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Preparation of porous polyacrylate/poly(ethylene glycol) interpenetrating network hydrogel and simplification of Flory theory

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Abstract In this article, we successfully designed and fabricated polyacrylate/poly(ethylene glycol) interpenetrating network (PAC/PEG IPN) hydrogel by a two-step technique. The influences of synthesis parameters, such as crosslinker dosage and neutralization degree of PAC, on the equilibrium swelling ratio (SR) of the PAC/PEG IPN hydrogel were investigated. Based on Flory theory, a simplified experiential formula $Q_{\mathrm{H_2O}}^{5/3} = 14.72I^{-1} + 207.43$ was proposed. The results revealed that the theoretical SR of the PAC/PEG IPN hydrogel was consistent with experimental value in the presence of univalent salt solution. In this case, the SR of the hydrogel can be calculated without measurement. While for multivalent salt solutions, the theoretical and experimental results are inconsistent owing to chelations between carboxylic and carboxylate groups of the PAC/PEG hydrogels and the cations in the solution.

Introduction

Hydrogels, such as polyacrylate, have a typical three-dimensional (3D) network structure with a suitable crosslinking density [1]. Not only can it absorb a large amount of water to form a stable hydrogel, but also the absorbed water cannot be removed under pressure. The hydrogel structures crosslinked physically or chemically are the results of covalent bonding, hydrogen bonds, and even Van der Waals interactions. There are numerous applications of these hydrogels, in particular in the medical and pharmaceutical fields.

Swelling behavior of hydrogel depends on its structure, composition, and the external environment. In recent years, great interests have been focused on intelligent hydrogels, which show responses to external stimuli changes, such as pH [2–4], temperature [5, 6], ionic strength [7, 8], electric field [9], and photics [10]. According to Flory theory [11], the swelling ratios (SRs) of hydrogels are affected by four factors: concentration of the fixed charges referred to the unswollen polymer, water affinity, ionic strength of the external solutions, and crosslinking density of hydrogel samples. The fixed charges in polymer, water affinity, crosslinking degree of hydrogels, ionic strength depend on nature of materials, neutralization degree, valences and concentration of external solutions, and dosages of crosslinker, respectively.

In this article, polyacrylate/poly(ethylene glycol) (PAC/PEG) hydrogel with an interpenetrating network (IPN) structure was synthesized by a simple two-step method. PEG is a cheap polyhydroxy polymer with interesting properties to be used as a biomaterial such as a polymeric drug carrier [12] and in encapsulation applications [13]. Here, PEG is introduced to form an IPN and porous structures. PAC is an inexpensive familiar hybrid polymer of polyacrylate and poly(acrylic acid) with –COO$^-$ and –COOH groups. A suitable degree of crosslinking PAC is a typical superabsorbent [14–16]. It is able to absorb hundreds to thousands times its own mass of water to form a stable hydrogel. Although the formation of IPN structure by introducing PEG depresses its SR, PAC/PEG is still expected to show unique swelling properties. Based on

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Flory theory, the influences of crosslinker, neutralization degree, and surrounding ionic solution on the equilibrium SR of the PAC/PEG IPN hydrogel were investigated, and a simplified experiential formula $Q_{H_2O}^{5/3} = 14.72I^{-1} + 207.43$ was proposed in this article.

Experimental

Materials

Acrylic acid (AA) monomer purchased from Sigma Chemicals was distilled under reduced pressure prior to use. Poly(ethylene glycol) (PEG, $M_n = 20{,}000$) was used without further purification. Ammonium peroxydisulfate (APS) was a radical initiator for the synthesis of oligo-acrylate (OAC) and polyacrylate (PAC). *N,N′*-methylene bisacrylamide (NMBA), as a crosslinker for the synthesis of the PAC with 3D network, was purified by recrystallization from 66 wt% ethanol/water solution. Potassium hydroxide was used to neutralize AA monomer to a desired neutralization degree (percentage of $-COO^-$ group in the functional groups of PAC chain). NaCl, $CaCl_2$, and $FeCl_3$ were used as received to prepare target ionic strength solutions. All aqueous solutions were prepared in 18 MΩ water obtained by purification of deionized water with a Millipore Milli-Q system. The above materials were all commercially purchased from Shanghai Chemical Reagents Co., China.

Preparation of PAC/PEG IPN composite

A mixed solution of AA monomer and AC monomer was made by agitating AA of 15 g, potassium hydroxide in deionized water of 15 mL at ambient temperature. Under nitrogen atmosphere, the mixture solution was heated at 80 °C for 10 min under stirring in a water bath, and then the APS (0.045 g, $M_{APS}/M_{AA+AC} = 0.003$) was added, a polymerization reaction of AA was carried out for a few minutes until the viscosity of the system reached 140 mPa s, indicating the formation of OAC. A mixed aqueous solution (20 mL) consisting of PEG and crosslinker NMBA was poured into the above OAC solution, then APS (0.045 g) was added for the further polymerization of OAC to PAC. Under a nitrogen atmosphere, the polymerization reaction was carried out under stirring until the viscosity of the system reached 180 mPa s, which resulted in the formation of 3D PAC network and IPN structure. Then polymerization reaction was slowered by transferring the system to room temperature. The half products were rinsed with deionized water and dried under vacuum at 80 °C for more than 12 h to a constant weight to remove low molecular weight polymers and any impurities. After being milled and sifted using a 40-mesh screen, a powdered product PAC/PEG IPN composite thus was obtained.

Measurements

Five grams of dried sample were immersed in enough salt solutions for 24 h to reach swelling saturation, and the swelling ratio (SR, g/g) was determined according to the Eq. 1 [17]. Each experiment was repeated three times to obtain a mean value of SR with errors of approximately ±4.5%.

$$\text{Swelling ratio (SR)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 was the mass of dried sample (g) and W_2 was mass of swollen hydrogel (g).

Characterizations

The morphology of PAC/PEG IPN hydrogel was examined using a scanning electron microscope (Hitachi S-5200, JAPAN). Swollen PAC/PEG IPN hydrogel was frozen in liquid nitrogen and then freeze-dried; its surface was subsequently observed and photographed by a scanning electron microscope (SEM). The sample was characterized by IR spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets.

Results and discussion

Synthesis

The PAC/PEG IPN hydrogel was synthesized by two-step method, which is different from the conventional routes to IPN hydrogel. In the first step, AA and AC monomers were initiated and polymerized to produce OAC. After viscosity of the reactant reached 140 mPa s, the second step was progressed, a mixture solution consisting of PEG and crosslinker NMBA was quickly poured into the above OAC solution, and APS was added to initiate the crosslinking of OAC and the formation of PAC/PEG IPN structure. The typical process can be expressed as follows:

$$\text{AA} + \text{AC} \xrightarrow[\text{Step I}]{\text{initiator}} \text{OAC} + \text{PEG} \xrightarrow[\text{Step II}]{\text{initiator} + \text{crosslinker}} \text{PAC/PEG IPN}$$

The OAC is a chainlike oligomer with low molecular weights in the absence of NMBA. While in the second step, NMBA is necessary for the formation of PAC network with a 3D structure. Once the PAC with full 3D network is formed and PEG interpenetrates into the PAC 3D network, the whole system becomes a typical IPN structure. The static polymerization is indispensable for the formation of excellent IPN structure. If the second step reaction is carried out continuously after the viscosity of the system exceeds 180 mPa s at 80 °C, the reaction will be accelerated and a sudden polymerization occurs which is unfavorable for the preparation of an even IPN hydrogel. In addition, the two-step synthesis technique is useful in preparing the IPN hydrogels with high mechanical strength. We have synthesized polyacrylamide/polyacrylamide, polyacrylamide/poly(vinyl alcohol) IPN hydrogels [18, 19] with a tensile strength of 2.4 MPa and a strain of 3000%, which is the highest report using the versatile technique.

Morphology of the PAC/PEG IPN hydrogel

Figure 1 shows the SEM micrograph of the typical PAC/PEG IPN hydrogel. It can be seen that the PAC/PEG IPN hydrogel exhibits even netlike structures with an average size of 1–4 µm. The structure is connective and oriented without any PEG agglomeration. A gel body with porous microstructure is expected to give rise to faster volume change, since the effective diffusion distance can be controlled by the average distance between neighboring pores [20]. Suzuki and Hirasa [21] synthesized bulky poly (methyl vinyl ether) (PMVE) hydrogel with a fine porous structure to obtain quick response gels. The swelling/deswelling properties of sponge-like gels are orders of much faster than any other responsive gels of comparable dimension, and the pore sizes have effects on swelling/deswelling properties of hydrogels. Based on the porous structures of PAC/PEG IPN hydrogel, it is expected to have excellent infiltration, swelling, and drug release properties.

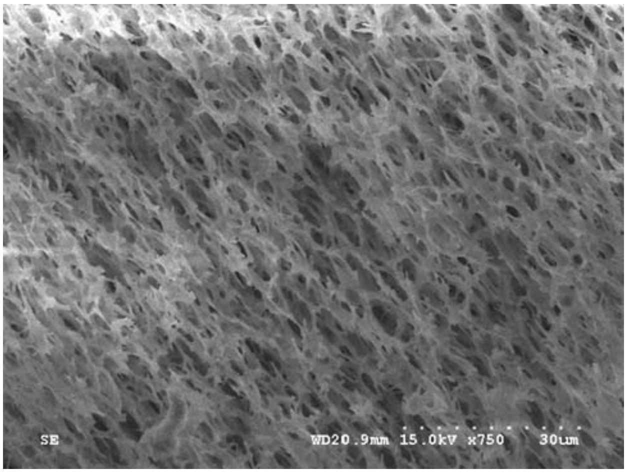

Fig. 1 SEM image of PAC/PEG IPN hydrogel

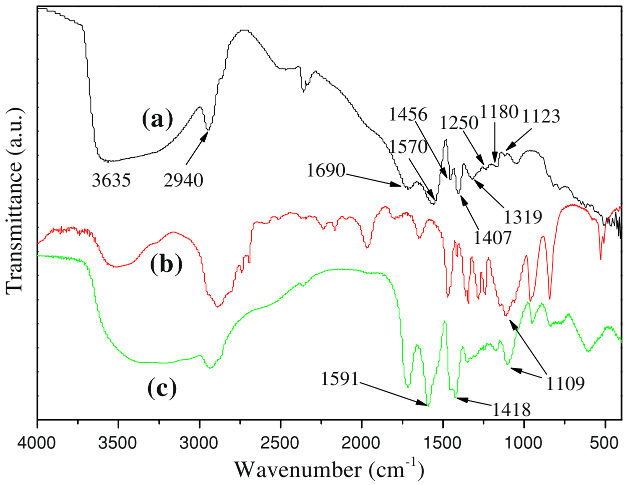

Fig. 2 FTIR spectra of PAC (*a*), PEG (*b*), and PAC/PEG IPN (*c*)

FTIR spectra of PAC/PEG IPN composite

The FTIR spectra of PAC, PEG, and PAC/PEG samples are shown in Fig. 2. For PAC, the absorption peak at ~3635 cm^{-1} attributes to the O–H stretching, the peak at ~2940 cm^{-1} is for the $–CH_2–$ dissymmetrical stretching, the peak at ~1690 cm^{-1} attributes to C=O stretching, the peak at ~1123 cm^{-1} is for C–H bending, the peaks at ~1570 cm^{-1} and ~1407 cm^{-1} are results of C=O bending in carboxylic and carboxylate groups, respectively. Peak at ~1250 cm^{-1} is corresponding to O–H distortion in carboxylic group, the peak at ~1180 cm^{-1} is for C–O stretching vibration, the peak at ~1456 cm^{-1} belongs to COO^- stretching, and ~1319 cm^{-1} peak is attributed to C–C stretching. In the case of PAC/PEG IPN, the absorption peak at ~1109 cm^{-1} is due to C–O–C stretching vibration of PEG, which indicates that PEG molecule chains have been introduced into the composite. The absorption peaks responsible for C=O bending in carboxylic and carboxylate groups have shifted to long wave number regions, which are ~1591 and ~1418 cm^{-1}, respectively. The shift of absorption peaks reveals a physical or chemical interaction between PAC and PEG in PAC/PEG IPN hydrogel [22, 23].

Swelling kinetics

The swelling kinetics at 0, 25, and 50 °C were measured and plotted in Fig. 3. It can be seen that the SRs decrease with increasing of the PEG amount. This may be due to the fact that the hydrophilicity of $–COO^-$ and –COOH groups on PAC is superior to the –OH group on PEG. With the increase of PEG content in the IPN hydrogel, the hydrophilic ability of the IPN hydrogel decreases, resulting in the decrease of SR. In addition, the density of the IPN hydrogel

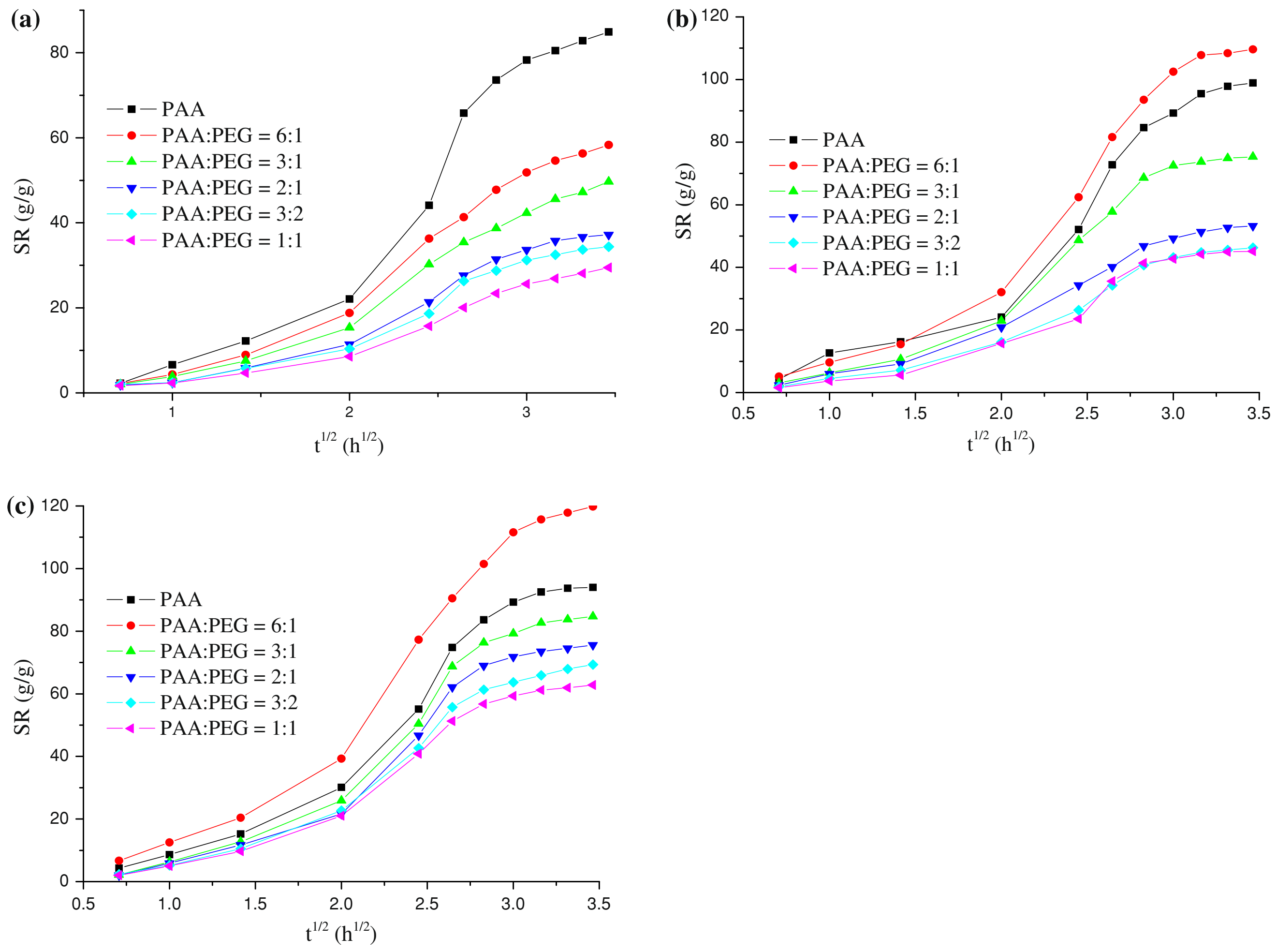

Fig. 3 SRs vs. $t^{1/2}$ for the PAC/PEG IPN samples at **a** 0 °C, **b** 25 °C, and **c** 50 °C under the same preparation conditions

is higher at higher PEG dosage, which leads to the decrease of water diffused into the gel and relaxation of the polymer chains [24].

It is known that swelling of hydrogel is a complicated process. Generally, three continuous processes are involved [25]: (i) water molecules enter hydrogel, (ii) relaxation of macromolecule chains, and (iii) stretch of whole macromolecule chains in water. If the first process is dominating in swelling of hydrogel network, the SR is directly proportional to square root of absorption time ($t^{1/2}$) [26]. If the second process is dominating, the plot of SR vs. $t^{1/2}$ is "S" shaped [27, 28]. From the above three figures of SR vs. $t^{1/2}$, it is obvious that all the curves are "S" shaped. Based on that, the second process was dominating in swelling of PAC/PEG IPN hydrogels. It is quick for water molecules to enter the hydrogel network and difficult for the relaxation of macromolecule chains in water, which result in the swelling controlled by step (ii). The result is consistent with Ref [27].

Influence of neutralization degree on SR

Neutralization degree of AA monomer in PAC/PEG hydrogel preparation has great influences on SR of hydrogel, which has been reported in our previous works [14–17]. From Table 1, the SR of PAC/PEG IPN samples increase with increasing of the neutralization degree in the range of 0–80%, and then gradually decrease beyond the neutration degree of 80%. The phenomenon can be explained by the Flory theory (Eq. 2) [11]:

$$\mathrm{SR}^{5/3} \approx \frac{\left(\frac{i}{2V_u I^{\frac{1}{2}}}\right)^2 + \frac{\frac{1}{2}-X_1}{V_1}}{\frac{V_e}{V_0}} \qquad (2)$$

where $\frac{i}{V_u}$ is the concentration of the fixed charges referred to the unswollen polymer, I is ionic strength in the external solution, $\frac{V_e}{V_0}$ is the crosslinking density of the hydrogel, and $\frac{\frac{1}{2}-X_1}{V_1}$ is relative to the water affinity of polymer.

Table 1 Values of k and c for the samples at different neutralization degrees and crosslinker dosage of 0.12 wt% (In our experiment, the k and c were all obtained from the sample with PAC:PEG = 6:1)

Neutralization degree (%)	0	20	40	60	80	100
SR (g/g)	3.550	60.259	95.232	108.197	122.7	69.829
k	0.030	4.373	9.634	11.837	14.717	5.706
c	2.508	87.583	138.257	186.514	207.427	89.767

Under the same crosslinking density, Eq. 2 can be simplified to Eq. 3, which is shown as follows:

$$\mathrm{SR}^{5/3} \approx kI^{-1} + c \tag{3}$$

where k is a parameter related to the ratio of charge density to crosslinking density, and c is a parameter related to the ratio of water affinity of polymer to crosslinking density. Ionic strength I can be expressed as (Eq. 4):

$$I = \frac{1}{2}\sum m_i z_i^2 \tag{4}$$

where m_i (mol kg^{-1}) and z_i are ionic concentration and valence of ion i, respectively.

Coefficients k and c at different neutralization degrees can be obtained by changing neutralization degree, measuring SR and ionic strength of solution, and combining Eqs. 3 and 4. The results are shown in Table 1. The parameters k and c both increase with increasing of neutralization degree ranging from 0 to 80% and then decrease in the neutralization degree range of 80–100%. It is known that –COOH group changes into COO$^-$ when AA monomer is neutralized by potassium hydroxide.

$$\mathrm{CH_2{=}CH{-}COOH + KOH \rightarrow CH_2{=}CH{-}COOK + H_2O}$$

Under a higher neutralization degree, more carboxylate groups with increased charge density and the water affinity will be produced, resulting in the increase of k and c (Table 1). However, under neutralization degree of 100%, a screening effect of the counter ions, i.e., K$^+$ ions shield the anions (–COO$^-$) and prevent an efficient repulsion, which decrease the SR. The same phenomenon was also found in PAC-based superabsorbents [14–17].

Influence of crosslinker on SR

In order to investigate the influence of crosslinker on SR of PAC/PEG IPN hydrogel, the neutralization degree of the samples was all fixed at 80%. From Table 2, the SR of PAC/PEG IPN hydrogel increases with increase of the crosslinker dosage in the range of 0–0.12 wt%, and then decreases in the crosslinker range of 0.12–0.50 wt%. It was also found that k and c increase in the crosslinker dosage ranging from 0 to 0.04 wt%, and decrease with increasing the amount of the crosslinker from 0.04 to 0.50 wt%. Under a lower crosslinker dosage, such as lower than 0.04 wt% the polymerization reaction does not occur adequately, and the 3D network of the polymer does not form effectively, which indicates water molecules cannot be held.

On the other hand, higher crosslinker concentrations result in the generation of more crosslinking points and the smaller network space of the polymer [16, 17], which has not enough space to hold water. This in turn causes a decrease of the coefficients k and c for the hydrogel. It has been reported by our and other groups that crosslinker plays an important role in adjusting the SR of superabsorbents or hydrogels [14–17, 29, 30]. Generally, two curves are found: (i) the SR of superabsorbents decreases gradually with the increase of crosslinker dosage; (ii) the SR increases with increasing of crosslinker dosage and reaches a highest value, beyond which, SR has a degressive tendency.

Influence of the ionic strength on SR

In order to investigate the swelling properties of PAC/PEG IPN hydrogels in univalent and multivalent salt solutions, we plotted the fitting curves of SR on effective ionic strength, which were shown in Figs. 4 and 5. In general, the salts cannot ionize completely. The effective ionic strength (I_{eff}) is introduced to obtain the exact relationship between ionic strength and SR. The I_{eff} of solutions can be obtained according to Eqs. 5–7 [31].

$$\lg \gamma_i = -0.509 \times z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30I \right) \tag{5}$$

$$\alpha_i = \gamma_i \times c_i \tag{6}$$

Table 2 k and c values for the samples with different crosslinking densities under neutralization degree of 80%

Crosslinker (wt%)	0	0.04	0.08	0.12	0.20	0.30	0.50
SR	81.800	137.685	131.516	122.703	88.021	75.595	70.625
k	7.383	17.551	16.357	14.717	8.332	6.581	5.914
c	125.442	305.225	264.086	207.427	143.706	89.351	72.451

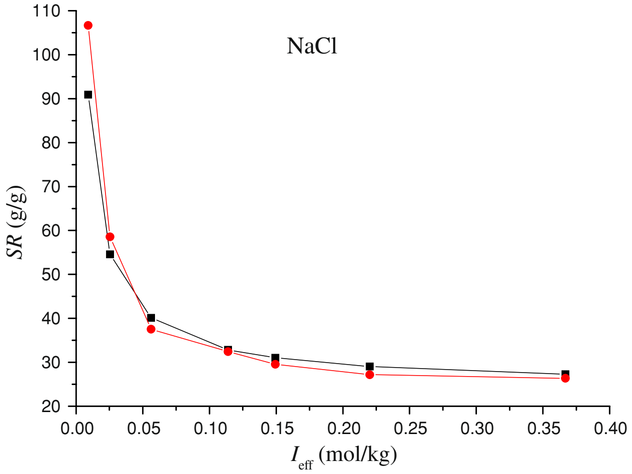

Fig. 4 Theoretical (*black square*) and experimental (*black circle*) curves of PAC/PEG IPN hydrogel in NaCl solutions

$$I_{\mathrm{eff}} = \frac{1}{2}\sum \alpha_i z_i^2 \qquad (7)$$

The relational data were listed in Table 3 with an ionic strength ranging from 0.01 to 0.5 mol kg^{-1} for sodium chloride, calcium chloride, and iron chloride. The PAC/PEG IPN hydrogels cannot react with univalent ions, the SRs at different I_{eff} in NaCl solution can be used as the theoretical values. So, we measured the SRs in NaCl solutions at different I_{eff}. When $I = 0.05$ ($I_{\mathrm{eff}} = 0.041$ mol kg^{-1}) and 0.1 mol kg^{-1} ($I_{\mathrm{eff}} = 0.078$ mol kg^{-1}), the SRs of PAC/PEG IPN hydrogel are 44.86 and 36.21 g/g, respectively. Substituting into Eq. 3, the theoretical values of k and c were 14.72 and 207.43 regardless of their units, respectively. Thus the Eq. 3 is simplified as:

$$\mathrm{SR}^{5/3} \approx 14.72 I^{-1} + 207.43 \qquad (8)$$

Table 3 The I_{eff} (mol kg^{-1}) of salts at various concentrations

I (mol kg^{-1})		0.01	0.03	0.07	0.15	0.20	0.30	0.50
NaCl	$\gamma\pm$	0.902	0.850	0.802	0.760	0.747	0.734	0.734
	$\alpha\pm$	0.009	0.026	0.056	0.114	0.149	0.220	0.367
	I_{eff}	0.009	0.025	0.056	0.114	0.149	0.220	0.367
$\mathrm{CaCl_2}$	$\gamma\pm$	0.773	0.666	0.576	0.504	0.482	0.462	0.461
	$\alpha\pm$	0.003	0.007	0.013	0.025	0.032	0.046	0.077
	I_{eff}	0.007	0.019	0.038	0.069	0.091	0.131	0.219
$\mathrm{FeCl_3}$	$\gamma\pm$	0.597	0.444	0.332	0.254	0.232	0.213	0.212
	$\alpha\pm$	0.001	0.002	0.004	0.006	0.008	0.010	0.017
	I_{eff}	0.005	0.012	0.021	0.038	0.048	0.069	0.115

Thus the theoretical SR ($\mathrm{SR_t}$) and experimental SR ($\mathrm{SR_e}$) can be plotted in Fig. 4. It can be seen that the two curves are nearly the same in NaCl solution, especially in higher ionic strength. It is known that there is no chemical crosslink occurring in NaCl solution apart from ion-exchange [32], which is in accordance with Flory theory. Consequently, the Eq. 8 is reliable and adoptable as a standard to estimate influences of ionic strength on $Q_{\mathrm{H_2O}}$ of PAC/PEG IPN hydrogels.

However, the analogous curves are not found in $\mathrm{CaCl_2}$ and $\mathrm{FeCl_3}$ solutions, as depicted in Fig. 5. It is obvious that $\mathrm{SR_e}$ are much lower than $\mathrm{SR_t}$ under the same conditions. In fact, the absorption of PAC/PEG hydrogels to water in multivalent salt solutions is far from physical interactions, in which chelation occurs in carboxylic and carboxylate groups on the PAC/PEG and cation ions in solution. Owing to the crosslinking of metal ions [33, 34] and heavy metal ions in solution [35–39] with carboxylic and carboxylate groups on the PAC/PEG, imaginably, the crosslinking density of the hydrogel increases, fixed charges and water

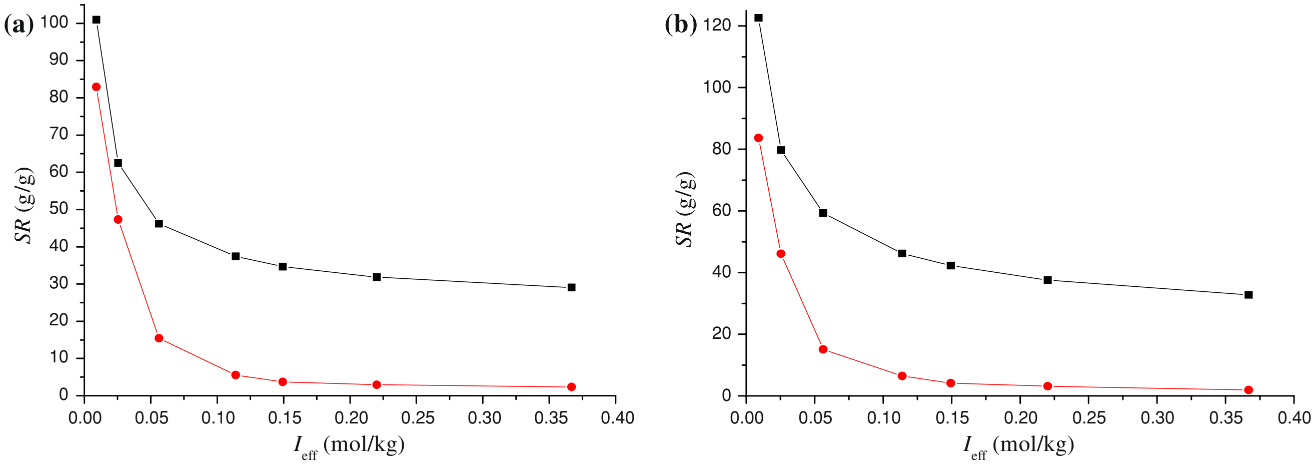

Fig. 5 Theoretical (*black square*) and experimental (*black circle*) curves of PAC/PEG IPN hydrogel in $\mathrm{CaCl_2}$ (**a**) and $\mathrm{FeCl_3}$ (**b**) solutions (The curves of SR_t for $\mathrm{CaCl_2}$ and $\mathrm{FeCl_3}$ were plotted based on Eq. 2 supposing without any chelations)

affinity on the hydrogel decreases with increasing of chelation degree, which results in the decrease of SR, *k*, and *c*.

Conclusions

PAC/PEG IPN hydrogels were synthesized using two-step aqueous solution polymerization. The SRs of PAC/PEG IPN hydrogels were proportional to square root of absorption time, indicating that the relaxation of macromolecule chains was dominating. The investigations on simplification of Flory theory revealed that the coefficients reflecting relations of fixed charges and water affinity to crosslinking density, *k*, and *c* could be obtained and compared via changing neutralization degree of acrylic acid monomer and crosslinker dosage. Fitting experiments showed that SR_t was consistent with SR_e when the hydrogels swelled in univalent salt solutions, whereas in the case of multivalent solutions, they were inconsistent owing to the changes of hydrogel structures.

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References

1. Buchholz F, Graham A (1997) Modern superabsorbent polymer technology. Wiley, New York
2. Asoh T, Kaneko T, Matsusaki M (2006) J Control Release 110:387
3. Zhang YX, Wu FP, Li MZ (2005) Polymer 46:7695
4. Pourjavadi A, Mirjalili BF, Entezami AA (2001) Eur Polym J 37:2111
5. Durme KV, Mele BV, Loos W (2005) Polymer 46:9851
6. Xiao XC, Chu LY, Chen WM (2005) Polymer 46:3199
7. Kaewpirom S, Boonsang S (2006) Eur Polym J 42:1609
8. Şolpan D, Torun M (2005) Colloid Surf A 268:12
9. Kim SJ, Yoon SG, Lee SM (2003) Sens Actuator B 96:1
10. Yang S, Aizenberg J (2005) Mater Today 8:40
11. Flory PJ (1953) Principles of polymer chemistry. Cornel University Press, New York
12. Gayet JC, Fortier G (1996) J Control Release 38:177
13. Bhattarai N, Ramay HR, Gunn J (2005) J Control Release 103:609
14. Wu JH, Lin JM, Zhou M (2000) Macromol Rapid Commun 21:1032
15. Lin JM, Wu JH, Yang Z (2001) Macromol Rapid Commun 22:422
16. Lin JM, Tang QW, Wu JH (2007) React Funct Polym 67:489
17. Wu JH, Wei YL, Lin JM (2003) Polymer 44:6513
18. Tang QW, Lin JM, Wu JH (2007) Carbohydr Polym 67:332
19. Tang QW, Wu JH, Lin JM (2008) e-Polymers 21:1
20. Arndt KF, Schmidt T, Reichelt R (2001) Polymer 42:6785
21. Suzuki M, Hirasa O (1993) Adv Polym Sci 110:241
22. Johansson HO, Magaldi FM, Feitosa E (2008) J Chromatogr A 1178:145
23. Touitou E, Donbrow M (1983) Int J Pharm 15:13
24. Li XY, Wu WH, Wang JQ (2006) Carbohydr Polym 66:473
25. Enscore DJ, Hopfraberg HB, Stannett VT (1977) Polymer 18:793
26. Crank J (1975) The mathematics of diffusion. Oxford University Press, London
27. Zhang XZ, Zhuo RX (2000) J Colloid Interface Sci 223:311
28. Zhang XZ, Zhuo RX, Yang Y (2002) Biomaterials 23:1313
29. Tang QW, Lin JM, Wu JH (2007) J Appl Polym Sci 104:735
30. Ge HC, Pang W, Luo DK (2006) Carbohydr Polym 66:372
31. Atkins PW (1986) Physical chemistry, 3rd edn. OUP, London, p 243
32. Mahdavinia GR, Pourjavadi A, Hosseinzadeh H (2004) Eur Polym J 40:1399
33. Tang QW, Sun XM, Li QH, Lin JM, Wu JH (2009) J Mater Sci 44:726. doi:10.1007/s10853-008-3173-1
34. Zimmermann H, Wählisch F, Baier C (2007) Biomaterials 28:1327
35. Singh B, Chauhan GS, Bhatt SS (2006) Carbohydr Polym 64:50
36. Chauhan GS, Singh B, Chauhan S (2005) Desalination 181:217
37. Li N, Bai RB (2005) Sep Purif Technol 42:237
38. Yan WL, Bai RB (2005) Water Res 39:688
39. Ali AE, Shawky HA, Abd El Rehim HA (2003) Eur Polym J 39:2337