \tag{4}$$

where C_0 is the initial monomer concentration (0.700×10^{-3} mol/cm^3) and $\bar{V}_r$ is the average molar volume of the network units in cm^3/mol, i.e.

$$\bar{V}_r = [229x_i + 71(1 - x_i)]/\rho \qquad \text{(for AAm/AMPS)} \tag{5a}$$

$$\bar{V}_r = [220.5x_i + 71(1 - x_i)]/\rho \qquad \text{(for AAm/MAPTAC)} \tag{5b}$$

The literature values of ρ found for the PAAm network and for poly(2-acrylamido-2-methylpropanesulfonamide) derived from poly(AMPS-H$^+$) are 1.35 and 1.443 g/cm^3, respectively [23,24]. For the calculations, we assumed a constant density of 1.35 g/cm^3 for all the hydrogels.

3. Theory

The experimental swelling data were analyzed in terms of the classical 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 ΔG_m, in the free energy of elastic deformation ΔG_{el} and in the free energy of electrostatic interactions ΔG_i :

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \tag{6}$$

According to the FH theory, ΔG_m is given by [25]:

$$\Delta G_m = RT\left(\sum_i n_i \ln v_i + \sum_{i<j} n_i v_j \chi_{ij}\right) \tag{7}$$

where n_i is the moles of the species i, v_i is its volume fraction, χ_{ij} is the interaction parameter between the species i and j, R is the gas constant and T is temperature. For the present (quasi) ternary system, the subscript $i = 1, 2$ and 3 denotes the solvent (water), the network (ionic PAAm) and the linear polymer (PEG), respectively. For the free energy of elastic deformation ΔG_{el}, several theories are available [26–34]. However, we will use here the simplest affine network model to describe qualitatively the elasticity of the PAAm network [25]:

$$\Delta G_{el} = (3/2)\left(\frac{RT}{NV_1}\right)(\alpha^2 - 1 - \ln \alpha) \tag{8a}$$

where N is the average number of segments in the network chains, V_1 is the molar volume of solvent and α is the linear swelling ratio with respect to the after synthesis stage of the gel, i.e.

$$\alpha = \left(\frac{D}{D_0}\right) = \left(\frac{v_2^0}{v_2}\right)^{1/3} \tag{8b}$$

The existence of fixed ions on the network chains results in non-equal distribution of mobile counterions between the inside and outside the gel. For ionic gels, this contribution (ΔG_i) may be written as follows [25]:

$$\Delta G_i = RTf\frac{v_2}{v_1}n_1 \ln(fv_2) \tag{9}$$

where f is the effective charge density of the network, i.e. the fraction of segments bearing ionic groups. Substitution of Eqs. (7)–(9) into Eq. (6) and differentiating with respect to the number of moles of solvent n_1 and linear polymer n_3 yield the following set of equations for the excess chemical potentials of the solvent and the polymer in both gel ($\Delta\mu_i^{gel}$)

and solution phases ($\Delta\mu_i^{\mathrm{sol}}$) :

$$\frac{\Delta\mu_1^{\mathrm{gel}}}{\mathrm{R}T} = \ln v_1 + (1 - v_1) - v_3/y + (\chi_{12}v_2 + \chi_{13}v_3)(1 - v_1) - \chi_{23}v_2v_3 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) - v_2 f \quad (10a)$$

$$\frac{\Delta\mu_1^{\mathrm{sol}}}{\mathrm{R}T} = \ln(1 - \phi) + \phi(1 - 1/y) + \chi_{13}\phi^2 \quad (10b)$$

$$\frac{\Delta\mu_3^{\mathrm{gel}}}{y\mathrm{R}T} = (1/y)\ln v_3 + (1/y)(1 - v_3) - v_1 + (\chi_{13}v_1 + \chi_{23}v_2) \times (1 - v_3) - \chi_{12}v_1v_2 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) - v_2 f \quad (11a)$$

$$\frac{\Delta\mu_3^{\mathrm{sol}}}{y\mathrm{R}T} = (1/y)\ln\phi - (1 - \phi) + (1/y)(1 - \phi) + \chi_{13}(1 - \phi)^2 \quad (11b)$$

where y is the number of segments in the linear polymer and ϕ is its volume fraction in the solution 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 μ of these components in both phases. Thus, at swelling equilibrium, we have:

$$\Delta\mu_1^{\mathrm{gel}} - \Delta\mu_1^{\mathrm{sol}} = 0 \quad (12a)$$

$$\Delta\mu_3^{\mathrm{gel}} - \Delta\mu_3^{\mathrm{sol}} = 0 \quad (12b)$$

In terms of the osmotic pressure π, Eq. (12a) can also be written as:

$$\pi = -\frac{(\mu_1^{\mathrm{gel}} - \mu_1^{\mathrm{sol}})}{V_1} = 0 \quad (12c)$$

Osmotic pressure π of a gel determines whether the gel tends to expand or to shrink. When non-zero, π provides a driving force for the gel volume change. The solvent moves into or out of the gel until π is zero, i.e. until the forces acting on the gel are balanced.

Combining Eqs. (10a)–(11b), we obtained the following two equations describing the thermodynamic equilibrium condition of an ionic gel immersed in a polymer solution:

$$\ln\left(\frac{1 - v_2 - v_3}{1 - \phi}\right) + (v_2 + v_3 - \phi) - (v_3 - \phi)/y + \chi_{12}v_2^2 + \chi_{13}(v_3^2 - \phi^2) + (\chi_{12} + \chi_{13} - \chi_{23})v_2v_3 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) - fv_2 = 0 \quad (13)$$

$$-\ln\left(\frac{1 - v_2 - v_3}{1 - \phi}\right) + (1/y)\ln(v_3/\phi) + 2\chi_{13}(v_3 - \phi) + (\chi_{23} - \chi_{12} - \chi_{13})v_2 = 0 \quad (14)$$

Eqs. (13) and (14) predict the equilibrium volume swelling ratio of the hydrogels in polymer solution ($q_\mathrm{v} = 1/v_2$) and the concentration of the linear polymer molecules penetrating into the gel phase (v_3) from the following parameters.

1. The concentration ϕ and the chain length y of the linear polymer in the external solution. These are the independent variables of the present study.
2. The network concentration after the gel preparation v_2^0. v_2^0 is fixed by the experimental condition and it is given by Eq. (4).
3. The interaction parameters between solvent–network, solvent–polymer and network–polymer, represented by χ_{12}, χ_{13}, and χ_{23}, respectively.
4. The crosslink (N^{-1}) and the effective charge densities of the network (f).

Eqs. (13) and (14) thus contain five unknowns, χ_{12}, χ_{13}, χ_{23}, N and f, which are going to be determined from the numerical analysis of the experimental data. After finding these parameters, they can be used to interpret the swelling behavior of the hydrogels in polymer solution.

4. Results and discussion

4.1. Swelling in a solvent

The equilibrium volume swelling ratios of the hydrogels in water q_v are shown in Fig. 1A plotted as a function of the mole fraction of the ionic comonomer in the network x_i. The filled and open symbols represent the swelling data of the hydrogels prepared using AMPS and MAPTAC as the ionic comonomer, respectively. As expected, q_v rapidly increases with increasing ionic group content of the hydrogels up to about $x_\mathrm{i} = 0.03$. This is a consequence of the osmotic pressure exerted by the counterions of AMPS or MAPTAC units in the network chains. This osmotic pressure increases as the concentration difference of the counterions between the inside and outside the gel phase increases. Between $x_\mathrm{i} = 0.03$ and 0.10, the equilibrium swelling of the hydrogels in water is almost independent on their ionic group content and the hydrogels attain a limiting value of $q_\mathrm{v} = 520 \pm 70$. Another point shown in Fig. 1A is that MAPTAC containing hydrogels with 1–3 mol% MAPTAC swell in water more than the corresponding hydrogels with AMPS units. This is probably due to the dependence of the swelling ratio of strong polyelectrolyte hydrogels on the chemical nature of the counterions (Na^+ versus Cl^- for AMPS and MAPTAC containing hydrogels).

For highly swollen hydrogels such as those of the present study, the swelling equilibrium is mainly determined by the mixing entropy of the counterions (Eq. (9)) which is

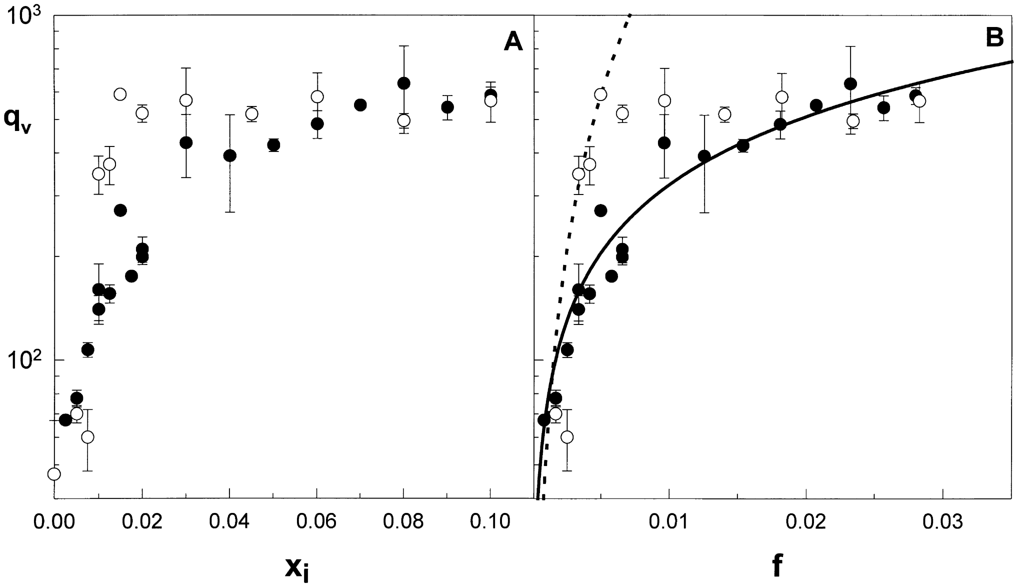

Fig. 1. The equilibrium volume swelling ratio of the hydrogels in water q_v shown as a function of: (A) the mole fraction of the ionic comonomer in the network x_i; and (B) of the fraction of network segments bearing ionic group f. Filled and open symbols represent the swelling data of the hydrogels prepared using AMPS and MAPTAC as the ionic comonomer, respectively. The dotted curve in (B) represents the prediction of the FH theory. The solid curve is the best fitting curve to the experimental swelling data of AMPS hydrogels.

balanced by the gel rubber-like elasticity (Eq. (8a)). Thus, balancing Eqs. (8a)–(9) by minimizing their sum with respect to the number of moles of solvent n_1 leads to:

$$q_v \propto (fN)^{3/2}(v_2^0)^{-1} \tag{15}$$

Since the crosslinker ratio and the monomer concentration used in the hydrogel synthesis were fixed in our experiments, Eq. (15) reduces to:

$$q_v \propto f^{3/2} \tag{16}$$

which indicates a scaling parameter of 1.5 between q_v and f.

It is important to note that the FH theory from which Eq. (16) was derived assumes an equivalent size both for the solvent molecules and the network segments [25]. Thus, due to the different molar volumes of the monomer units and solvent of the present system, the fraction of network segments bearing the ionic group f does not correspond to x_i. In the following, f was calculated from x_i using the equation:

$$f = x_i \frac{V_1}{\bar{V}_r} \tag{17}$$

where $\bar{V}_r$ is the average molar volume of the network chains which is given by Eqs. (5a) and (5b) for AAm/AMPS and AAm/MAPTAC based hydrogels, respectively. The f values of the hydrogels calculated using Eq. (17) are shown in Fig. 2 as the solid curve plotted as a function of the real mole fraction of AMPS units in the network x_i. It is seen that f is much smaller than x_i and, it becomes rather insensitive to x_i at high ionic comonomer concentrations. This is due to the fact that each AMPS unit in the gel occupies a volume equal to nine-fold the volume of a solvent molecule, i.e. each AMPS unit forms nine segments but produces only one mobile ion in the gel. This size effect of the ionic comonomer, which was not taken into account in many of previous works, results in a considerable lower charge

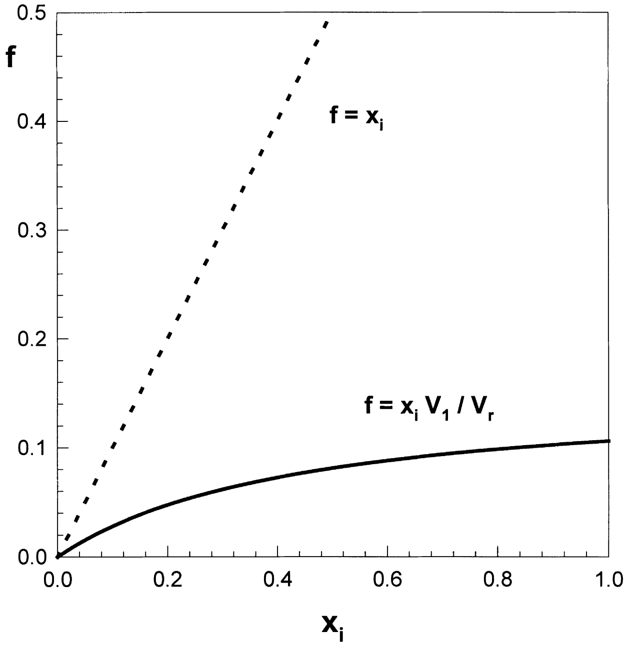

Fig. 2. The charge density of the networks f shown as a function of the real mole fraction of AMPS units in the network x_i. Owing to the different molar volumes of the monomer units and solvent, f deviates from x_i as shown by the solid curve.

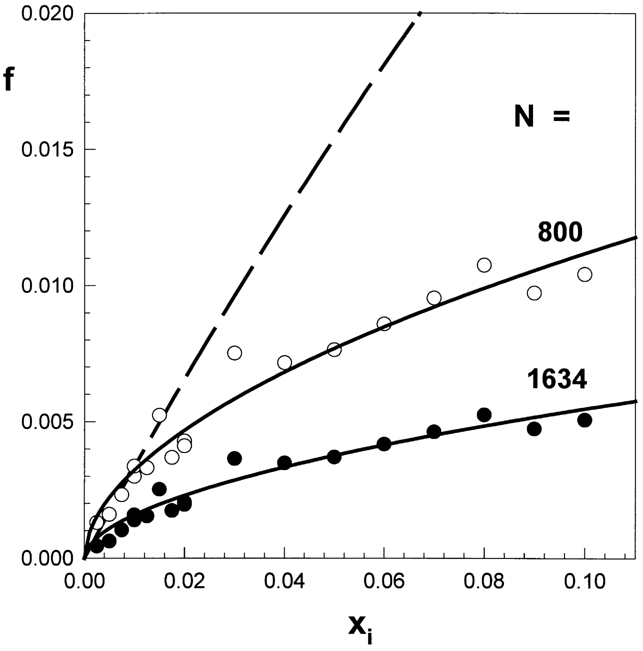

Fig. 3. The effective charge density of the network f calculated from the experimental swelling data of the hydrogels shown as a function of the real mole fraction of AMPS units in the network x_i. Calculations were for $N = 1635$ (filled symbols) and 800 (open symbols). The solid curves were calculated using Eq. (22) for the two different N values. The dashed curve represents the f values if all the counterions in the hydrogel are effective in the swelling process.

density than expected from the chemical composition of the network chains.

In Fig. 1B, the independent variable x_i was replaced with f using Eq. (17). A plot similar to Fig. 1A is seen in this figure but, the swelling ratio becomes almost independent of f for $f > 0.01$. The dotted curve in Fig. 1B represents the prediction of the FH theory (Eq. (16)) with a scaling parameter of 1.5. The solid curve in this figure is the best fitting curve to the experimental swelling data of AMPS hydrogels, which gives a scaling relation:

$$q_v \propto f^{0.66} \tag{18}$$

The scaling parameter 0.66, thus found, is much smaller than the predicted value of 1.5 of the FH theory. An exponent between 0.6 and 0.63 has been observed previously for weak and strong polyelectrolyte hydrogels swollen in water [21,35,36]. In these works, however, instead of f, the mole fraction of the ionic comonomer x_i was used in the calculations. Converting the reported values into an f-scale also gives an exponent close to 0.66. Following are two explanations for the discrepancy between theory and experiments.

4.1.1. Non-Gaussian behavior of the network chains

Eq. (16) assumes that the polymer network is a collection of Gaussian chains, which can be extended to infinity. However, due to the finite extensibility of the network chains, a deviation from the Gaussian statistics may appear at high swelling ratios. Indeed, the network chains in the swollen hydrogels with $x_i > 0.03$ are in an eight-fold elongated configuration than their dry state. Moreover, cyclization and multiple crosslinking reactions are known to occur predominantly during the gel formation process of AAm and BAAm monomers [37–40]. These reactions result in an inhomogeneous distribution of crosslinks in the final network and, thus, also contribute to the deviation from the Gaussian statistics of the network chains. For Gaussian chains, the elastic free energy ΔG_{el} increases with the square of the linear swelling ratio α (Eq. (8a)). As the network chains deviate from the Gaussian statistics, ΔG_{el} will increase with a higher power of α. For example, assuming that ΔG_{el} increases with fifth power of α:

$$\Delta G_{el} \propto \alpha^5/N \tag{19}$$

minimizing the sum of Eqs. (9) and (19) gives:

$$q_v \propto (fN)^{3/5}(v_2^0)^{-1} \tag{20}$$

For a fixed crosslinker ratio and monomer concentration, a scaling parameter 0.6 can be obtained, which is close to the observed value. Moreover, assuming $\Delta G_{el} \propto \alpha^4/N$, a scaling parameter value of 0.75 can be obtained. Thus, an elastic free energy that scales between the fourth and the fifth powers of the linear swelling ratio of the network chains may explain the observed swelling behavior of the hydrogels in water.

4.1.2. Osmotically passive counterions

An alternative explanation for the discrepancy between theory and experiment is the existence of "wasted" counterions inside the swollen gel which do not contribute to the swelling process. Following Manning's theory [41], if the distance between two consecutive charges on the network chains reduces to the Bjerrum length, the counterions start to condense on the network chains. For hydrogels derived from vinyl monomers, the critical value of x_i for the onset of counterion condensation was calculated as 0.35 [21], which is much larger than the values of x_i of the present hydrogels. Therefore, counterion condensation in Manning's sense cannot explain the observed deviation from the FH theory. Alternatively, the hydrophobic interactions between the alkyl groups of AMPS or MAPTAC units leading to the formation of aggregates may be responsible for the wasted counterions. The counterions in these aggregates may condense and lead to a decrease in the osmotic pressure.

In the following, we used the FH theory to calculate the charge densities of the AAm/AMPS networks, which are effective in the swelling process. For polymer gels swollen in a solvent ($y = 1$, $\phi = 0$), Eqs. (10a) and (10b) simplify to:

$$\ln(1 - v_2) + v_2 + \chi_{12}v_2^2 + N^{-1}(v_2^{1/3}v_2^{0^{2/3}} - v_2/2) - fv_2 = 0 \tag{21}$$

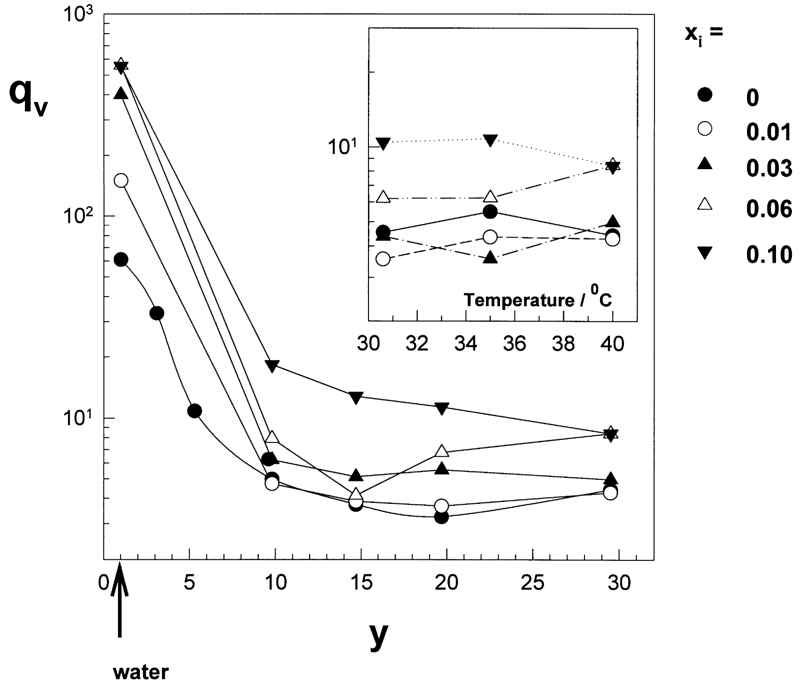

Fig. 4. The equilibrium volume swelling ratio q_v of the hydrogels with different ionic group contents x_i shown as a function of the number of segments y on PEG. The inset shows the q_v values of the hydrogels in PEG-600 ($y = 29.5$) at various temperatures between 30.6 and 40°C. The curves only show the trend of the data.

Solution of Eq. (21) for the charge density f of the networks requires the values of the parameters χ_{12} and N, characterizing the extent of the network–solvent interactions and the network. The χ_{12} parameter value for the PAAm–water system was recently evaluated from the swelling data for uncharged PAAm hydrogels swollen in water [42]. A best-fit value for χ_{12} of 0.48 was obtained [43]. This value of the χ_{12} parameter provided a good fit to the experimental swelling data of acrylamide-based anionic, cationic and ampholytic hydrogels of various compositions [43–45]. In the following calculations, χ_{12} was held constant at this value. The value N of the hydrogels was calculated from the equilibrium-swelling ratio of the non-ionic PAAm gel in water. The value $q_v = 47 \pm 10$ found by experiments together with Eq. (21) for $f = 0$ gives $N = 1635 \pm 800$. This value of N should be valid for all other hydrogels because the crosslinker ratio and the monomer concentration were fixed.

Solution of Eq. (21) using the χ_{12} and N values together with the experimental swelling data leads to the effective charge densities f of the hydrogels in water. These are shown in Fig. 3 as filled symbols plotted as a function of the AMPS mole fraction in the network x_i. The dashed line represents the f values expected if all the counterions are free and effective in gel swelling. It is seen that the effective charge density of the networks is much smaller than the theoretical value represented by the dashed curve and this deviation increases as the x_i increases. Reanalysis of the experimental data using Eq. (21) indicated, however, a considerable sensitivity of f to the standard deviation in N (1635 ± 800) used in the calculations, i.e. to the equilibrium swelling ratio q_v of the reference PAAm gel without an ionizable group. For example, calculations using $N = 800$ result in the f values shown in Fig. 3 as open symbols. Although the charge density of the hydrogels f is sensitive to the network crosslink density N, the number of charges per network chain (fN) was found to be insensitive to N. Analysis of the experimental data together with Eq. (21) leads to the following relation between the effective charge density of AAm/AMPS hydrogels in water and the AMPS mole fraction in the network x_i:

$$f = \frac{31}{N} x_i^{0.54} \tag{22}$$

This equation is represented by the solid curves in Fig. 3.

4.2. Swelling in polymer melt

Fig. 4 shows the equilibrium volume swelling ratio q_v of the hydrogels in pure PEG of various molecular weights plotted as a function of the number of segments y on PEG. All the swelling experiments in polymer melts, except in PEG-600, were carried out at room temperature (24 ± 1°C). Because PEG-600 is a solid at room temperature, the swelling measurements in this polymer were conducted at 40°C. However, as seen from the inset of Fig. 4, which shows the q_v values of the hydrogels in PEG-600 at various temperatures between 30.6 and 40°C, the swelling ratio is almost independent of the temperature. Therefore, the swelling ratio in PEG-600 measured at 40°C was also

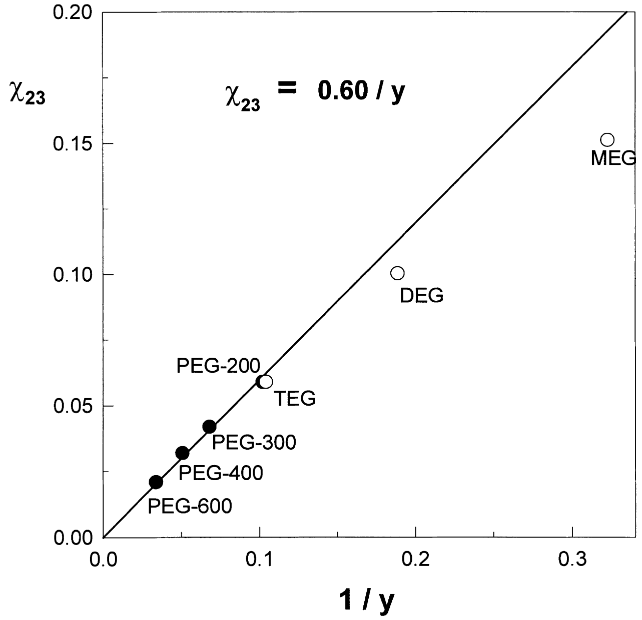

Fig. 5. The value of the polymer–network interaction parameter χ_{23} calculated from the equilibrium swelling data of the non-ionic gel in PEG of various molecular weights and using Eq. (24) shown as a function of $1/y$, where y is the number of segments on the polymer.

used for the following calculations. The number of segments, y, was calculated using the equation:

$$y = \frac{MW_{\mathrm{PEG}}}{\rho_3 V_1} \tag{23}$$

where ρ_3 is the density of PEG (1.13 g/cm^3 for PEG-200 to PEG-600, 1.113, 1.114 and 1.124 g/cm^3 for mono-, di- and tetraethyleneglycol (MEG, DEG and TEG), respectively) and MW_{PEG} is its molecular weight, reported by the manufacturer. The q_{v} values of MEG, DEG and TEG, respectively) with $y = 3.1$, 5.3 and 9.6 were taken from the literature [46]. Fig. 4 shows that both non-ionic and ionic gels deswell significantly with increasing chains length of PEG outside the gel phase. This decrease is first rapid up to $y = 10$, which corresponds to a molecular weight of 200, but then it slows down and q_{v} attains an almost constant value.

For polymer gels swollen in polymer melt (no solvent), Eq. (11a) simplifies to:

$$\frac{\Delta\mu_3^{\mathrm{gel}}}{y\mathrm{R}T} = (1/y)\ln(1 - v_2) + v_2/y + \chi_{23}v_2^2 + N^{-1}(v_2^{1/3}{v_2^0}^{2/3} - v_2/2) - v_2 f \tag{24}$$

which is equal to zero for gels in equilibrium with a polymer melt, i.e. for the present hydrogels equilibrium swollen in pure PEG. Eq. (24) in conjunction with the swelling data of non-ionic gels ($f = 0$) can be used to calculate the network–polymer interaction parameter χ_{23}. Respective calculations showed that the χ_{23} parameter is insensitive to the standard deviation in N used in the calculations. The calculated values of χ_{23} are shown in Fig. 5 plotted as a function of $1/y$. χ_{23} decreases as the molecular weight of PEG increases. The smaller the molecular weights are, the larger χ_{23} is. This trend of χ_{23} is similar to that of the second virial coefficient A_2 in a binary solution, which also decreases with increasing molecular weight [47]. The molecular weight dependence of χ_{23} was also observed previously in several systems [10,47,48]. It must be noted that, if the linear polymer chains are short, the combinatorial entropy of mixing in the FH expression (the first two terms of Eq. (24)) is incorrect [49]. Therefore, the molecular weight dependence of χ_{23} may also appear to compensate the inaccuracy in the FH theory for short polymer chains. Fig. 5 indicates that a straight line gives a good fit with the data points. The solid line in Fig. 5 is a linear best fit to the data points for PEG of molecular weights of 200 up to 600 g/mol passing through the origin, which gives:

$$\chi_{23} = \frac{0.60}{y} \tag{25}$$

The deviation from Eq. (25) observed for DEG and MEG may be a consequence of their action as an organic solvent instead of linear polymer in the gel swelling [46].

χ_{23} parameter values thus found using the swelling degrees of the non-ionic gel in PEG should also be valid for ionic gels because, as pointed out in the previous section, the value of χ_{23} parameter is independent of the number of the charges created on the network chains. Simulation of q_{v} versus y dependencies of the ionic gels using Eqs. (24) and (25) gives, however, in contrast to the experimental results shown in Fig. 4, almost no change in the volume of the ionic gels over the whole molecular weight ranges of PEG. To explain this discrepancy, one has to consider the effect of the medium polarity on the degree of ionization of AMPS units on the network chains. As is well known, the fraction of ions forming ion pairs in the gel strongly depends on the dielectric constant ε of the gel phase. The formation of ion pairs is more pronounced for solutions with a lower solvent dielectric constant ε [50–53]. A decrease in ε increases the probability of ionpairing and results in the deswelling of the gel. Because the dielectric constant ε of polymers is close to unity, compared to the value of $\varepsilon = 80$ for water, the counterions that are free in water bind tightly in the PEG environment to the AMPS units to form ion pairs. Thus, the deswelling of the ionic gels in PEG shown in Fig. 4 is due to the decreasing charge density of the networks caused by the ion pair formation. Indeed, calculations using Eqs. (24) and (25) indicate that the effective charge densities f of the ionic gels with $x_{\mathrm{i}} < 0.10$ are close to zero in PEG, whereas in the hydrogel with $x_{\mathrm{i}} = 0.10$ some counterions still exist in PEG. Thus, the effective charge density of the hydrogels in PEG solutions may be assumed, as a first approximation, to be related to the PEG volume fraction in the external PEG–water solution by an expression of the form:

$$f = f_0(1 - A\phi) \tag{26}$$

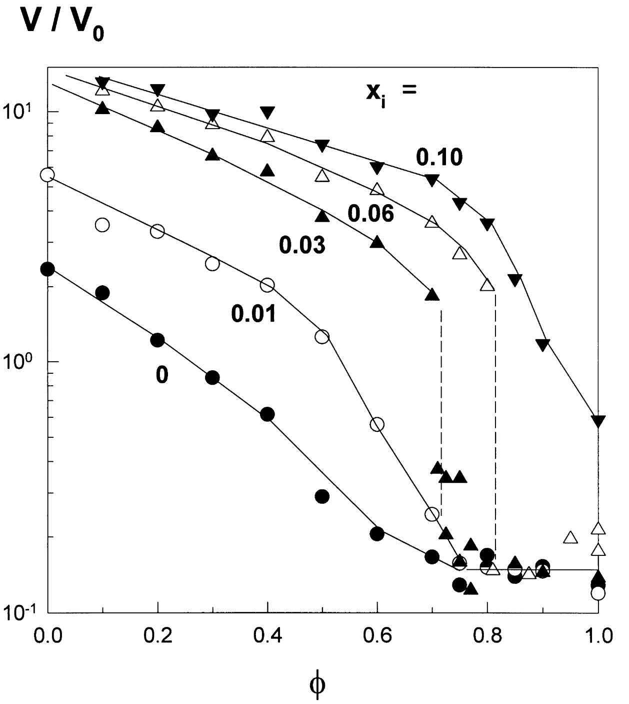

Fig. 6. The equilibrium volume swelling ratio V/V_0 of the hydrogels with different ionic group contents x_i shown as a function of the volume fraction of PEG-300 in the aqueous PEG-300 solution. The curves only show the trend of the data.

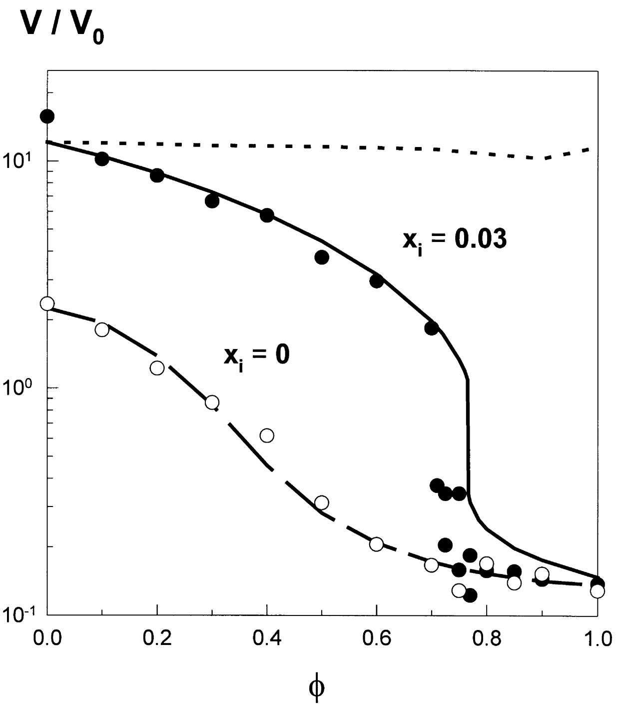

Fig. 7. The equilibrium volume swelling ratio V/V_0 of the hydrogels with $x_i = 0$ and 0.03 shown as a function of the volume fraction of PEG-300 in the aqueous PEG-300 solution. The solid curves were calculated using the FH theory. The dotted curve assumes a constant charge density for the networks in PEG solutions.

where f_0 is the network charge density measured in water, and A is a constant describing the fraction of trapped counterions forming ion pairs in pure PEG. From the experimental swelling data in Fig. 4 together with Eq. (24), the value of A was estimated as 1 and 0.9 for hydrogels with $x_i < 0.10$ and $x_i = 0.10$, respectively.

In conclusion, the decrease in the swelling ratio of non-ionic hydrogels with increasing size of the linear polymer is due to the mixing entropy of the linear polymers. An increase in y decreases the osmotic pressure of the solution phase so that the gel shrinks. However, for ionic gels, this effect is negligible, compared to the strong osmotic pressure of the counterions inside the gel phase. Formation of ion pairs due to the decrease in the polarity of the medium is responsible for the deswelling behavior of ionic hydrogels in the polymer melt.

4.3. Swelling in polymer solution

Fig. 6 shows the degree of swelling of the AAm/AMPS hydrogels, in terms of V/V_0, plotted as a function of the volume fraction of PEG-300 in the external solution ϕ. In these series of experiments, hydrogels with five different charge densities ($x_i = 0$, 0.01, 0.03, 0.06 and 0.10) were studied. The experimental swelling data are shown as symbols. The curves only show the trend of the data. As the PEG-300 concentration outside the gel phase increases, the volume of the gels decreases. The gel without any ionizable group exhibits a continuous change in the swelling volume over the entire concentration ranges. This behavior is in contrast to the non-ionic NIPA gels which undergo a discontinuous phase transition in PEG solutions [15]. At PEG concentrations as high as 80%, the non-ionic PAAm gel volume becomes rather insensitive to the composition of the external solution. Similar to the non-ionic gel, gels with the lowest and highest number of ionic groups ($x_i = 0.01$ and 0.10, respectively) decrease their volume smoothly over the entire range of the external PEG-300 concentration.

The ionic gels with $x_i = 0.03$ and 0.06 are swollen at low PEG concentrations, whereas they are collapsed at high concentrations. In the concentration range marked with vertical dashed lines in Fig. 6, both a swollen and a collapsed state can be observed but never an intermediate state. These findings indicate a first-order transition. The jump of the network volume occurs at the critical volume fraction of PEG $\phi = 0.70$–0.71 and 0.80–0.81 for $x_i = 0.03$ and 0.06, respectively. Thus, the critical value of ϕ at which transition takes place increases with increasing ionic group content of the network. Also, the magnitude of the collapse becomes larger as the ionic group content of the network increases.

In order to predict the swelling behavior of the hydrogels in PEG solutions, in addition to the parameters found in the previous sections (N, f and χ_{23}), the interaction parameter between water and PEG (χ_{13}) must also be known. Solution of Eqs. (13) and (14) using the reported value for $\chi_{13} = 0.45$

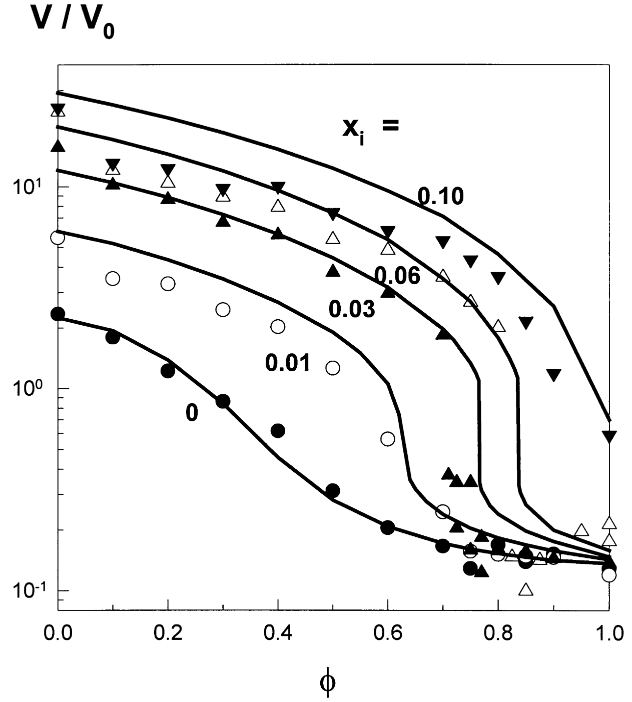

Fig. 8. The equilibrium volume swelling ratio V/V_0 of the hydrogels shown as a function of the volume fraction of PEG-300 in the aqueous PEG-300 solution. The solid curves were calculated using the FH theory.

[54] gives an initial gel swelling on rising the external PEG solution, which was not observed experimentally. Therefore, these two equations were solved for χ_{13} in order to reproduce the experimental swelling data of the non-ionic gel in PEG-300 solutions. The analysis of the swelling data leads to the following expression for the PEG–water interaction parameter:

$$\chi_{13} = 0.31 - 0.21\phi + 0.11\phi^2 \qquad (27)$$

The results of calculation of the swelling ratio of the non-ionic gel in PEG-300 solutions using Eq. (27) are shown in Fig. 7 as the dashed curve together with the experimental swelling data (open symbols).

The following parameters are now available for the (quasi) ternary system consisting of AAm/AMPS network, PEG and water:

$$v_2^0 = C_0\bar{V}_r \qquad \bar{V}_r = [229x_i + 71(1 - x_i)]/\rho$$

$$N = 1635 \pm 800 \qquad \chi_{12} = 0.48$$

$$f_0 = \frac{31}{N}x_i^{0.54} \qquad \chi_{13} = 0.31 - 0.21\phi + 0.11\phi^2$$

$$f = f_0(1 - A\phi) \qquad \chi_{23} = \frac{0.60}{y}$$

These parameters together with Eqs. (13) and (14) can be used to predict the equilibrium swelling ratio of ionic gels in PEG solutions. The solid curve in Fig. 7 shows the prediction of the theory for the ionic gel with $x_i = 0.03$ swollen in PEG-300 solution. It is seen that the FH theory correctly predicts the swelling and collapsing behavior of the ionic gel in polymer solution. Note that these calculations take into account the decrease of the effective charge density of the network with increasing PEG concentration in the external solution due to ion pair formation (Eq. (26)). Otherwise, if one assumes a constant charge density for the network ($f = f_0$), the theory predicts almost no change in the volume of the ionic gel over the whole concentration ranges of PEG, as shown in Fig. 7 as the dotted curve. The simulation results for all hydrogels with different ionic group contents are collected in Fig. 8 as solid curves together with the experimental data. In general, satisfactory agreement between the theory and experiment is observable. For example, for the hydrogels with $x_i = 0.03$ and 0.06, respectively, the theory predicts a first-order volume phase transition at $\phi = 0.766$ and 0.837 compared to the experimental measured values of $\phi = 0.70$–0.71 and 0.80–0.81. For the hydrogel with $x_i = 0.1$, the theory predicts, in accordance with the experimental data, a continuous deswelling over the entire range of the external PEG-300 concentration. This is due to the fact that, according to Eq. (26), 10% of the counterions in this hydrogel are free, even in pure PEG-300, which prevents the collapsing of the network in the PEG solution. If all the charges in this hydrogels were screened in PEG-300, a first-order volume phase transition at $\phi = 0.875$ should be expected for this hydrogel.

Calculations were repeated using an elastic free energy term with scales with the fifth power of α. In this way, the deviation from the Gaussian statistics of the network chains was included into the calculations. Moreover, calculations were also carried out by changing the network crosslink density N within the limit of its standard deviation. No further improvements can be obtained using these procedures.

5. Conclusions

In this work, the swelling behavior of strong polyelectrolyte hydrogels was investigated in a good solvent, in polymer melts and in polymer solutions. The system under study was a polymer network of AAm/AMPS (or MAPTAC) chains interacting with water and/or linear PEG chains of various molecular weights. The following conclusions were drawn from the experimental data.

1. The equilibrium volume swelling ratio q_v of the hydrogels in water scales with the network charge density f by the relation $q_v \propto f^{0.66}$. The scaling parameter 0.66 indicates a non-Gaussian behavior of the network chains and/or the existence of counterions in the gel phase, which are ineffective in the gel swelling. Assuming that the network chains behave Gaussian, it was shown that the effective charge density of the hydrogels relates to the mole fraction of AMPS in the network x_i through the

equation $f = (31/N)x_i^{0.54}$ where N is the number of segments on the network chains.

2. The swelling degree of the hydrogels in a polymer melt decreases as the number of segments y on the linear polymer increases. This deswelling occurs, for the non-ionic hydrogels, due to the mixing entropy of the linear polymer, whereas, for ionic gels, due to trapping of counterions with the formation of ion pairs caused by the decreased polarity of the medium. The network–polymer interaction parameter χ_{23} was found to vary with y by the relation $\chi_{23} = 0.60/y$.
3. The hydrogels deswell in aqueous polymer solutions as the polymer concentration increases. This deswelling occurs smoothly or jumpwise, as a first-order phase transition, depending on the ionic group content of the hydrogels. The FH theory correctly predicts the swelling and collapsing behavior of the hydrogels in polymer solutions, if the variation of the effective charge density depending on the medium polarity is taken into account.

Acknowledgements

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