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Swelling Behaviors of pH- and Salt-Responsive Cellulose-Based Hydrogels

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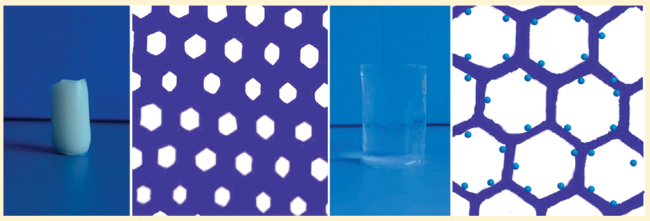
Supporting Information

ABSTRACT: Ampholytic hydrogels with pH and salt responsive properties have been synthesized by cross-linking quaternized cellulose (QC) and carboxymethyl cellulose (CMC) with epichlorohydrin (ECH) in NaOH aqueous solution. The swelling behaviors of the QC/CMC hydrogels were studied as a function of the polymer composition, pH, and salt concentration. The equilibrium swelling ratio of the hydrogel in ultrapure water strongly depended on the composition, and increased dramatically from 8.6 to 498 g/g with the change of the weight ratio of QC to CMC from 3:1 to 1:3 (w/w). The hydrogel (Gel32) consisted of QC and CMC in the ratio of 3:2 (w/w) had the minimum swelling ratio, and it was electrically neutral. The results from ξ-potential experiments were in good agreement with the theoretically calculated stoichiometry for balanced charge, confirming that the weight ratio of QC and CMC was 1.5, corresponding to Gel32. Furthermore, all hydrogels exhibited excellent pH sensitivity in the range of pH from 1 to 13 and shrunk significantly at pH 12 on the whole. The hydrogels displayed smart swelling behaviors in NaCl, $CaCl_2$, and $FeCl_3$ aqueous solutions. The results revealed that CMC mainly contributed to increasing the swelling as a result of strong water adsorption, whereas QC played a role in the controlling of the charges in the QC/CMC system, leading to the pH sensitivity.



INTRODUCTION

Responsive behavior has become a key requirement for advanced artificial materials and devices.[1] Especially, environmentally sensitive hydrogels which contain functional groups have received increasing attention in many applied scientific fields including medicine, pharmaceutics, agriculture, and material science.[2−9] The smart behavior of hydrogels is generally based on noncovalent dynamic bonding, e.g., hydrogen bonding, hydrophobic, $\pi-\pi$ stacking, and electrostatic interactions.[10−15] Depending on the backbone structure and composition, such hydrogels can be designed to respond to external stimuli such as temperature, pH, salt, light, and electric field.[16−20] The majority of the work in environmentally sensitive hydrogels has been focused on synthesized polymers. There has also been significant attention on natural polymers.[21] It is noted that the hydrogels prepared from natural polymers, such as alginate,[22] chitosan,[23,24] gelatin,[25] starch,[26] cellulose,[27] and collagen,[28] have many inherent advantages such as biodegradability, biocompatibility, and their natural abundance. As a result of their good biocompatibility, these hydrogels can be used to deliver a number of therapeutics, such as enzymes, antibacterial, antibodies, vaccines, contraceptives, and hormones.[29]

Cellulose, the most abundant resource in nature, has been chosen as a good candidate for fabricating hydrogels owing to its hydrophilicity, biodegradability, and safety. Moreover, the utilization of cellulose to prepare materials is in accord with the theme of "Chemistry for a Sustainable World" in 239th ACS National Meeting. Recently, we have developed a novel solvent for the dissolution of cellulose in a precooled (−12 °C) 7 wt % NaOH/12 wt % urea aqueous solution.[30] Moreover, a series of studies have been reported by our laboratory indicating: (1) The dissolution of cellulose in this solvent system is a "green" process.[31] (2) Macroporous hydrogels have been prepared by using cellulose as the support of pore wall and acidic polysaccharide as pore expander;[32] in particular, cellulose/CMC hydrogels have high swelling ratio in ultrapure water.[36] (3) Strong fluorescent hydrogels have been fabricated by embedding quantum dots in cellulose matrices through electrostatic attraction and hydrophobic interaction.[33] (4) By using 3-chloro-2-hydroxypropyltrimethylammonium chloride, quaternized cellulose (QC) has been synthesized in NaOH/urea systems.[34] On the other hand, Heinze et al. have reported that carboxymethyl cellulose (CMC) can be synthesized by carboxylmethylation of cellulose with sodium monochloroacetate in the same solvent system.[35] These works have indicated that novel cellulose-based smart hydrogels with pH and salt sensitivity from QC and CMC have attracted much attentions. It is well-known that hydrogel networks can be constructed by both chemical and physical cross-linking. As shown above, the NaOH/urea aqueous solution is a good homogeneous derivation system obtainable via "green" processes, and cellulose is an excellent candidate for smart materials because of the abundance of OH groups. Therefore,

Received: December 10, 2010
Revised: January 25, 2011
Published: February 23, 2011

we are interested in fabricating cellulose-based hydrogels by employing two cellulose derivatives to exploit new ways for preparing smart hydrogels by chemical cross-linking. However, ampholytic cellulose-based hydrogels have been scarcely reported. A worthwhile endeavor would be to explain why the cellulose/acidic polysaccharides hydrogels exhibit large swelling ratio, the relationship between structure and swelling properties, the influence of the two polysaccharides contents, and how to predict the formulation of smart hydrogels. In this work, a series of ampholytic hydrogels which contained both acidic ($-COO^-$) and basic groups ($-(CH_3)_3N^+$) in the polysaccharides networks were created through chemical cross-linking cellulose derivatives with epichlorohydrin (ECH), where QC and CMC were employed as the polycations and polyanions, respectively. The swelling behavior of the ampholytic hydrogels under different pH and salt concentrations were investigated to evaluate their smart behaviors. Our findings may lead to a new approach for the preparation of smart hydrogels with ampholytic character from natural polymers.

EXPERIMENTAL SECTION

Materials. The cellulose samples (cotton linter pulps) were supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). Its weight-average molecular weight (M_w) was determined by static laser light scattering (DAWN DSP, Wyatt Technology Co.) to be 9.2×10^4. Sodium carboxymethylcellulose (CMC, 2.4×10^4) was analytical-grade reagent purchased from Shanghai Chemical Agents Co. Ltd. The degree of carboxymethyl substitution (DS) is 0.7, which is the number of substituents per sugar ring. 3-Chloro-2-hydroxypropyltrimethylammonium chloride was purchased from Guofeng Fine Chemical Co. Ltd. (Shandong, China), and epichlorohydrin (ECH, Chemical Agents, Ltd. Co., Shanghai, China) (1.18 g/mL) was analytical grade.

Preparation of QC/CMC Hydrogels. Quaternized cellulose (QC) was prepared according to the previous method.[31] Its degree of substitution was determined by an elemental analyzer (CHN-O-Rapid, Hanau, Germany) to be 0.59. For the preparation of ampholytic hydrogels, QC and CMC were dissolved in 2 wt % NaOH aqueous solutions to obtain a 4 wt % polymer concentration. The QC/CMC hydrogels were prepared by dissolving QC and CMC in 2 wt % NaOH aqueous solution and cross-linking them with epichlorohydrin (ECH). By changing the weight ratio of QC to CMC by wt % of 3:1, 2:1, 3:2, 1:1, 1:2, and 1:3, the hydrogels were coded as Gel31, Gel21, Gel11, Gel12, and Gel13, respectively. ECH (1 mL) as cross-linker was added to the QC/CMC mixture (10 mL). The resulting mixtures were stirred at 25 °C for 2 h to obtain a homogeneous solution and then kept at 60 °C for 4 h to complete the reaction. The hydrogels were taken out and immersed in ultrapure water to remove the residual NaOH to obtain pure samples.

Characterization. The dried samples were analyzed in KBr disks by FTIR (Perkin-Elmer Spectrum One, Wellesley, MA) in the region of 400−4000 cm^{-1}. The liquid ^{13}C NMR spectrum of QC (or CMC)/D_2O solution was recorded on a Mercury NMR spectrometer (600 MHz) (Varian) at 20 °C, and the sample concentration was about 4 wt %. Solid-state ^{13}C NMR spectra were recorded on an Infinity Plus 400 Spectrometer (^{13}C frequency = 100.12 MHz) with a CP/MAS unit at ambient temperature. The spinning rate and the contact time were 5.0 kHz and 5.0 ms, respectively. The pulse width was 2.1 μs, spectral width 5.0 kHz, acquisition time 20.48 ms, and 2000 scans were accumulated for each spectrum.

Swelling Studies. The gravimetric method[37] was employed to measure the swelling ratios of the hydrogels in the ultrapure water, salt solution, and different pH solutions with different feed ratios. The swelling ratio of these hydrogels changed hardly with the temperature

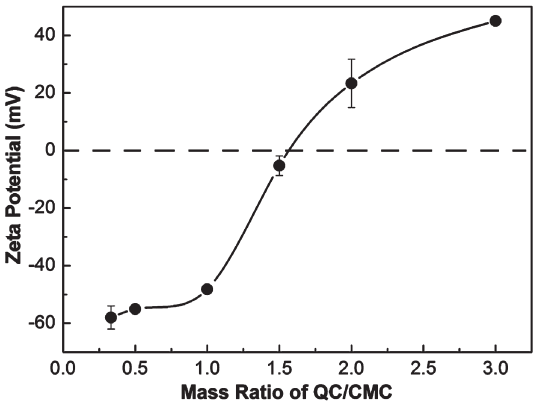


Figure 1. ζ-potential of QC/CMC solution as a function of the mass ratio of QC/CMC.

(Figure S1). The swelling temperature was set as 37 °C to simulate body temperature for exploring potential biomedical and also other applications. The pH values were adjusted by HCl and NaOH solutions, ranging from 1.01 to 13.12, which were determined by using a pH-meter (BEBCH/PHS-25, ±0.01). The ionic strength of the pH solution was 0.1 M, which was obtained by adding an appropriate amount of NaCl. The equilibrium swelling ratio (ESR) was calculated as

$$\mathrm{ESR} = W_s/W_d \quad (1)$$

where W_s is the weight of the swollen gel at 37 °C and W_d is the weight of the gel in the dry state.

The swelling kinetics of the swollen hydrogels in different salt solutions was measured gravimetrically. At predetermined time intervals, the hydrogel samples were taken out from the aqueous solution and weighed after removing the excess water on the surfaces with wet filter paper. Water retention (WR) in the hydrogel was defined as

$$\mathrm{WR} = (W_t - W_d)/W_s \times 100 \quad (2)$$

where W_t is the weight of wet hydrogel at time t and W_s is the weight of swollen hydrogel in ultrapure water. The other symbols are the same as defined above.

RESULTS AND DISCUSSION

Determination of Charge Balance Stoichiometry. Charge balance stoichiometry (CBS) of the hydrogel network was studied by both theory and experiment. At charge balance point, it should satisfy

$$Q_+ = Q_- \quad (3)$$

where Q_+ and Q_- are the number of positive and negative charges in the hydrogel network, respectively. We assume that one of the hydroxyl groups in each glucose unit of cellulose could be substituted by $-(CH_3)_3N^+$ or $-COO^-$ in QC and CMC (due to $DS < 1$), respectively. So the average mass of per glucose unit for QC ($\overline{M_q}$) and CMC ($\overline{M_c}$) can be calculated as follows:

$$\overline{M}_q = S_q M_1 + (1 - S_q) M_0 \quad (4)$$

$$\overline{M}_c = S_c M_2 + (1 - S_c) M_0 \quad (5)$$

where S_q and S_c are the DS of QC and CMC, respectively. M_1, M_2, and M_0 are the molecular masses of the glucose units substituted with quaternary ammonium, substituted with carboxymethyl group, and unsubstituted glucose unit, respectively. Therefore,

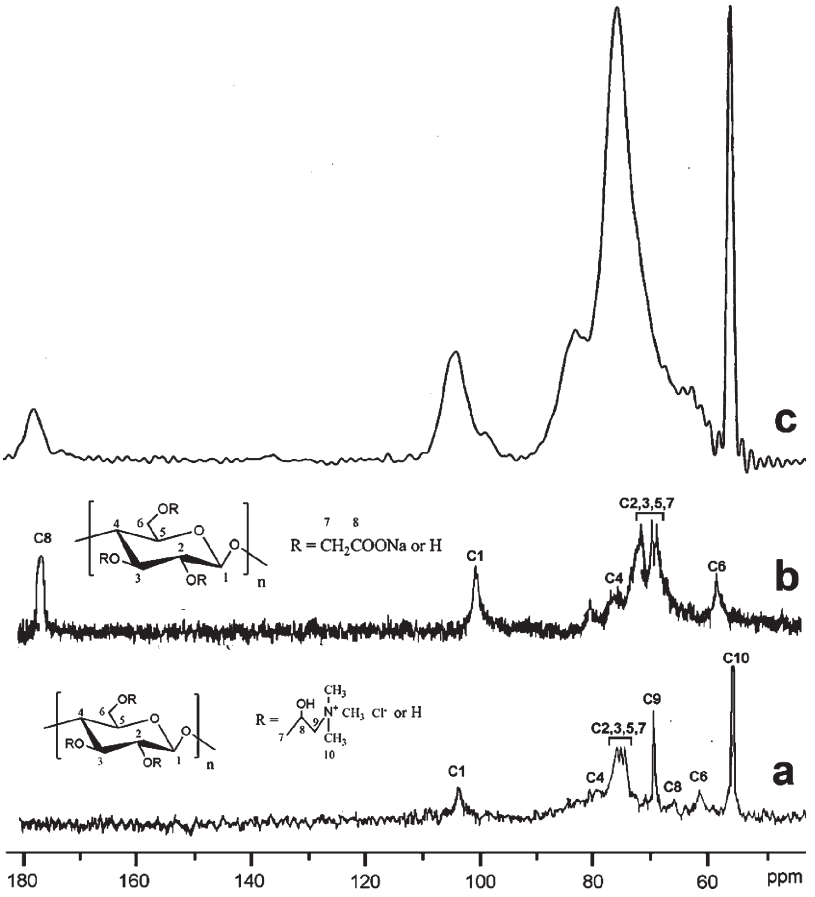


Figure 2. ^{13}C NMR spectra of QC (a) and CMC (b) in D_2O and solid-state ^{13}C NMR of Gel32 (c) at 25 °C.

the number of positive or negative charges in the hydrogel network is given by

$$Q_+ = \frac{m_q}{n_q \overline{M}_q} N_A n_q S_q \quad (6)$$

$$Q_- = \frac{m_c}{n_c \overline{M}_c} N_A n_c S_c \quad (7)$$

where m_q and m_c are the mass of QC and CMC to prepare hydrogel, respectively. n_q and n_c are the number of glucose units in QC and CMC, respectively. N_A is Avogadro's number. Finally, the mass ratio of QC and CMC (m_q/m_c) was determined to be 1.5 when the system reached charge balance ($Q_+ = Q_-$).

To verify the result of the above theory, the ζ-potential of the mixed systems by blending QC and CMC solution as a function of their mass ratio is shown in Figure 1. The ζ-potential of QC/CMC increased from −58 to 45 mV with the increase of the QC/CMC mass ratio. The least absolute value of ζ-potential was observed to be −5.8 mV, when the QC/CMC mass ratio was 1.5:1. This result was in good agreement with the charge balance which was obtained by theoretical calculations (m_q/m_c = 1.5). It was demonstrated that Gel32 corresponding to composite of QC:CMC = 3:2 was electrically neutral.

Structure of QC/CMC Hydrogels. The etherification of cellulose-based polyelectrolyte and cross-linker created a complex network containing the $-(CH_3)_3N^+$ and $-COO^-$ groups on the cellulose chains with the same backbone in the QC/CMC hydrogels. To determine the structures of QC, CMC, and the hydrogel networks, ^{13}C NMR and FTIR spectra were obtained.

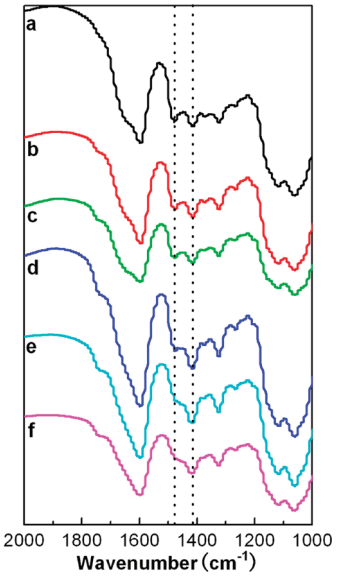


Figure 3. FTIR spectra of QC/CMC hydrogels: (a) Gel31, (b) Gel21, (c) Gel32, (d) Gel11, (e) Gel12, and (f) Gel13.

Figure 2 shows the ^{13}C NMR spectra of QC, CMC, and Gel32. In Figure 2a, the typical signal of the $-(CH_3)_3N^+$ groups appeared at 55.1 ppm, and the signals at 104.1, 80.3, 69.9, 65.9, and 62.0 ppm can be attributed to the chemical shifts of C1, C4,

C9, C8, and C6, respectively. Three peaks around 75.0 ppm is the overlapping signals of C2, C3, C5, and C7. It was thus revealed that QC was successfully fabricated, and its structure was similar to our previous works.[34] For CMC, the sharp peak at 174.2 ppm was attributed to the carboxyl carbons, indicating the presence of carboxymethyl groups on the CMC (see Figure 2b). These characteristic peaks of QC and CMC, such as 178.3 ppm for C8′ and 55.8 ppm for C10, could be observed in the solid-state ^{13}C NMR spectrum of Gel32, as shown in Figure 2c. It indicated that hydrogels were constructed by combining QC and CMC by cross-linking with ECH.

FTIR spectra can be used to monitor the change of the chemical composition in the hydrogel networks (Figure 3). The peak at 1482 cm^{-1} can be attributed to the methyl groups of ammonium (Figure 3a), indicating that the presence of QC in hydrogel networks. However, it disappeared in the spectra of hydrogel networks with lower QC contents (see Figure 3e,f), whereas strong peaks appeared at 1420 cm^{-1}. This confirmed the presence of COO^- groups in CMC.[24] In view of these results, $-(CH_3)_3N^+$ groups of QC, COO^- groups of CMC, and signals of other carbons could be observed in the Gel32, indicating that ampholytic hydrogels based on QC and CMC were successfully fabricated.

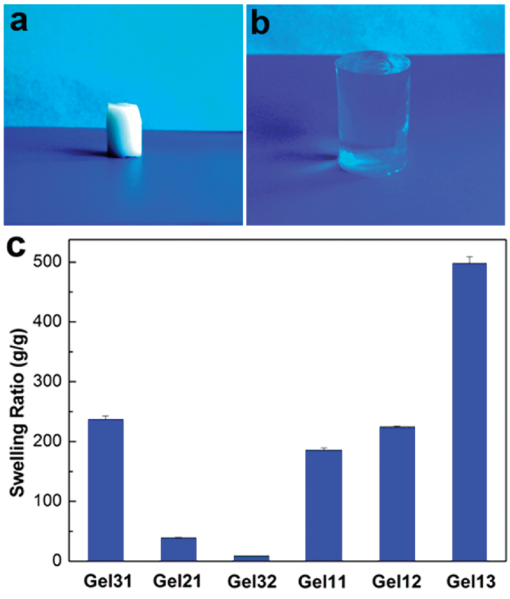


Figure 4. Photographs of Gel32 (a) and Gel21 (b) and equilibrium swelling ratio of the QC/CMC hydrogels after immersing in ultrapure water as a function of the composition of CMC and QC at 37 °C (c).

Effect of Chemical Composition on the Swelling Ratio. As in all polyelectrolyte gels, swelling resulted from the competition between the Donnan osmotic pressure and the elasticity of the gel network. The osmotic pressure increased monotonically with the number of molecules and/or bound charges but began to decrease at high ionic strengths.[38,39] The swelling ratio of hydrogels usually depends on the chemical composition of the hydrogels.[40] As mentioned above, the charge balance stoichiometry was determined to be m_q/m_c = 1.5 by both theory and by experimental data. The photographs of Gel32 and Gel12 are shown in Figure 4a,b.

The appearance of Gel32 (m_q/m_c = 1.5) was opaque and smaller in comparison with Gel12, which was transparent and swollen. Usually, hydrogels swell because of the presence of osmotic pressure, which is resulted from a difference in the concentrations of the mobile ions between the interior of the hydrogel and the exterior solution. For Gel32, the number of positive charge was equal to that of negative charge in the hydrogel as shown in Figure 1, and the strong electrostatic interaction between $-COO^-$ and $-(CH_3)_3N^+$ on polysaccharide backbone led to the dense structure and the more compact appearance. In Gel12, the number of negative charges exceeded that of the positive charges in the hydrogel, and the networks were expanded as a result of the electrostatic repulsions between excess COO^- groups on the networks backbone. Therefore, Gel12 exhibited transparent properties and high swelling ratio. These QC/CMC hydrogels could not be dissolved in water or organic solvents because of the presence of chemical cross-linking in the hydrogel networks.

Furthermore, the influence of QC/CMC mass ratio on the swelling ratio of QC/CMC hydrogel was also investigated. Figure 4c shows the equilibrium swelling ratio (ESR) of the QC/CMC hydrogels after immersing in ultrapure water as a function of the compositions of QC and CMC at 37 °C. The electrostatic force between unbound fixed charges made a contribution to the expansion (or swelling) of the hydrogels, and the number of unbound fixed charges in the hydrogel network (charge density) played an important role in the swelling ratio of hydrogels. Therefore, the ESR values of hydrogels were found in the following order: Gel13 > Gel31 > Gel12 >

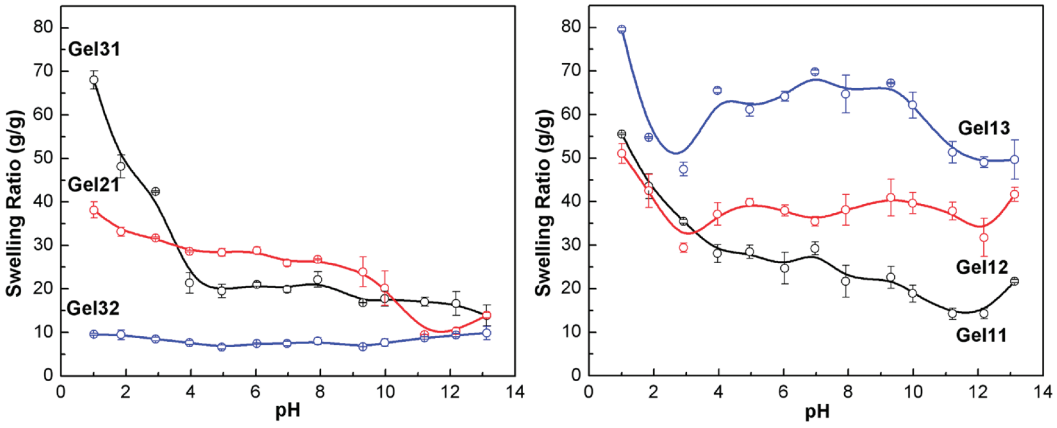


Figure 5. Effects of pH on the swelling behaviors of QC/CMC hydrogels in buffer solutions.

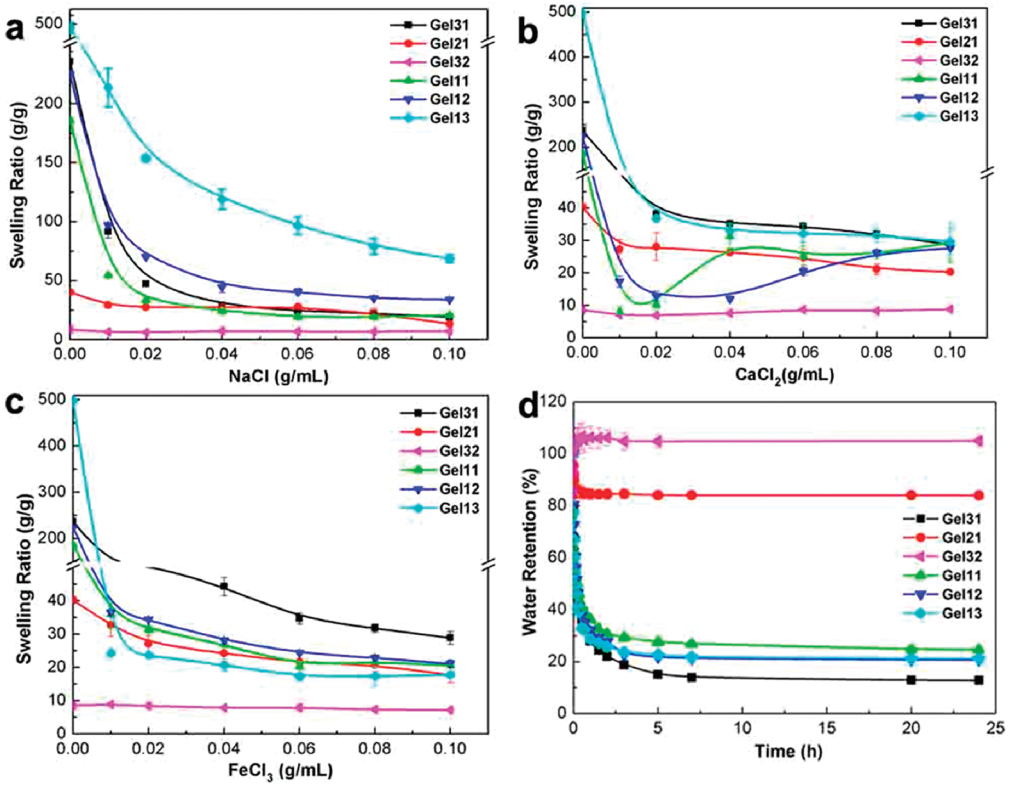


Figure 6. Swelling ratio of QC/CMC hydrogels in NaCl solution (a), $CaCl_2$ solution (b), $FeCl_3$ solution (c), and water retentions of QC/CMC hydrogels in physical saline water (d).

Gel11 > Gel21 > Gel32, which was in agreement with the number of unbound fixed charges of hydrogels. Clearly, the ESR values of the hydrogels in ultrapure water was strongly dependent on the composition and increased dramatically from 8.6 to 498 g/g within the range of the weight ratio of QC to CMC from 3:1 to 1:3. The CMC in the hydrogel contributed mainly to increasing the swelling as a result of the high absorbability of water.[36]

pH Sensitivity. The swelling behavior of hydrogels, usually, is sensitive to ionic strength.[35] In our findings, ionic strength of various pH solutions was controlled to be 0.1 M by adjusting NaCl content. Figure 5 shows the effects of pH on the swelling behaviors of the QC/CMC hydrogels. All hydrogels exhibited lower swelling ratio in buffers with 0.1 M ionic strength in comparison with that in ultrapure water.

Six samples of the QC/CMC hydrogels exhibited clearly pH sensitive behavior in buffers, i.e. significant swelling at pH = 1 and shrinking at pH = 12. Gel31 had the maximum swelling ratio at pH 1. It can be postulated that the QC chains having unbounded fixed positive charges in the hydrogel networks expanded at low pH due to the strong electrostatic repulsion between $-(CH_3)_3N^+$ groups in acidic medium. The swelling ratio of Gel31 decreased sharply with increasing pH from 1 to 13, owing to the positive charges in hydrogel networks being screened in the basic region, leading to the shrinking of hydrogel. Therefore, QC in the hydrogels played an important role in the domination of the amount of charges, leading to the high pH sensitivity. However, the electrostatic repulsion was clearly weakened when the QC content decreased, leading to the low swelling ratio of Gel32 (Figure 5, left). It can be explained that at m_q/m_c = 1.5 the charge stoichiometry is balanced, and the electrostatic screen effect dominated in the

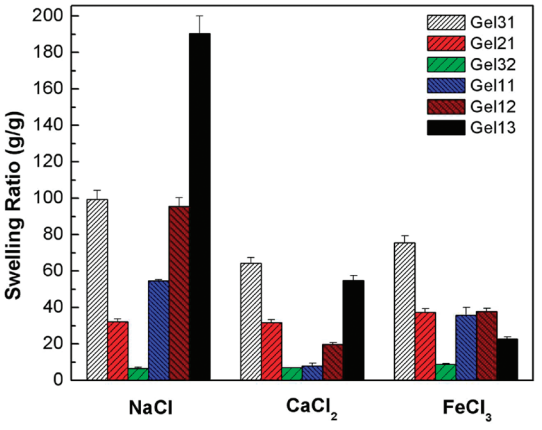


Figure 7. Swelling ratio of hydrogels in different salt solutions (0.01 M): NaCl, $CaCl_2$, and $FeCl_3$.

network, as a result of the electrostatic bonding between $-COO^-$ and $-(CH_3)_3N^+$.

Interestingly, Gel13 with the highest CMC content exhibited relatively low dependence of swelling ratio on pH and increased slightly in the range from pH 6 to pH 8 (Figure 5, right). This could be attributed to the contribution from the highly hydrophilic CMC to the high swelling ratio of the QC/CMC hydrogels.[36] Moreover, there were a number of bound water molecules attached on the CMC chains, which prevented the shrinking of the hydrogels. In view of these results, the electrostatic repulsion between the hydrogel backbone ($-(CH_3)_3N^+/-COO^-$) and the pH solution (H^+/OH^-), the electrostatic repulsion among cellulose chains, electrostatic screening between the

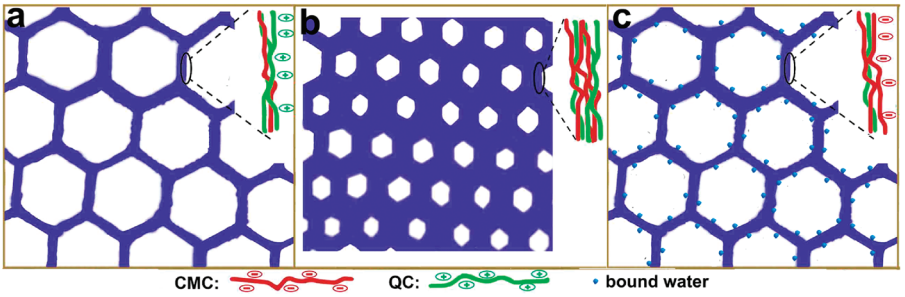


Figure 8. Schematic illustrations of the structures of QC/CMC hydrogels: (a) Gel31, (b) Gel32, and (c) Gel13.

hydrogel backbone and the pH solution, and electrostatic screening of the $-(CH_3)_3N^+$ and $-COO^-$ groups led to the pH responses of the hydrogels. The increase in the solution pH induced deprotonation of the ionizable functional groups bound onto the polymeric network, causing the increase in the osmotic pressure and thus enhancing the hydration of the hydrogel.[41] In the complex system, an increase of $-(CH_3)_3N^+$ group conversion to $-(CH_3)_3NOH$ groups could decrease the swelling ratio of hydrogel at pH 12.[42] Therefore, QC, known as strong polyelectrolyte, played an important role in the pH sensitivity of hydrogels, whereas CMC mainly contributed to the increasing of the equilibrium swelling ratio of the hydogels.

Salt Sensitivity. In general, the salt sensitive hydrogel consists of three phases, namely the three-dimensional polymeric network matrix, the interstitial fluid, and the ionic species.[43] The swelling behavior of the QC/CMC hydrogels in various salt solutions with different concentrations is shown in Figure 6.

In NaCl, $CaCl_2$, and $FeCl_3$ solutions, the swelling ratio of all hydrogel samples mostly decreased with the increase of the salt concentration. The swelling and shrinking behaviors of hydrogels in salt solution can be determined by the ionic interactions between mobile ions and the fixed charges which make great contributions to the osmotic pressure between the interior hydrogel and the external solution.[44] In higher Na^+ concentrations, the gels began to shrink because of the decrease in the Donnan osmotic pressure. Moreover, the QC/CMC hydrogels with different chemical composition exhibited different shrinking behavior, which can be attributed to the charge density in the hydrogel networks.

The swelling ratio of Gel13 exhibited sharp decrease with an increase of salt concentration in $CaCl_2$ and $FeCl_3$ solution, as shown in Figure 6b,c. The results indicated that the swelling ratio of hydrogels in salt solution depended on not only the salt concentration but also the ionic charge. Under the presence of excess salt, the counterion contribution to the osmotic pressure increased with the increasing of the ionic charge ($Fe^{3+} > Ca^{2+} > Na^+$).[45] However, the swelling ratio of the hydrogel samples were different in different salt solution. Figure 7 shows the swelling ratio of the hydrogels with different weight ratio of the components in various salt solutions (0.01 M). The shrinking trend of Gel13 increased with the increasing of ionic charge, and the swelling ratio depended significantly on the ionic species, indicating maximum swelling ratio in NaCl solution and minimum value in $FeCl_3$. However, the ionic species exhibited very small influence on the swelling ratio for Gel21 and Gel 32. On the other hand, Gel 31, Gel 11, and Gel 12 displayed the minimum swelling ratio in $CaCl_2$ solution. Therefore, the hydrogel had smart swelling behaviors in NaCl, $CaCl_2$, and $FeCl_3$ aqueous solutions.

Furthermore, the swelling kinetic of QC/CMC hydrogels in physical saline water is shown in Figure 6d. All of the swollen hydrogels displayed fast responsive properties once transferred into physical saline water and reached equilibrium within 5 h. The water retention of the hydrogels were 15%, 22%, 23%, 28%, and 84% for Gel31, Gel12, Gel13, Gel11, and Gel21, respectively. These hydrogels revealed shrinking behavior with different water retention. The osmotic pressure increased monotonically with the number of bound charges but began to decrease at high ionic strengths.[46,47] However, Gel32 showed a rather unique swelling behavior in physical saline water; namely, the water retention increased slightly with the increase of immersing time and then reached equilibrium value of about 105%. The association of QC and CMC by electrostatic force was weakened in physical saline water, leading to the increase of bound water on CMC backbone. This could explain the above observation. From the above results, these QC/CMC hydrogels had pH- and salt-sensitive properties. However, the swelling ratios of hydrogels were not dependent on the temperature (Figure 1S); namely these hydrogels were not temperature sensitive.

Effect of Structure on Swelling Behavior. Generally, the expansion of the ionic hydrogel is related to a balance between the osmotic pressure (driven by ions inside and outside the hydrogel), polymer−solvent interactions, and the elastic retractile force of the polymer.[48] In view of the above results, the schematic structures of QC/CMC hydrogels with different chemical composition are proposed in Figure 8.

The osmotic pressure in the gels of polyelectrolyte and the repulsive force between fixed charges play an important role in the expansion of the hydrogel.[49] On the basis of the results in Figure 4, Gel31 had relatively higher swelling ratio as a result of the excess positive charges fixed in the hydrogel networks. When the number of fixed positive charges was equal to that of fixed negative charges in the hydrogel, strong electrostatic attractions formed in the hydrogel networks, leading to the decrease of water amount bound by hydrogen bonds and resulting in a dense network. Gel32 had minimum swelling ratio due to the absence of free charges in the hydrogel network (Figure 8b). However, excess negative charges were fixed in the network of Gel 13 (Figure 8c), leading to an expandable structure, which can more easily absorb and bind water. Therefore, Gel13 exhibited an expandable structure and did not change significantly with an increase in pH.

■ CONCLUSION

A series of ampholytic hydrogels through chemical cross-linking were prepared successfully from two cellulose-based polyelectrolytes (QC and CMC). The swelling ratios of these QC/CMC

hydrogels changed dramatically from 8.6 to 498 g/g, depending on the chemical composition of QC and CMC. Therefore, ampholytic hydrogels with required swelling ratio could be obtained by fine-tuning the mass ratio of QC and CMC. These hydrogels exhibited multiple responsive behaviors, including pH and salt. QC in the Gel31with high QC content contributed to pH sensitivity, and the swelling ratio decreased sharply at pH 13. CMC in the hydrogels with high CMC content contributed to the expansion of the hydrogel network, and the swelling ratio changed slightly in different pH solutions. Furthermore, these QC/CMC hydrogels exhibited smart swelling behaviors in NaCl, $CaCl_2$, and $FeCl_3$ aqueous solutions, and their swelling ratio decreased with an increase of the salt concentration on the whole. These smart hydrogels from cellulose will have wide applications in the fields of agriculture, foods, tissue engineering, and drug delivery.

■ ASSOCIATED CONTENT

Supporting Information. Effect of temperature on the swelling behavior of the hydrogels. The material is available free of charge via Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by National Basic Research Program of China (973 Program, 2010CB732203), National Supporting Project for Science and Technology (2006BAF02A09), and the National Natural Science Foundation of China (20874079). We acknowledge the Center of Nanoscience and Nanotechnology and the Center for Electron Microscope of Wuhan University for their technical support.

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