

# Preparation and Characterization of Hydrophilic, Spectroscopic, and Kinetic Properties of Hydrogels Based on Polyacrylamide and Methylcellulose Polysaccharide

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**ABSTRACT:** Hydrogels with potential technological applications has been prepared using polyacrylamide (PAAm) and methylcellulose (MC) polymers by free radical polymerization reaction. The spectroscopic, morphological, swelling, and kinetic properties were investigated by solid state <sup>13</sup>C VACP-MAS nuclear magnetic resonance (NMR), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), water uptake (WU) measurements, respectively. FTIR and NMR analysis confirmed the formation of semi-IPN structured hydrogel. Data from WU and SEM revealed that the addition of MC into the solution-forming hydrogel leads to increase in average pore size and

hydrophilicity. By varying of AAm, MC, pH and ionic-strength of swelling medium, it was possible to obtain hydrogels with hydrophilic properties controlled and optimized. The water uptake mechanism is dependent of the AAm concentration, which can follow the Fickian diffusion and anomalous transport process. In this way, PAAm-MC hydrogels are promising materials for technological applications, such as agricultural field. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3004–3013, 2011

**Key words:** biodegradable; crosslinking; hydrogels; hydrophilic polymers; polysaccharides

## INTRODUCTION

Hydrogels constitute a select class of polymeric materials because they can swell in specific conditions by absorbing a large amount of water<sup>1,2</sup> and de-swell by pushing out the total or a fraction of the absorbed water according to the environmental conditions such as temperature, pH, ionic-strength, solvent polarity, etc. Hydrogels are constituted of hydrophilic chains in a three-dimensional polymer network.<sup>3</sup> Because of their common characteristics, hydrogels are extensively used in different applications, for instance, implants,<sup>4</sup> contact lenses,<sup>5</sup> controlled delivery systems,<sup>6</sup> soil conditioning,<sup>7</sup> and others. There are divergences in relation the use of polyacrylamide

hydrogels as matrix for specific application as bio-materials. For instance, surface-grafted polyacrylamide brushes and presented inhibition for microbial adhesion due to the high hydrophilic characteristics.<sup>8</sup> However, there are findings showing that the polyacrylamide presents some incompatibility with human body.<sup>9,10</sup> In this way, the copolymerization of acrylamide with polysaccharides would provide more biocompatibility as well as biodegradability, what seems to be a quite important approach.<sup>11</sup>

In the last years, much attention has been given to polysaccharide-based hydrogels,<sup>12–14</sup> mainly in agricultural applications. An important fraction of such studies focused on emerging applications such as delivery carriers of fertilizers, pesticides, and other agricultural raw materials loaded onto hydrogels.<sup>15–18</sup> Bajpai and Giri, 2003<sup>19</sup> investigated hydrogel formation by polyacrylamide-grafted carboxy methylcellulose for the controlled delivery of potassium nitrate. There is high concern in obtaining hydrogels from renewable sources for reduced production cost and environmental friendliness,<sup>20,21</sup> but mainly because of the biodegradability requirements of specific applications. Large number of hydrophilic groups in the chains of the polysaccharide, mainly hydroxyl and carboxyl groups may help to become or improve

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**TABLE I**  
**AAm, and MC Concentrations in Feed Solutions Used**  
**in (PAAm X-MC Y)<sup>a</sup> hydrogel synthesis:  $V_{\text{Final}}$ : 30 mL;**  
**[MBAAm] = 1.0 mol % relative to the AAm conc.;**  
**[TEMED]<sub>Final</sub> = 3.21  $\mu\text{mol mL}^{-1}$  and [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]<sub>Final</sub> =**  
**3.38  $\mu\text{mol mL}^{-1}$**

| Hydrogels      | Acrylamide (AAm) (g) | Methylcellulose (g) |
|----------------|----------------------|---------------------|
| PAAm3.6-MC0.0  | 1.08                 | 0                   |
| PAAm3.6-MC0.5  | 1.08                 | 0.15                |
| PAAm3.6-MC1.0  | 1.08                 | 0.30                |
| PAAm7.2-MC0.0  | 2.16                 | 0                   |
| PAAm7.2-MC0.5  | 2.16                 | 0.15                |
| PAAm7.2-MC1.0  | 2.16                 | 0.30                |
| PAAm14.7-MC0.0 | 4.41                 | 0                   |
| PAAm14.7-MC0.5 | 4.41                 | 0.15                |
| PAAm14.7-MC1.0 | 4.41                 | 0.30                |
| PAAm21.7-MC0.0 | 6.51                 | 0                   |
| PAAm21.7-MC0.5 | 6.51                 | 0.15                |
| PAAm21.7-MC1.0 | 6.51                 | 0.30                |

<sup>a</sup> X and Y corresponds to AAm and MC concentrations, both in wt %.

hydrogel hydrophilic properties and potentially enhance biodegradability.<sup>22–25</sup> Zhao et al.,<sup>22</sup> observed an enhancement in the hydrophilicity of poly(*N*-vinyl pyrrolidone) (PVP) with the addition of carboxymethyl chitosan.

This work reported the synthesis of semi-IPN hydrogels constituted by methylcellulose (MC) entrapped in polyacrylamide (PAAm) network by crosslinking polymerization (gelling process) of acrylamide (AAm) using sodium persulfate as an initiator, *N,N,N',N'*-tetramethylethylene-diamine as an accelerator and *N',N'*-methylene-bisacrylamide as a crosslinker. The aim of this article was to propose strategies for improving the water uptake (hydrophilicity) of PAAm hydrogel. Hydrophilic and kinetic properties were investigated as function of pH and ionic-strength. In addition, solid state <sup>13</sup>C VACP-MAS nuclear magnetic resonance, fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy techniques were used to investigate the spectroscopic and morphological properties, respectively.

## EXPERIMENTAL

### Materials

Methylcellulose (MC,  $M_n = 40,000 \text{ g mol}^{-1}$ , viscosity 400 cP, 27.6–31.5% in methoxy groups; 68.5–72.4% in hydroxyl groups, data provided by the supplier), and *N',N'*-methylene-bisacrylamide (MBAAm) crosslinker were purchased from Aldrich. *N,N,N',N'*-tetramethylethylene-diamine (TEMED), and sodium persulfate (SP) were obtained from Sigma. The acrylamide (AAm) monomer was purchased from Fluka. All reagents were of analytical grade and used as received.

### Preparation of hydrogels

PAAm-MC hydrogels were obtained from the polymerization/crosslinking of AAm with MBAAm using water as solvent. After the addition of AAm, MBAAm, MC, and TEMED (3.21  $\mu\text{mol mL}^{-1}$ ) (total volume = 29 mL), the resultant mixture was deoxygenated by bubbling N<sub>2</sub> gas for 25 min. Thereafter, 1.0 mL of deoxygenated aqueous sodium persulfate 0.10 mmol L<sup>-1</sup> was added to start the reaction.

The gelling process is believed to occur through a typical free-radical polymerization mechanism. At the end of reaction, the hydrogel was immersed in distilled/deionized water to remove the unreacted chemicals, e.g., monomers, catalyst, initiator. The water was changed to each 10 h for 10 days. AAm and MC concentrations (both in wt %) used in the feed solutions were given in Table I. MBAAm content was fixed in 1.0 mol % relative to the AAm concentration.

The radical reaction of AAm and MBAAm was not affected by the presence of MC, as expected. However, as known, that reaction must be performed in absence of O<sub>2</sub> because oxygen atoms react instantaneously with some radical moieties that prevent the polymerization. As TEMED catalyzes the homolytic scission of the SP, that polymerization may be performed at room temperature.<sup>26</sup>

### Scanning electron microscopy

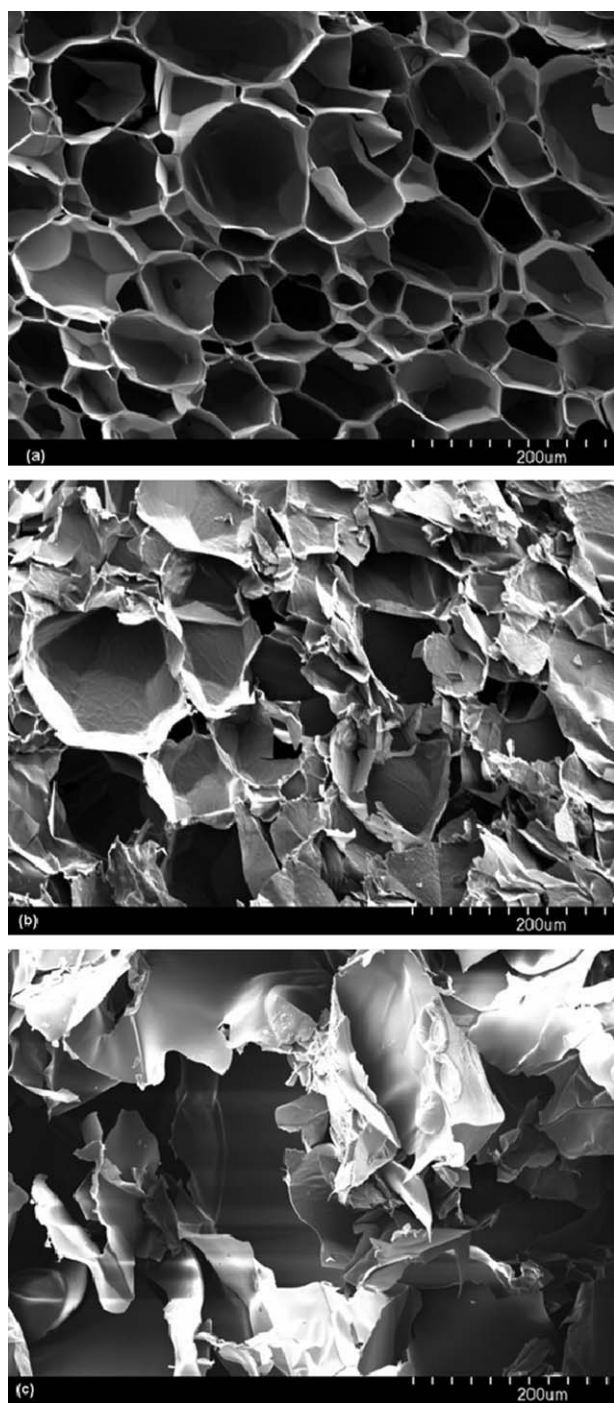
Morphological properties of equilibrium swollen hydrogels were investigated using a scanning electron microscope Hitachi, model S-4700 with 200 X magnification and an accelerating voltage of 15 keV. The samples were removed from water and quickly frozen by immersion in liquid nitrogen. Hydrogels were freeze dried at –80°C to maintain the porous structure without any collapse.<sup>27,28</sup> After 48 h lyophilization, the dried sample was deposited onto an aluminum stub and sputter-coated with gold for 60 s to enhance conductivity.

### Fourier transform infrared spectroscopy

Spectra of PAAm, MC, and PAAm-MC hydrogel in range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> were recorded on a FTIR (Perkin–Elmer, model Spectrum Paragon 1000).<sup>29</sup> Prior to the measurement, the samples were dried under vacuum until reaching a constant weight. Powdered samples were prepared into pellets with KBr (1 wt %). To reach a resolution of 2 cm<sup>-1</sup>, 128 scans were acquired for each spectrum.

### Solid state <sup>13</sup>C VACP-MAS nuclear magnetic resonance

Hydrogels and MC high resolution <sup>13</sup>C-NMR experiments with cross-polarization (CP) and magic-angle



**Figure 1** SEM micrographs for semi-IPN hydrogels: (a) PAAm3.6-MC0.0; (b) PAAm3.6-MC0.5 and (c) PAAm3.6-MC1.0. The gels were lyophilized after swelling in distilled water at 25.0°C. All micrographs were taken at  $\times 200$  magnification.

spinning (MAS) with variable amplitude (VA) method<sup>30</sup> were carried out in a Varian Inova 400 spectrometer (9.4 T). The samples were placed in a cylindrical 5-mm diameter zirconium rotor spinning at 4.5 kHz in a Doty Supersonic probe. Each spectrum was acquired using a standard pulse sequence, consisting of a 4- $\mu$ s preparation  $\pi/2$  pulse, 12.8 ms

time acquisition, 1 ms contact time, and 1-s recycle delay. The chemical shift values were calibrated using hexamethyl benzene (HMB) at 17.2 ppm. All spectra were filtered by an exponentially decaying function (line broadening factor of 10 Hz).

### Water uptake

The swelling capability of hydrogels was investigated by measuring their water uptake (WU) at different pH and ionic-strength conditions. The buffer solutions were prepared according to Morita and Assumpção.<sup>31</sup> The ionic strength was adjusted with NaCl salt for 0.025, 0.10, and 0.20 mol L<sup>-1</sup>.

For the water uptake studies, the swollen hydrogels in membrane form were cut in cylindrical form with radius of 13 mm, and the average of dry hydrogels used was  $\sim 150$  mg. After removing the water on the surface with wet filter paper, the weight of hydrogels was recorded. WU values were obtained by the mass ratio of the swollen hydrogel to dried hydrogel. Measurements were performed in replicate at 25.0°C to check reproducibility and the error bars indicate the standard deviation ( $n = 3$ ).

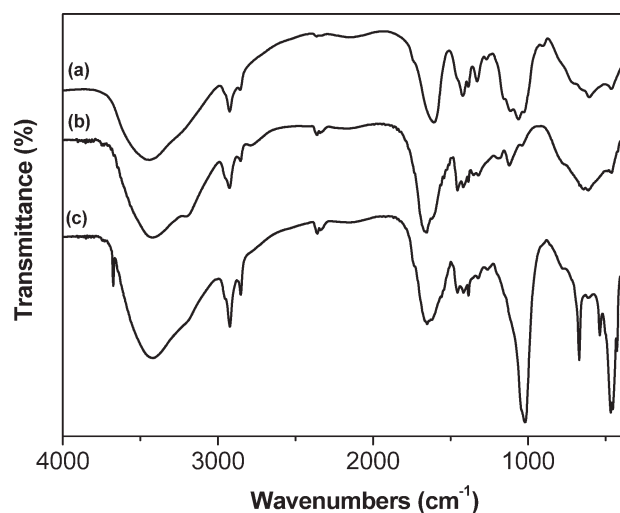
## RESULTS AND DISCUSSION

### Scanning electron microscopy

SEM technique was used to analyze the morphology of PAAm and PAAm-MC hydrogels. Average pore size values were estimated by considering at least 20 individual pore size values.<sup>32</sup> The SEM image of PAAm3.6-MC0.0 (3.6% AAm and 0% MC), shown in Figure 1(a), indicates the formation of homogeneous and highly porous material with average pore size of 90 ( $\pm 20$ )  $\mu$ m. The addition of MC into the solution-forming hydrogel caused changes on morphologic aspects, mainly in the size and shape of the pores. From SEM micrographics showed in Figure 1(b,c), it was possible to see that hydrogel pores are more foliaceous, larger, and highly heterogeneous than those showed in Figure 1(a). Because of the formation of pore with high heterogeneity, is not possible to estimate with precision the pore size of these hydrogels.

### FTIR spectroscopy

FTIR spectra of MC, PAAm3.6-MC0.0, and PAAm3.6-MC1.0 semi-IPN hydrogels are presented in Figure 2. The bands at 3425-3193 cm<sup>-1</sup> (N-H stretch), and 800-664 cm<sup>-1</sup> (N-H out-of-plan bend), in the PAAm hydrogel spectrum, can be assigned to amide groups.<sup>33,34</sup> Axial deformation relative to carbonyl and C-N bonds can be observed at 1668 cm<sup>-1</sup> and 1466 cm<sup>-1</sup>, respectively. Two bands of medium intensity appearing around 1375 and 825 cm<sup>-1</sup> are



**Figure 2** FTIR spectra of: (a) methylcellulose (MC), (b) PAAm3.6-MC0.0 and (c) PAAm3.6-MC1.0 semi-IPN hydrogel.

associated with the  $\text{CH}_2$  vibration modes. The  $\text{CH}_2$  asymmetric and symmetric stretching vibrations occur at  $2925\text{--}2860\text{ cm}^{-1}$  region. The strong bands observed at  $1120\text{--}1030\text{ cm}^{-1}$  (symmetric) and  $466\text{ cm}^{-1}$  (asymmetric) has been assigned to  $\text{C}\text{--}\text{C}$  stretching modes.

A wide band in the MC spectrum corresponded to the hydroxyl groups<sup>35,36</sup> is observed at spectral range of  $3760\text{--}2990\text{ cm}^{-1}$ . The band at  $1614\text{ cm}^{-1}$  is due to the adsorbed water molecular vibration (hydration water). The band at  $1426\text{ cm}^{-1}$  is attributed to planar deformation of  $\text{H}\text{--}\text{C}\text{--}\text{H}$  and  $\text{O}\text{--}\text{C}\text{--}\text{H}$  groups. The bands appearing at the spectral range from  $1230\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  are characteristics to  $\beta$ -glycosides among MC saccharide units. A band attributed to pyronisidic ring is observed at  $620\text{ cm}^{-1}$ .

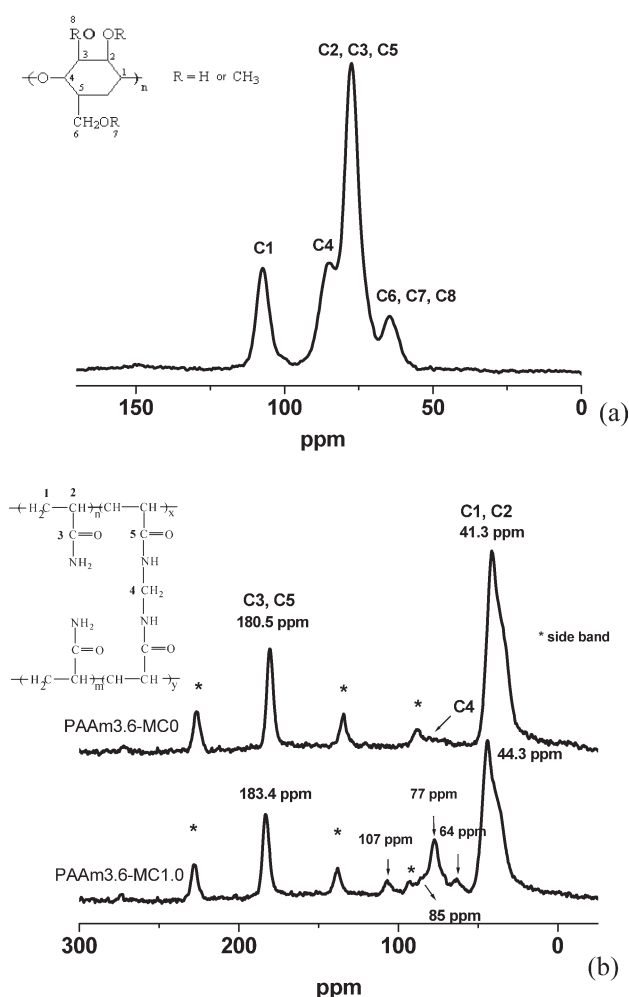
Intensification of the bands at wavenumbers  $1030\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  can be observed in the PAAm3.6-MC1.0 hydrogel spectrum when compared to MC spectrum.<sup>37,38</sup> Such bands are attributed to  $\beta$ -glycosides bonds among saccharide and the pyronisidic rings, respectively. Finally, the axial deformation of the carbonyl of amide group is observed at  $1680\text{ cm}^{-1}$  in the semi-IPN and the PAAm hydrogel spectra. These data show that methylcellulose is present in the hydrogel. In addition, as there is no covalent bond among polyacrylamide and methylcellulose chains, it can be inferred that the formation of polyacrylamide network entrapped methylcellulose hydrogel occurred.

### Solid state $^{13}\text{C}$ Vacp-MAS NMR spectroscopy

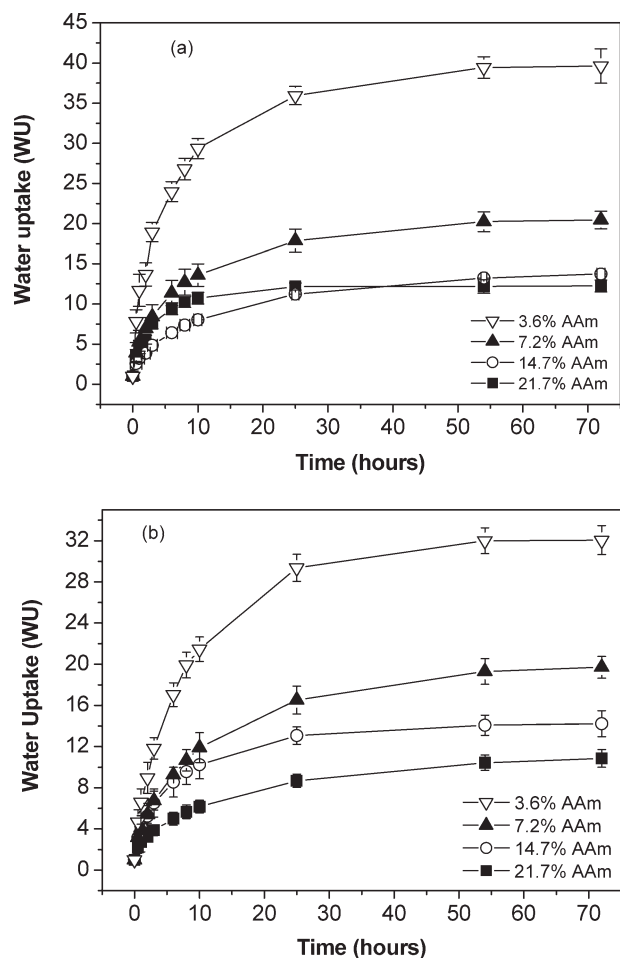
Signals ranging from  $\delta 64\text{ ppm}$  to  $\delta 108\text{ ppm}$  corresponding to carbons  $\text{C}_1$  to  $\text{C}_8$  can be observed in the MC spectrum [Fig. 3(a)]. Signals at  $\delta 64\text{ ppm}$  and  $\delta 77\text{ ppm}$  are attributed to  $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_8$ , and to  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_5$ , respectively. Signals related to  $\text{C}_4$  and  $\text{C}_1$  appear

at  $\delta 86\text{ ppm}$  and  $\delta 107\text{ ppm}$ , respectively.  $^{13}\text{C}$  VACP-MAS NMR of PAAm3.6-MC0.0 and PAAm3.6-MC1.0 hydrogels are shown in Figure 3(b), respectively. Two strong signals attributed to  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$ ,  $\text{C}_5$  carbons can be observed in the PAAm spectrum at  $\delta 41.3\text{ ppm}$  and  $\delta 180.5\text{ ppm}$ , respectively. There is also a little band between  $\delta 70\text{--}75\text{ ppm}$  attributed to  $\text{C}_4$  carbons.

Some spectral changes at higher frequencies can be noticed in PAAm3.6-MC1.0 semi-IPN hydrogel spectrum. The signal corresponding to  $\text{C}_1$  and  $\text{C}_2$  carbons changed from  $\delta 41.3\text{ ppm}$  to  $\delta 44.3\text{ ppm}$ .  $\text{C}_4$  carbons changed from  $\delta 70\text{--}75\text{ ppm}$  to  $\delta 85\text{ ppm}$ , and  $\text{C}_3$  and  $\text{C}_5$  shifted from  $\delta 180.5\text{ ppm}$  to  $\delta 183.4\text{ ppm}$ . These changes are strong indications of the structural and conjugation ( $\text{C}=\text{C}$  bonds between  $\text{C}_1$  and  $\text{C}_2$  carbons) modifications of the PAAm-MC network. The signals at  $\delta 64\text{ ppm}$ ,  $77\text{ ppm}$ , and  $107\text{ ppm}$  observed for the semi-IPN hydrogels, coming from MC macromolecule, are strong evidences of



**Figure 3** VACP-MAS  $^{13}\text{C}$ -NMR spectrum of (a) methylcellulose; (b) PAAm3.6-MC0 and PAAm3.6-MC1.0 semi-IPN hydrogel. The structures correspond to MC and PAAm hydrogel.



**Figure 4** Dependence of water uptake as a function of time for: (a) PAAm-MC0.5 and (b) PAAm-MC1.0, in pH 4.0, at 25.0°C. Different concentrations of AAm were tested as indicated. Error bars represent standard deviations for the three experiments.

the formation of semi-IPN structured hydrogel, as proposed in this article.

### Water uptake

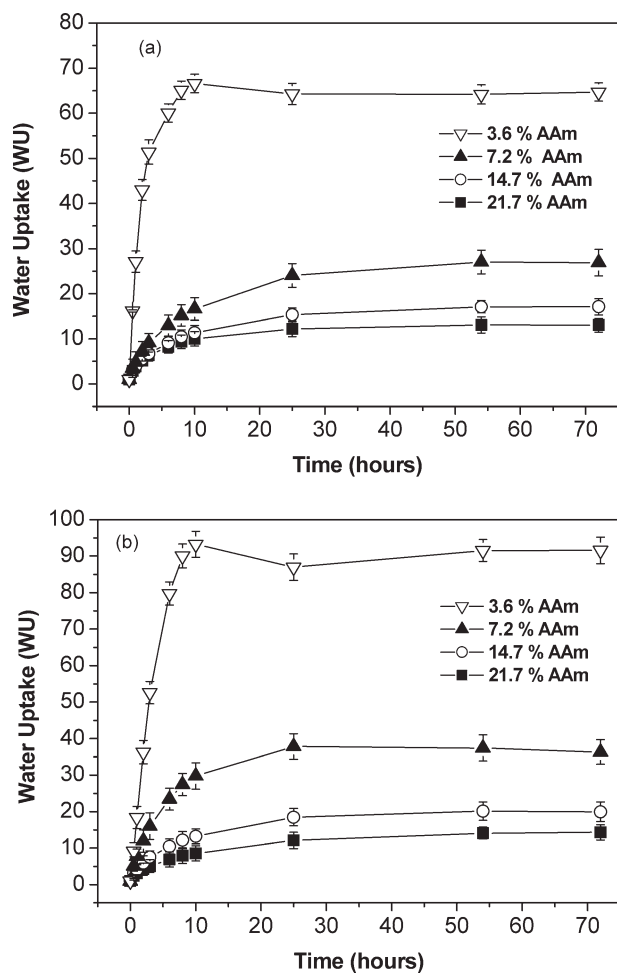
The dependence of water uptake (WU) as a function of time for PAAm-MC0.5 and PAAm-MC1.0

hydrogels is shown in Figures 4(a,b), respectively. At pH 4.0, the WU values for PAAm hydrogel without MC (not shown) obtained from solutions with AAm concentrations of 3.6, 7.2, 14.7, and 21.7 wt % were  $31.4 \pm 1.5$ ,  $19.8 \pm 0.8$ ,  $13.4 \pm 0.6$ , and  $11.5 \pm 0.5$  g/g, respectively. For PAAm-MC0.5 hydrogels, the WU values at the same feed AAm concentrations were  $39.6 \pm 2.2$ ,  $20.5 \pm 1.1$ ,  $13.7 \pm 0.6$ , and  $12.2 \pm 0.7$  g/g. For PAAm-MC1.0 hydrogels, the respective WU values were  $32.1 \pm 1.4$ ,  $19.7 \pm 1.1$ ,  $14.2 \pm 1.3$ , and  $10.9 \pm 0.9$  g/g. In general, in PAAm-MC1.0 hydrogels the WU is lower than PAAm-MC0.5 hydrogels. In this condition, the density of network may have increased so much that both the diffusion of solvent molecules and relaxation of macromolecular chains are reduced (see results presented in Table II). This explains the fall in the swelling ratio of the hydrogel. Similar results have also been obtained by other workers in swelling studies of hydrogels containing hydrophilic polymers.<sup>19,39</sup>

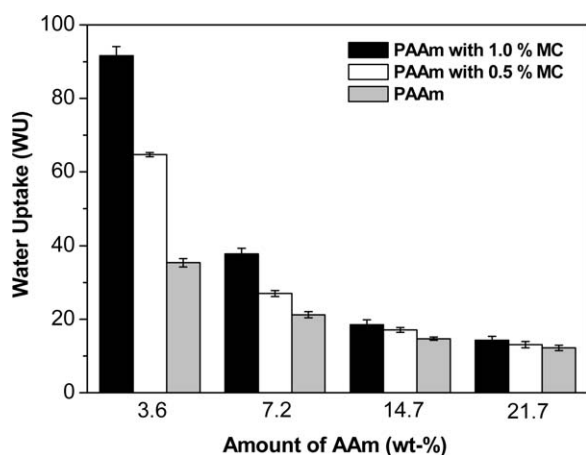
The dependences of WU as a function of the immersion time of the semi-IPN hydrogels swelled in distilled water are shown in Figure 5. Changes on equilibrium WU values as a function of the AAm concentration in the feed solution are shown in Figure 6. It can be pointed out that WU value decreases abruptly when the concentration of AAm in the gel-forming solution increases. This reduction is related to the increase of network rigidity, where the flexibility of a hydrogel network is directly related with the amount of total water absorbed by hydrogel.<sup>40</sup> The highest WU value was obtained for 3.6 (wt %) AAm and 1.0 (wt %) MC, around 90 g/g. Also, the WU values abruptly increased when concentration of MC in feed solution increased. This trend is attributed to the increase in the hydrogel hydrophilicity (and thus the increase in water absorption capacity) due to incorporation of hydroxyl groups from MC segments. This tendency was also observed in the PAAm/poly((-glutamic acid) hydrogels studied by Rodríguez et al.<sup>41</sup>

**TABLE II**  
Effect of Acrylamide and Methylcellulose Concentrations on Swelling Exponent ( $n$ ) and Diffusion Constant ( $k$ ) of Water in PAAm-MC Hydrogels at Different pH Values

| Hydrogels        | pH = 4.0        |                        | pH = 6.7        |                        | pH = 10.0       |                        |
|------------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
|                  | $n$             | $k$ (s <sup>-1</sup> ) | $n$             | $k$ (s <sup>-1</sup> ) | $n$             | $k$ (s <sup>-1</sup> ) |
| PAAm3.6-MC0.5    | $0.44 \pm 0.01$ | $0.315 \pm 0.041$      | $0.60 \pm 0.02$ | $0.616 \pm 0.082$      | $0.36 \pm 0.04$ | $0.905 \pm 0.102$      |
| PAAm7.2-MC0.5    | $0.42 \pm 0.02$ | $0.169 \pm 0.025$      | $0.53 \pm 0.04$ | $0.063 \pm 0.011$      | $0.44 \pm 0.05$ | $0.156 \pm 0.025$      |
| PAAm14.7-MC0.5   | $0.39 \pm 0.01$ | $0.137 \pm 0.018$      | $0.45 \pm 0.02$ | $0.104 \pm 0.020$      | $0.38 \pm 0.01$ | $0.192 \pm 0.015$      |
| PAAm21.7-MC0.5   | $0.38 \pm 0.02$ | $0.215 \pm 0.021$      | $0.41 \pm 0.01$ | $0.132 \pm 0.013$      | $0.38 \pm 0.02$ | $0.165 \pm 0.008$      |
| PAAm 3.6-MC 1.0  | $0.52 \pm 0.03$ | $0.092 \pm 0.006$      | $0.78 \pm 0.06$ | $0.030 \pm 0.004$      | $0.55 \pm 0.02$ | $0.063 \pm 0.001$      |
| PAAm 7.2-MC 1.0  | $0.45 \pm 0.02$ | $0.106 \pm 0.007$      | $0.60 \pm 0.04$ | $0.058 \pm 0.004$      | $0.45 \pm 0.03$ | $0.110 \pm 0.002$      |
| PAAm 14.7-MC 1.0 | $0.40 \pm 0.01$ | $0.159 \pm 0.015$      | $0.49 \pm 0.01$ | $0.078 \pm 0.003$      | $0.39 \pm 0.01$ | $0.135 \pm 0.010$      |
| PAAm 21.7-MC 1.0 | $0.36 \pm 0.01$ | $0.147 \pm 0.009$      | $0.43 \pm 0.02$ | $0.097 \pm 0.008$      | $0.37 \pm 0.01$ | $0.127 \pm 0.008$      |

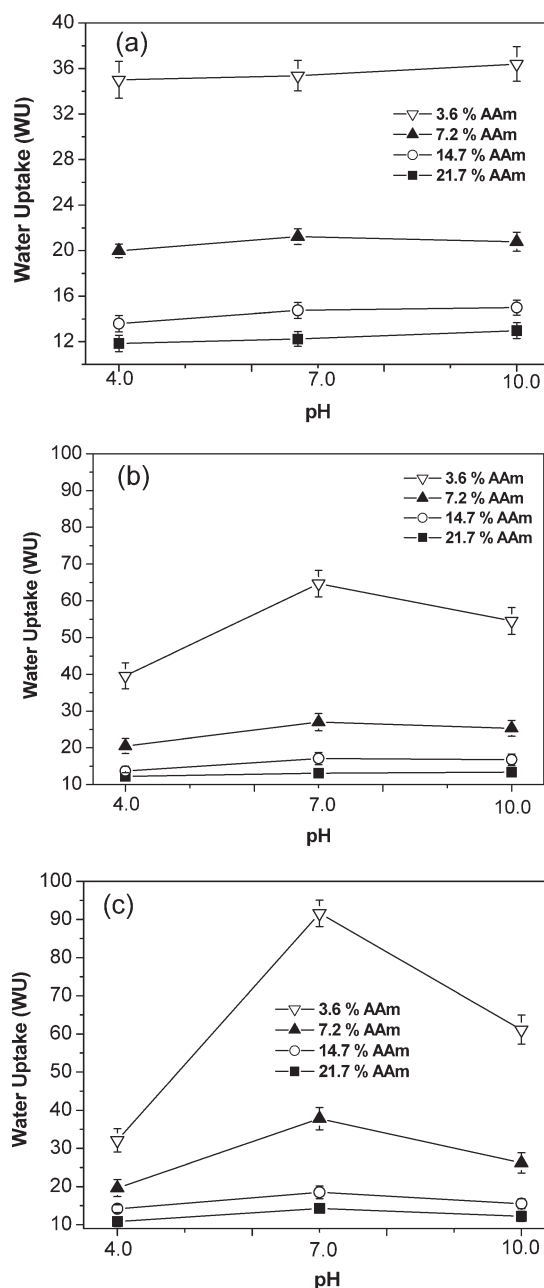


**Figure 5** Dependence of water uptake as a function of time for: (a) PAAm-MC0.5 and (b) PAAm-MC1.0, in distilled water ( $\text{pH} = 6.7$ ), at  $25.0^\circ\text{C}$ . Different concentrations of AAm were tested as indicated. Error bars represent standard deviations for the three experiments.

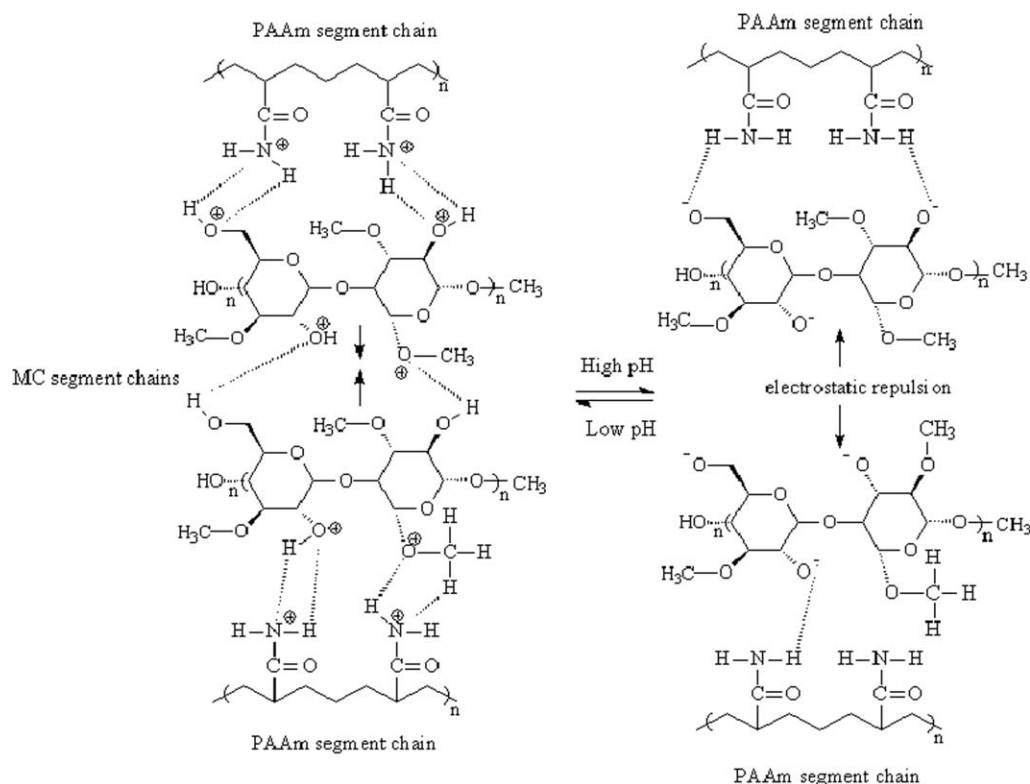


**Figure 6** Dependence of equilibrium water uptake as a function of acrylamide for PAAm, PAAm-MC0.5 and PAAm-MC1.0 hydrogels, in distilled water ( $\text{pH} = 6.7$ ), at  $25.0^\circ\text{C}$ . Error bars represent standard deviations for the three experiments.

One of the most widely studied types of responsive hydrogels is pH-responsive hydrogels. These hydrogels are swollen ionic network containing acidic or basic groups. In aqueous solution of appropriate pH and ionic strength, the groups can ionize and to develop charges on the gel.<sup>42</sup> The effect of pH on WU property of the PAAm hydrogels (without MC) is shown in Figure 7(a). The water uptake values are practically constant for any of the AAm concentrations studied, indicating that the hydrophobicity is not affected by pH environment.



**Figure 7** Dependence of equilibrium water uptake as a function of pH, at  $25.0^\circ\text{C}$ : (a) PAAm; semi-IPN hydrogels with (b) 0.5 and (c) 1.0 wt % in MC. Error bars represent standard deviations for the three experiments.



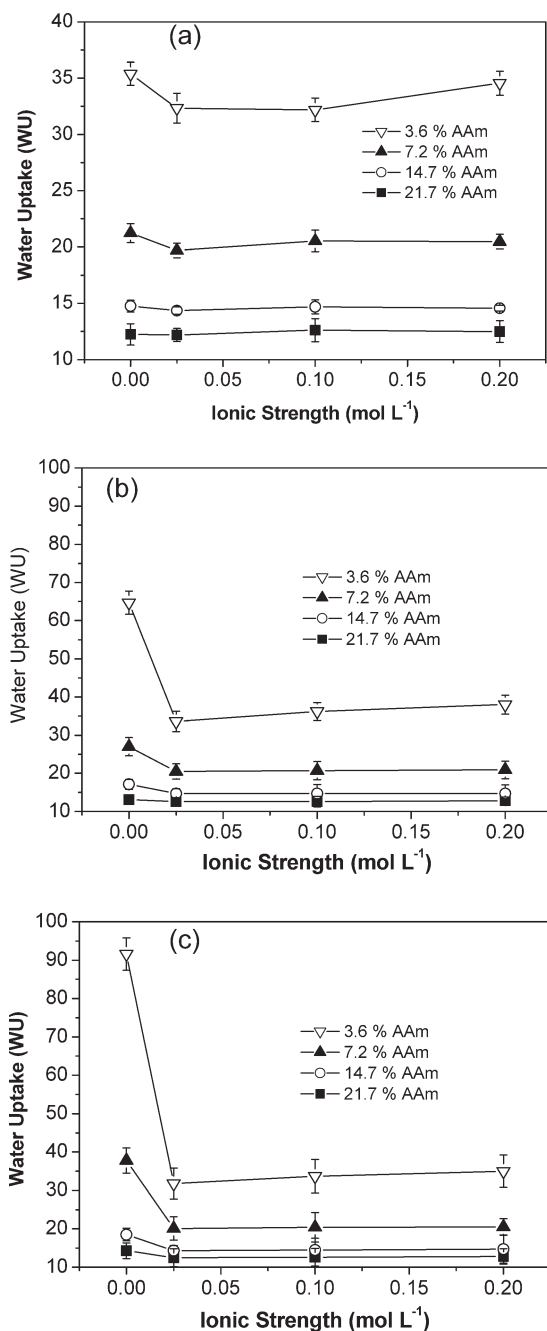
**Scheme 1** Schematic illustration of the swelling behavior of PAAm-MC hydrogel in different pH.

In contrast, as shown in Figures 7(b,c), the WU values for PAAm-MC hydrogels is strongly influenced by changes on pH of swelling medium. In the pH range from 4.0 to 7.0, the water uptake of the PAAm-MC hydrogels increase with increasing pH values. At lower pH values, a fraction of  $\text{—O}^-$  groups in MC could be protonated to  $\text{—OH}$  groups, and the hydrogen bonds between  $\text{—OH—OH}$  and  $\text{—OH—amide}$  groups (from PAAm segments) could be formed, which result in a decrease of water uptake (Scheme 1). The lower pH values of the medium, the stronger the hydrogen bonds and thus the smaller the swelling ratios of hydrogels. When pH value is increased to 7.0, the fraction of hydroxyl groups become ionized and the electrostatic repulsion between the molecular chains is predominated which leads to the network more expanding.<sup>43</sup> There exhibits a maximum water uptake ratio at pH 7.0. Beyond this value, a screening effect of the counter ions, i.e.,  $\text{Na}^+$ , shielding the charge of the hydroxyl anions may prevents from an efficient repulsion. Similar behavior were observed by Bajpai and Giri, 2002<sup>44</sup> and Chen et al. 2009.<sup>45</sup>

The increase of average pore size also corroborates this hypothesis, as early discussed in SEM section [Fig. 1(a–c)]. It should be also emphasized that the MC chains are not itself crosslinked. Thus, their polymer segments may have high mobility, leading a high water uptake.

The change on the water uptake as a function of AAm concentration for PAAm, PAAm-MC0.5, and PAAm-MC hydrogels was also analyzed in alkaline solution medium (pH = 10.0). This dependence was very similar to those obtained in distilled water; therefore their results were not shown.

The presence of ions in the swelling medium has a profound effect on the swelling behavior of the hydrogel. The underlying principal behind this ionic dependence of swelling is that it is the balance between the osmotic pressure of the swelling system and elastic response of the polymeric material that controls the extent of swelling. The osmotic pressure results from the difference between the mobile ion concentrations between the interior of the hydrogel network and the external immersion medium.<sup>19</sup> The effect of ionic strength concentration on the water uptake for PAAm hydrogels is shown in Figure 8. WU values shown in Figure 8(a) are not seriously affected by the changes on ionic strength of the swelling medium, with exception of the matrix less rigidity, i.e., 3.6 wt % AAm. On the other hand, the PAAm-MC water uptake can be controlled by varying the salt content [Fig. 8(b,c)]. The presence of salt minimizes the ion-ion electrostatic repulsion forces (Scheme 2) within the hydrogel because the ions coming from salt are more strongly solvated than the ions that are fixed to polymer chains.



**Figure 8** Dependence of equilibrium water uptake on the NaCl concentration, in distilled water (pH = 6.7) and 25.0°C: (a) PAAm; semi-IPN hydrogels with (b) 0.5 and (c) 1.0 wt % in MC. Error bars represent standard deviations for the three experiments.

From results presented in Figure 8, it was possible to determine the relative decrease of the WU ( $\Delta WU$ ) using the eq. (1):

$$\Delta WU = \frac{WU_{0.2\% \text{ NaCl}}}{WU_{0\% \text{ NaCl}}} \times 100 \quad (1)$$

where  $WU_{0.2\% \text{ NaCl}}$  and  $WU_{0\% \text{ NaCl}}$  are the swelling medium used in the water uptake measurements.

Figure 9 shows the  $\Delta WU$  as a function of acrylamide for hydrogels obtained with different methylcellulose concentrations. For the same AAm concentration, the discrepancy of the  $\Delta WU$  values between PAAm hydrogels (without MC) and PAAm hydrogels with 1.0 wt % MC is more accentuated for flexibility matrices. As the polymeric matrix becomes rigid due to the increase in the concentration of acrylamide in the hydrogels, there is a decrease in the difference between  $\Delta WU$  values between PAAm and PAAm-MC hydrogels, which is attributed to the loss of mobility of MC in the PAAm matrix.

### Diffusion studies

The water sorption process has been investigated by monitoring the change in the amount of water absorbed by the hydrogel at various time periods. For this, the swollen hydrogel was taken out at different time intervals and its weight recorded. Equation (2) was used to determine the kinetics of the swelling process,<sup>44</sup> which stands for the first 60% of fractional water uptake ( $W_t/W_\infty \leq 0.60$ ).

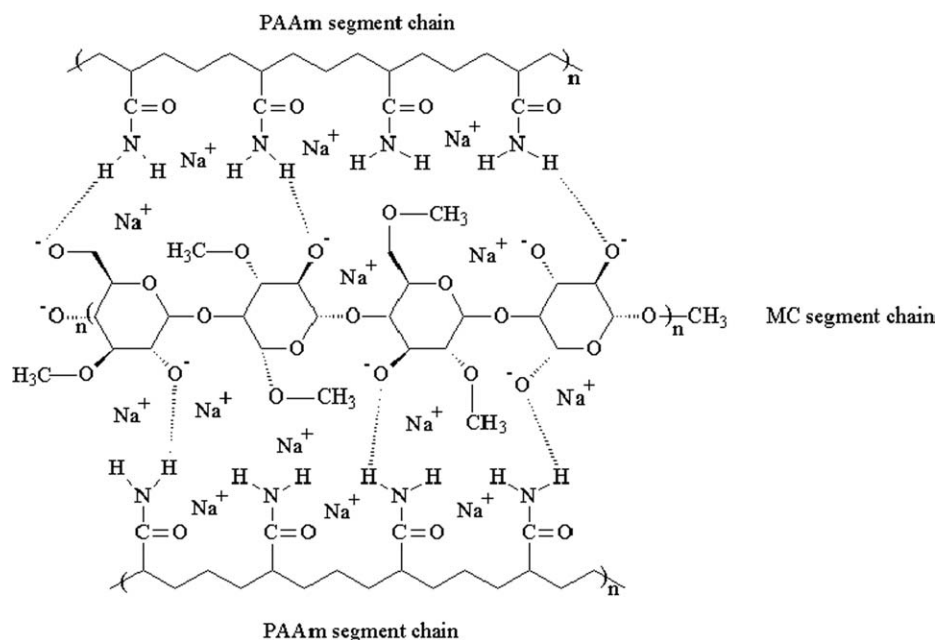
$$W_t/W_\infty = kt^n \quad (2)$$

where  $k$  is the diffusion constant,  $W_t$  and  $W_\infty$  are the water intakes at time  $t$  and equilibrium time,  $n$  is swelling exponent, which is often used to determine the transport mechanism mode.

According to the literature<sup>47</sup> for Fickian diffusion, in which the rate of diffusion of the water is rate limiting,  $n = 0.5$ . Values of  $n$  between 0.5 and 1 indicate the contribution of non-Fickian processes (anomalous processes) such as polymer relaxation. Non-Fickian or anomalous diffusion occurs when the diffusion and relaxation rates are comparable. In this condition, the process depends on two simultaneously rate processes, water migration into the beads and diffusion through continuously swelling hydrogels.<sup>48</sup>

The swelling exponent,  $n$ , and diffusion constant,  $k$ , are calculated from the slopes and intercepts of the curves obtained from eq. (2), and are given in Table II. It was found that the increase of AAm content provoked a pronounced decrease in  $n$  values for the three different pH values. Also, an increase in  $n$  constant was observed when the MC concentration was increased, for the same pH and AAm concentration. In distilled water, the  $n$  values are larger than pH 4.0 or 10.0 medium due to the minimization in the electrostatic repulsion between the polymeric chains. The water-uptake mechanism of the PAAm 7.2 and 14.7 wt % - MC 0.5 and 1.0 wt % followed the Fick's law. Hydrogels synthesized with 3.6% or





**Scheme 2** Schematic illustration of the swelling behavior of PAAm-MC hydrogel in presence of sodium salt.

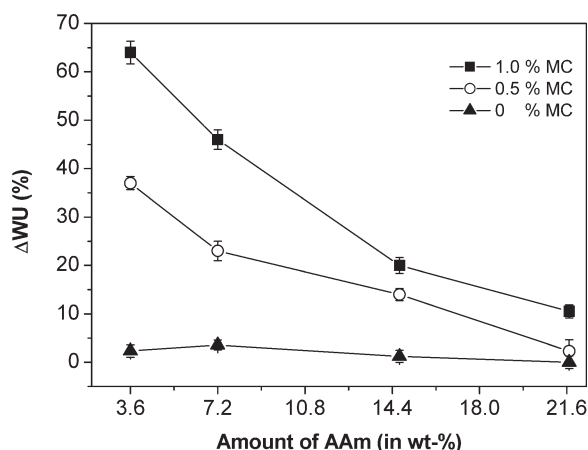
21.7 wt % in AAm concentrations followed the anomalous transport process and is mainly governed by the swelling of the hydrogel.

It can be observed that the diffusion constant was strongly dependent of AAm and MC concentration. For instance, when the AAm content was increased from 3.6 to 21.7 wt %, the  $k$  values decreased from  $0.616 \pm 0.082$  to  $0.132 \pm 0.013 \text{ s}^{-1}$  for MC = 0.5 wt %. The reduction of the  $k$  with the increase of the AAm content is related to the increased polymer density that limits its water absorption capability of the hydrogel. For PAAm-MC hydrogels with MC content of 1.0 wt %

presented practically the same kinetic behavior of water-uptake,  $k \approx 0.1 \text{ s}^{-1}$ , showing that these hydrogels reached the equilibrium in the swelling degree at the same time. This trend is related with the large number of MC hydroxyl groups.

## CONCLUSIONS

FTIR and NMR analysis confirmed the formation of semi-IPN structured hydrogel. Data from water uptake and scanning electron microscopy revealed that the addition of MC into the solution-forming hydrogel leads to increase in average pore size and hydrophilicity. By varying of AAm, MC, pH and ionic-strength of swelling medium, it was possible to obtain hydrogels with hydrophilic properties controlled and optimized for some specific application: WU values varied from 10 to 95 g/g. Kinetic properties revealed that the increase of AAm content provoked a pronounced decrease in  $n$  values. Also, an increase in  $n$  constant was observed when the MC concentration was increased, for the same pH and AAm concentration. The water uptake mechanism of the hydrogels synthesized with intermediary PAAm concentrations followed the Fickian diffusion. Already, hydrogels synthesized with highest or lowest AAm concentrations followed the anomalous transport process. The reduction of the  $k$  constant with the increase of the AAm content is related to the increased polymer density that limits its water absorption capability of the hydrogel. In this way, PAAm-MC hydrogels are promising materials for technological applications, such as agricultural field.



**Figure 9** Relative decrease of the WU ( $\Delta WU$ ) as a function of AAm concentration for hydrogel prepared with different formulations, in distilled water (pH = 6.7) and 25.0°C. Different concentrations of MC were tested as indicated. Error bars represent standard deviations for the three experiments.

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