

# Swelling behavior of poly(acrylamide-co-sodium acrylate) hydrogels in aqueous salt solutions: theory versus experiments

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Received 4 August 1998; received in revised form 4 January 1999; accepted 29 January 1999

## Abstract

The predictions of the Flory–Rehner theory of swelling equilibrium including the ideal Donnan equilibria were compared with the experimental swelling data obtained from poly(acrylamide-co-sodium acrylate) hydrogels swollen in water and in aqueous salt (NaCl) solutions. For this comparison, the fraction of counterions which are effective in the gel swelling was taken into account. The ionic hydrogels were prepared from acrylamide and sodium acrylate (NaAc) monomers with 0 to 5 mol% NaAc and using *N,N'*-methylenebis(acrylamide) as the crosslinker. As expected, at a fixed crosslinker ratio, the volume swelling ratio of hydrogels in water increases sharply when the mole fraction of NaAc increases or the NaCl concentration in the external solution decreases. Taking into account the wasted counterions within the hydrogels, the theory correctly predicts the swelling behavior of hydrogels in water and in aqueous salt solutions. Not predicted by the theory is the increased swelling ratio of hydrogels with less than 4 mol% NaAc content with increasing salt concentration from 10<sup>-1</sup> to 10<sup>0</sup> M. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Hydrophilic gels called hydrogels are crosslinked materials absorbing large quantities of water without dissolving. Investigations of the swelling behavior of acrylamide (AAm)-based hydrogels have received considerable attention in the last four decades. These hydrogels are prepared by free-radical crosslinking copolymerization of AAm monomer with a small amount of a hydrophilic crosslinker, e.g., *N,N'*-methylenebis(acrylamide) (BAAm). In order to increase their swelling capacity, an ionic comonomer is also included

into the reaction mixture [1,2]. The equilibrium swelling degree of hydrogels is known to depend on the crosslink and charge densities of the network as well as on the polymer network concentration after the gel preparation. These three factors are related to the concentrations of BAAM, the ionic comonomer and the total monomers in the initial reaction mixture, respectively. The Flory–Rehner theory including the ideal Donnan equilibria gives the following well-known relation between the equilibrium swelling ratio of hydrogels in water and the three synthesis parameters [3]:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1} \left[ v_2^{1/3} (v_2^0)^{2/3} - v_2/2 \right] - V_1 \frac{f}{V_r} v_2 = 0 \quad (1)$$

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where  $v_2$  is the volume fraction of polymer in the equilibrium swollen hydrogel, i.e., the inverse of the volume swelling ratio  $q_v$ ,  $\chi$  is the polymer–solvent interaction parameter,  $N$  is the number of segments between two successive crosslinks of the network,  $v_2^0$  is the volume fraction of polymer network after preparation,  $V_1$  and  $\bar{V}_r$  are the molar volumes of solvent (water) and the polymer repeat unit, respectively, and  $f$  is the mole fraction of effective charged units in the network.

The calculated equilibrium volume swelling ratio  $q_v$  versus crosslink density ( $N^{-1}$ ), effective charge density ( $f$ ), and the polymer concentration ( $v_2^0$ ) plots shown in Fig. 1 indicate that, according to the theory, highly swollen hydrogels can be obtained at high network charge densities  $f$ , at low crosslink densities  $N^{-1}$ , or at low monomer concentrations  $v_2^0$ . Superabsorbent materials with  $q_v$  in the order of  $10^3$  could be obtained by adjusting one of the three network parameters.

Experimental results indicate, however, only qualitative agreement between the experimental swelling

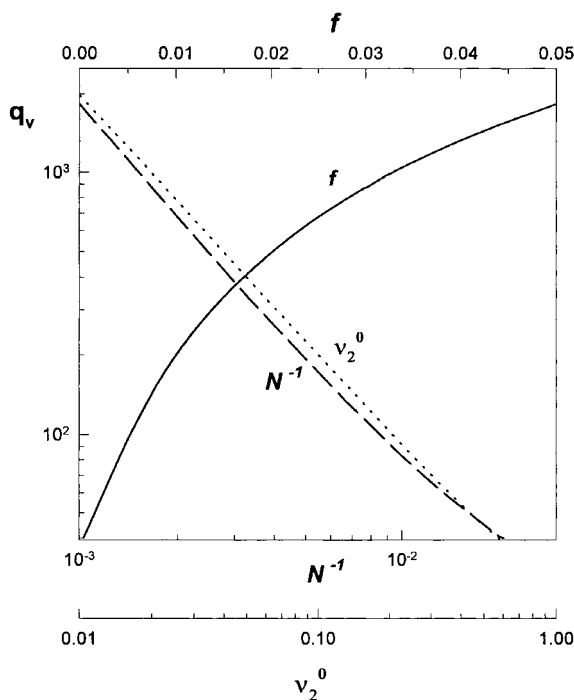


Fig. 1. The prediction of the Flory–Rehner theory [3] for the volume swelling ratio  $q_v$  of hydrogels in water shown as a function of the crosslink density  $N^{-1}$ , the effective charge density of the network  $f$ , and the polymer network concentration after gel preparation  $v_2^0$ . Calculations were using Eq. (1) with  $\chi = 0.48$ ,  $V_1 = 18$  ml/mol, and  $\bar{V}_r = 53$  ml/mol. Solid curve:  $N^{-1} = 10^{-3}$ ,  $v_2^0 = 0.04$ . Dashed curve:  $f = 0.05$ ,  $v_2^0 = 0.04$ . Dotted curve:  $N^{-1} = 10^{-3}$ ,  $f = 0.02$ .

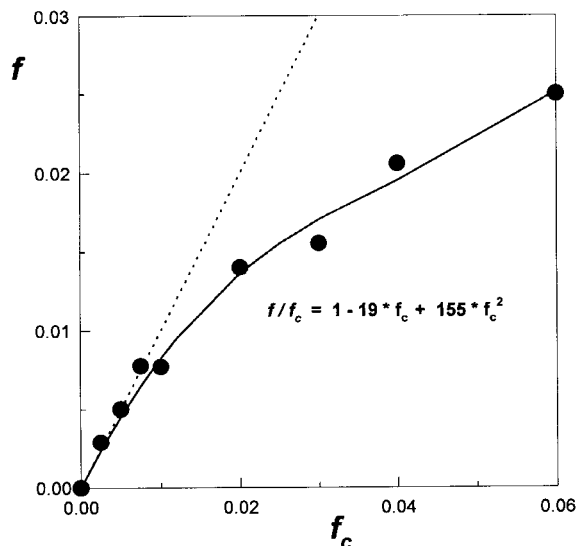


Fig. 2. Variation of the effective network charge density  $f$  with the chemical charge density  $f_c$  in AAm/AMPS hydrogels. The dotted line represents the relation  $f = f_c$ .

data and the theoretical curves shown in Fig. 1 [4–7]. In fact, due to the several assumptions and approximations of the classical theory, no agreement between theory and experiment can be expected, especially in case of highly swollen hydrogels [8,9]. This is, of course, for the case where the experimental values of  $f$  and  $N^{-1}$  obtained from the condition of gel preparation were used in the calculations [5,7]. Although many new theories have been proposed to modify the classical theory [10–17], recent results show a good agreement between the classical theory and the experimental swelling data, if the parameters  $N^{-1}$  and  $f$  are taken as adjustable parameters [5]. Recently, we have also shown that the classical theory correctly predicts the swelling behavior of strong polyelectrolyte AAm/2-acrylamido-2-methylpropanesulfonic acid (AMPS) hydrogels swollen in water and in aqueous salt solutions [18]. For AMPS mole fractions  $f_c < 0.05$ , a good agreement between the measured and calculated results was obtained if  $f$  is taken as a fit parameter, which was found to be a function of the AMPS mole fraction  $f_c$  [18]. The variation of the effective charge density  $f$  with chemical charge density  $f_c$  found in Ref. [18] is illustrated in Fig. 2 as filled circles. In the figure, the dotted line represents the relation  $f/f_c = 1$ , i.e., on this line the ionic group content of hydrogels is equal to their effective charge density. It is seen that up to 1% AMPS content ( $f_c = 0.01$ ), all AMPS units act as charged units in the gel swelling. However, as  $f_c$  further increases, deviations appear from the straight line dependence. A polynomial regression yields:

$$\frac{f}{f_c} = 1 - 19f_c + 155f_c^2 \quad (2)$$

in the range of  $f_c \leq 0.06$  (solid curve in Fig. 2). Eq. (2) suggests that not all the fixed charges inside the gel are effective in the gel swelling. Thus, only a certain fraction of mobile counterions ( $f/f_c$ ) inside the gel are effective in creating an osmotic pressure that expands the gel. According to Fig. 2, the fraction of effective counterions decreases on raising the chemical charge density of the network. This experimental finding is in accord with recent experimental and theoretical results indicating the existence of 'osmotically passive' counterions inside the swollen gel which do not contribute to the swelling process [5,19].

The scope of the present work was to establish whether it is possible to predict the swelling behavior of weak polyelectrolyte AAm/sodium acrylate (NaAc) hydrogels using the empirical equation (2). For this purpose, we prepared a series of AAm/NaAc hydrogels with chemical charge densities  $f_c$  between 0 and 0.05 and measured their swelling capacities in water and in aqueous NaCl solutions ranging in concentration from  $10^{-5}$  to 1 M. The measured swelling data of the hydrogels were compared with that predicted by the Flory–Rehner theory in combination of Eq. (2). As will be shown below, the theory correctly predicts the swelling behavior of hydrogels in water and in aqueous NaCl solutions if the fraction of effective counterions given by Eq. (2) is taken into account.

## 2. Experimental

### 2.1. Materials

Acrylic acid (AA, Fluka) was distilled under a vacuum. Acrylamide (AAm, Merck), *N,N'*-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Merck), and NaCl (Merck) were used as received. Sodium acrylate (NaAc) was prepared in situ by adding equimolar amounts of AA and NaOH in the polymerization mixture. Double distilled and deionized water was used in the hydrogel preparation and in the swelling measurements.

### 2.2. Hydrogel synthesis

The hydrogels were prepared by free-radical cross-linking copolymerization of AAm and NaAc with a small amount of BAAm as a crosslinker in aqueous solution. APS and TEMED were respectively the initiator and the accelerator. The reactions were carried out at room temperature ( $21 \pm 2^\circ\text{C}$ ). The gels were prepared according to the following procedure.

Five grams of AAm–AA mixture, NaOH (in amount corresponding to the number of moles of AA), 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. The polymerization was conducted for 24 h. Homologous series of anionic hydrogels were prepared in this way allowing systematic variation of the NaAc concentration between 0 and 5 mol% (with respect to the monovinyl monomers). The total monomer concentration and the crosslinker ratio  $X$  (mole ratio of divinyl to vinyl monomers) were fixed at 5% (w/v) and  $82^{-1}$ , respectively.

After polymerization, hydrogel samples were cut into specimens of approximately 10 mm in length. The samples (usually 10 pieces) were then immersed in a large excess of distilled water for at least one 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 less than 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  $60^\circ\text{C}$  to constant weight. The weight swelling ratio of hydrogels after preparation,  $q_F$ , was calculated as:

$$q_F = \frac{\text{mass gel after preparation}}{\text{mass dry gel}} \quad (3)$$

The volume fraction of polymer network after preparation,  $v_2^0$ , was calculated from  $q_F$  values as:

$$v_2^0 = \left[ 1 + \frac{(q_F - 1)\rho}{d} \right]^{-1} \quad (4)$$

where  $\rho$  and  $d$  are the densities of polymer and solution, respectively. The values  $\rho$  and  $d$  used were 1.35 and 1 g/ml, respectively. The experimental value of  $v_2^0$  was found to be 0.056 and  $0.039 \pm 0.002$  for non-ionic and ionic hydrogels, respectively.

### 2.3. 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  $25 \pm 0.1^\circ\text{C}$ . In order to reach the equilibrium degree of swelling, the gels were immersed in water at least for one 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 1.0 to  $10^{-5}$  M. The gel samples were allowed to swell in the solution at least for one week, during which aqueous NaCl was refreshed to keep the concentration as feeded. After the swelling equilibrium was established, the samples were weighed and then transferred into the next dilute NaCl solution. The swelling measurements in aqueous NaCl were carried out both in direction of decreasing salt concentration from 1 M to water and in reverse direction from water up to 1 M 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:

$$q_{w(\text{H}_2\text{O})} = q_F \frac{\text{mass gel in water}}{\text{mass gel after preparation}} \quad (5a)$$

$$q_{w(\text{NaCl}_{\text{aq}})} = q_{w(\text{H}_2\text{O})} \frac{\text{mass gel in aqueous NaCl}}{\text{mass gel in water}} \quad (5b)$$

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

$$q_v = 1 + \frac{(q_w - 1)\rho}{d} \quad (6)$$

Each swelling ratio reported in this paper is an average of at least five separate measurements; standard deviations of the measured swelling ratios were less than 4% of the mean.

### 3. Results and discussion

Fig. 3 shows the equilibrium volume swelling ratio  $q_v$  of AAm/NaAc hydrogels in water and in aqueous NaCl solutions plotted as a function of  $f_c$ , the mole fraction of NaAc used in the hydrogel preparation. In Fig. 4,  $q_v$  of hydrogels is shown as a function of the NaCl concentration in the external solution. The experimental data are shown as symbols. As expected,  $q_v$  increases sharply when the mole fraction  $f_c$  of NaAc increases from 0 to 0.05 (Fig. 3). This is due to the fact that, as  $f_c$  increases, the mobile ion ( $\text{Na}^+$ ) 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

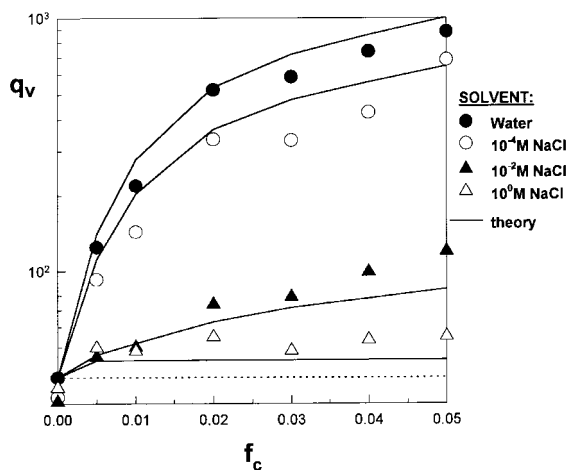


Fig. 3. Variation of the volume swelling ratio  $q_v$  of AAm/NaAc hydrogels in water and in aqueous NaCl solutions with the mole fraction of NaAc used in the gel preparation  $f_c$ . The experimental data are shown as symbols. The solid lines were calculated using the swelling theory and using Eq. (2). The dotted line represents the prediction of the theory without the Donnan term (Eq. (10)).

external solution (Fig. 4); this is due to a decrease in the concentration difference of counterions inside and outside the hydrogel. The decrease in  $q_v$  is first rapid up to  $10^{-2}$  M NaCl concentration. As the NaCl concentration further increases, the decrease in  $q_v$  slows down and, between  $10^{-1}$  and  $10^0$  M NaCl,  $q_v$  remains almost constant or slightly increases with increasing salt concentration (Fig. 4A).

To interpret the experimental swelling data shown in Figs. 3 and 4 within the framework of the Flory–Rehner theory, the osmotic pressure  $\pi$  of a hydrogel during swelling is given as the sum of the pressures due to polymer–solvent mixing (mix), due to deformation of network chains to a more elongated state (el), and due to the nonuniform distribution of mobile counterions between the gel and the external solution (ion) [20,21]:

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} + \pi_{\text{ion}} \quad (7)$$

According to the Flory–Huggins theory,  $\pi_{\text{mix}}$  is given by [3]:

$$\pi_{\text{mix}} = -\frac{RT}{V_1} (\ln(1 - v_2) + v_2 + \chi v_2^2) \quad (8)$$

where  $R$  is the gas constant and  $T$  is temperature. To describe the elastic contribution  $\pi_{\text{el}}$  to the swelling pressure, we will use here the simplest affine network model to describe the behavior of our gels [3]:

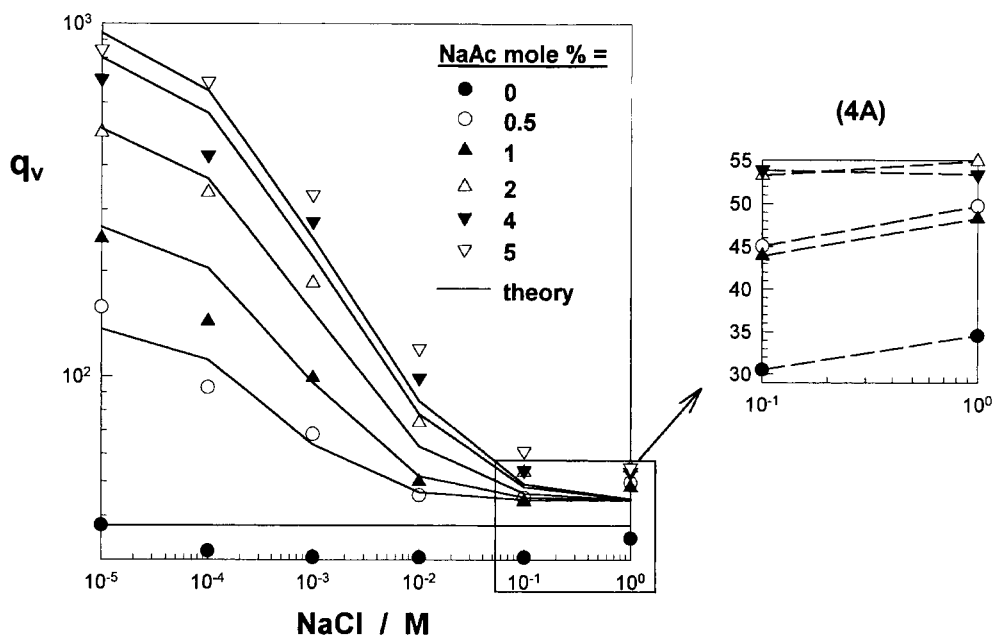


Fig. 4. Variation of the volume swelling ratio  $q_v$  of hydrogels with the NaCl concentration in the external solution. The experimental data are shown as symbols. The curves were calculated using the swelling theory and using Eq. (2). Fig. 4A is a magnification of the small box. The dashed lines in Fig. 4A only show the trend of data.

$$\pi_{el} = -\frac{RT}{V_1} N^{-1} \left[ v_2^{1/3} (v_2^0)^{2/3} - v_2/2 \right] \quad (9)$$

Ionic contribution  $\pi_{ion}$  to the swelling pressure is caused by the concentration difference of counterions between the gel and the outer solution. The ideal Donnan theory gives  $\pi_{ion}$  as the pressure difference of mobile ions inside and outside the gel [3]:

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s) \quad (10)$$

where  $C_i^g$  and  $C_i^s$  are the concentrations of the mobile ions of species  $i$  inside and outside the gel, respectively. According to ideal Donnan equilibria, for aqueous solutions of univalent salts, we have the equality:

$$C_+^g C_-^g = C_+^s C_-^s = (C_{salt}^s)^2 \quad (11)$$

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:

$$C_+^g = C_-^g + \frac{f}{\bar{V}_r} v_2 \quad (12)$$

Solution of Eqs. (7)–(12) for the thermodynamic equilibrium state of a gel ( $\pi = 0$ ) gives the following system of equations describing the equilibrium value of  $v_2$  of hydrogels in aqueous salt solution and the distribution coefficient  $K$  of counterions between the gel and sol-

ution phases:

$$\begin{aligned} \ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1} \left[ v_2^{1/3} (v_2^0)^{2/3} - v_2/2 \right] \\ - 2(K - 1) V_1 C_{salt}^s - V_1 \frac{f}{\bar{V}_r} v_2 \\ = 0 \end{aligned} \quad (13a)$$

$$K \left( K + \frac{f v_2}{\bar{V}_r C_{salt}^s} \right) - 1 = 0 \quad (13b)$$

where  $K = C_-^g / C_{salt}^s$ . Note that, in the case of swelling of hydrogels in water free of ionic species ( $C_{salt}^s = 0$ ), Eq. (13a) reduces to Eq. (1) given in Section 1.

The system of equations (13a) and (13b) were solved numerically to calculate the equilibrium swelling ratio of AAm/NaAc hydrogels in aqueous salt solutions ( $q_v = 1/v_2$ ). For calculations, the values used were  $V_1 = 18$  ml/mol and  $\bar{V}_r = 52.6 + 17 f_c$  (obtained using the values 71 and 94 g/mol for the molecular weights of AAm and NaAc units, respectively). The  $\chi$ -parameter value for PAAm–water system was recently evaluated from the swelling data for uncharged PAAm hydrogels swollen in water [22]. A best-fit value for  $\chi$  of 0.48 was obtained [5]. This value of  $\chi$ -parameter provided a good fit to the experimental swelling data of acrylamide-based anionic, cationic, and amphoteric

Table 1  
Calculated effective charge densities  $f$  of AAm/NaAc hydrogels with various chemical charge densities  $f_c$

$10^2 \times f_c$	$10^2 \times f$
0.50	0.45
1.0	0.83
2.0	1.36
3.0	1.71
4.0	1.95
5.0	2.19

hydrogels of various compositions [5,6]. In the following calculations,  $\chi$  was held constant at this value. The  $f$  value of the hydrogels was calculated using Eq. (2) derived from the equilibrium swelling degrees of AAm/AMPS hydrogels in water [18]. Table 1 shows the  $f$  values used in the calculations.  $C_{\text{salt}}^s$  (in mM) is the independent variable of Eqs. (13a) and (13b), which was varied between  $10^{-5}$  and 1.0 M in our experiments (Fig. 3 Fig. 4).

In order to solve Eqs. (13a) and (13b), the crosslink density of the network  $N^{-1}$  characterizing the hydrogels must also be known. Both the crosslinker ratio  $X$  (mole ratio of crosslinker to monomer) and the total monomer concentration were fixed in our experiments, while only the mole fraction of NaAc varied between the hydrogels from 0 to 0.05. Therefore, it is reasonable to assume a constant crosslink density for all the hydrogels. Thus, using the swelling ratio of non-ionic gel in water  $q_v = 37.9$  and using Eq. (1) for  $f = 0$ , we calculated  $N$  as  $1.5 \times 10^3$ , which should be valid for all other ionic hydrogels. In fact, from the crosslinker ratio  $X = 82^{-1}$  used in the hydrogel synthesis, one may expect the chemical value of  $N$  as 41, if all BAAM molecules form effective crosslinks in the final hydrogel. It is seen that more than 90% of BAAM used in the hydrogel synthesis were consumed in cycles, multiple crosslinks or, in units with pendant vinyl groups. This high fraction of wasted BAAM monomer is in accord with our previous result on PAAM gels [23]. For the same copolymerization system, Tobita et al. [24] and Naghash et al. [25] used an analytical titration technique to calculate the fraction of BAAM units involved in formation of cycles. They showed that, in AAm/BAAM copolymerization, at least 80% of the pendant acryl groups are consumed by cyclization reactions, which is also comparable with the present result. However, contrary to these results Baselga et al. pointed out that the difference in the vinyl group reactivity leading to the spatial inhomogeneity in PAAM gels is mainly responsible for the observed deviations and cyclization has a very low probability [26,27].

Calculation results using Eqs. (13a) and (13b) are shown in Figs. 3 and 4 as the solid curves. The dotted

line in Fig. 3 represents the prediction of the theory without the Donnan term (Eq. (10)). It is seen that the predictions of the classical theory including the ideal Donnan equilibria agree reasonably well with the experimental swelling data of hydrogels in water and in aqueous salt solutions. It must be pointed out that no adjustable parameter was used in the calculation of the swelling data of ionic hydrogels. This good agreement also means that the fraction of effective counterions found in AAm/AMPS hydrogels also corresponds to that in the present hydrogels. We can thus conclude that the empirical Eq. (2) in connection with the Flor—Rehner theory can be used to predict the swelling behavior of hydrogels in aqueous salt solutions.

Another point shown in Fig. 4A is that the equilibrium swelling ratio  $q_v$  of hydrogels with less than 4 mol% NaAc content increases again, when the salt concentration further increases from 0.1 to 1.0 M. This interesting feature, not predicted by the theory, was also observed previously in ampholytic, cationic, and non-ionic AAm-based hydrogels [6,22] and in AAm/AMPS hydrogels [18]. Specific interactions between AAm units and mobile ions seem to be responsible for this behavior.

#### 4. Conclusions

A series of hydrogels from AAm and NaAc monomers were prepared by free-radical crosslinking copolymerization using  $N,N'$ -methylenebis(acrylamide) 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 1 M. The volume swelling ratio  $q_v$  of hydrogels increases sharply as the mole fraction  $f_c$  of NaAc increases from 0 to 0.05, or as the NaCl concentration in the external solution decreases. The results of swelling measurements were compared with the theory of swelling equilibrium. It was shown that the theory correctly predicts the swelling behavior of hydrogels in water and in aqueous salt solutions if their effective charge densities are taken into account.

#### Acknowledgements

This work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK) under Grand Number TBAG-1561. The authors wish to thank Dr. Sibel Zor from the Kocaeli University for the technical assistance during a part of this work.

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