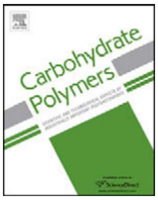
Carbohydrate Polymers 86 (2011) 171–176

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Alkaline hydrolysis and flocculation properties of acrylamide-modified cellulose polyelectrolytes

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ARTICLE INFO

Article history:
Received 2 December 2010
Received in revised form 30 March 2011
Accepted 13 April 2011
Available online 21 April 2011

Keywords:
Cellulose
Polyelectrolytes
Acrylamide
Hydrolysis
Flocculation

ABSTRACT

By controlling the saponification hydrolysis of acylamino groups to carboxyl groups in alkaline medium, a series of acrylamide-modified cellulose polyelectrolyte (AMC) samples with various degree of hydrolysis (DH) were successfully obtained. The structure and solution properties of AMC were characterized by using elemental analysis, FT-IR, ^{13}C NMR, viscometer, and zeta potential measurement. The results revealed that DH value of AMC samples could be controlled by adjusting the hydrolysis reaction time. The carboxyl group content and intrinsic viscosity ($[\eta]$) value increased with increasing DH value. Moreover, ferric hydroxide ($Fe(OH)_3$) colloid was selected as a model to evaluate the flocculation properties of AMC. The results showed that AMC was an effective flocculant to $Fe(OH)_3$ colloid, and the $Fe(OH)_3$ colloid was almost removed (up to nearly 100%). Therefore, acrylamide-modified celluloses are applicable as novel flocculants with high flocculation efficiency, non-toxicity as well as biodegradability.

1. Introduction

Flocculation has been the well-known simple, cheap and effective technique in solid/liquid separation (Boltoa & Gregory, 2007), and been employed in a wide range of applications in both wastewater treatment and industrial processes, such as water treatment, paper manufacturing, food processing, and agriculture (Bratby, 2006; Krentz et al., 2006; Sabah & Cengiz, 2004; Sableviciene, Klimaviciute, Bendoraitiene, & Zemaitaitis, 2005). Flocculation processes can bring the smaller colloidal particles together to form larger floes, which may cause significant changes in the colloidal stability and facilitate the removal of suspended solids and colloids (Pal, Sen, Karmakar, Mal, & Singh, 2008). The efficient flocculants play the dominant role in the flocculation processes. Nowadays, various anionic, cationic and nonionic flocculants have been increasingly utilized for the treatment of water and wastewater in industrial processes. Anionic polyelectrolyte flocculants are generally used in industry (Aly, 2006; Khalil & Aly, 2002), and are very useful for sedimentation of copper flotation tailings, fine clay particles, waste water of porcelain manufacture, phosphatic clay waste, selective flocculation for dolomite–apatite system, and cane mud flocculation (Abd-El Rahman, 2000; Aly, 2006; Besra, Sengupta, Roy, & Ay, 2003; Khalil & Aly, 2002). Anionic polyelectrolyte flocculants have been prepared via polymerization of acrylic acid or copolymerization of acrylamide with comonomers bearing acidic groups (Liu, Wang, & Hua, 2000).

Among various anionic flocculants, partially hydrolyzed polyacrylamide (HPAM) is the most prevalent one due to its outstanding properties, practical applications, and important roles (Feng et al., 2005; Xin, Xu, Gong, Bai, & Tan, 2008). HPAM molecules have the extended conformation in aqueous solution attributing to the charge repulsion produced by the charged carboxyl groups, which facilitates polymer bridging of the primary amide ($-CONH_2$) functional groups (Hogg, 2000; Rivas, Pereira, & Maureira, 2009; Yu, Liu, & Chen, 2000). As a result, HPAM is one of the most efficient flocculants with excellent flocculation property. However, HPAM shows poor biodegradability and the residual toxic monomers may cause potential health impacts (e.g., carcinogenic effects) (Roussy, Van Vooren, Dempsey, & Guibal, 2005). Therefore, the use of HPAM flocculants is questionable in water treatment and will be strictly prohibited in many countries. For example in Japan, even where the research on preparation and application of the polyacrylamide-based flocculants are relatively mature, HPAM is seldom used as flocculants in the treatment of pipe-water (Semsar, Scholz, & Kulicke, 2007).

With the increasing demand for environmentally friendly and healthy technologies, natural polysaccharides have been researched widely in order to replace synthetic polymer flocculants and have become more popular in water treatment (Mishra & Bajpai, 2006). Polysaccharides are by far the most abundant renewable resource on the earth, and are expected to play an increasingly important role in, for example, industrial, biochemical, and medical fields with decreasing supply of

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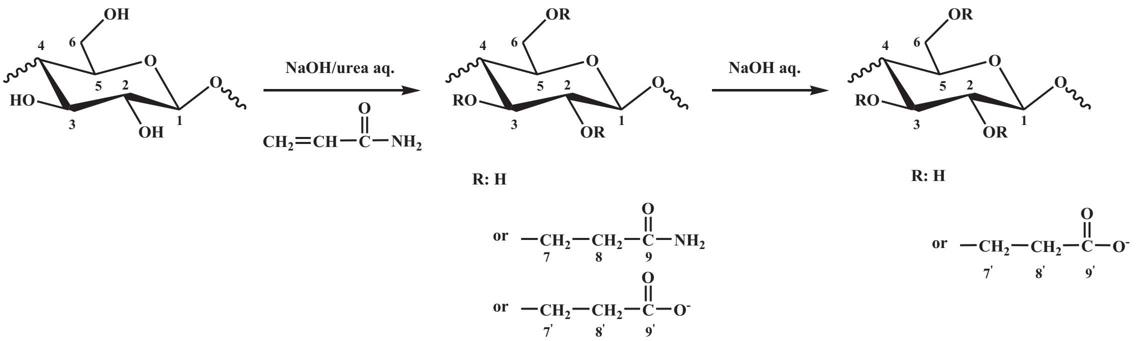
doi:10.1016/j.carbpol.2011.04.025



Scheme 1. Synthesis and hydrolysis of AMC in alkaline aqueous medium.

oil resources (Dumitriu, 1998). Moreover, it is well known that polysaccharides such as chitin and starch, and their derivatives (chitosan, cyclodextrin) containing required functional groups, have received increasing attention in water and wastewater treatment in recent years. Resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains, these biopolymers represent an interesting and attractive alternative as potential flocculants, because of their particular structure, physicochemical characteristics, chemical stability, and excellent capacity to associate by physical and chemical interactions with a wide variety of molecules (Crini, 2005). During the past several years, a variety of flocculants have been developed on the basis of polysaccharides, including cationic, non-ionic and anionic modification of different polysaccharides (Boltoa & Gregory, 2007). It has been found that these polysaccharide-based flocculants provide comparatively higher flocculation efficiency than many commercially available synthesized flocculants (Pal et al., 2008).

As we know, cellulose is the most abundant natural polymer available today worldwide and can be a primary chemical resource in the future. Moreover, cellulose is biodegradable and usually safe for human health (Klemm, Heublein, Fink, & Bohn, 2005; Liu et al., 2008). So the modification and utilization of cellulose as flocculants in water is of important significance (Song, Zhang, Gan, Zhou, & Zhang, 2010). In our previous works (Song, Zhou, Li, Lue, & Zhang, 2009; Song, Zhou, Zhang, & Wu, 2008), based on the Michael addition and the saponification hydrolysis of acylamino groups to carboxyl groups in alkaline medium (Scheme 1), we synthesized acrylamide-modified cellulose (AMC) polyelectrolytes homogeneously in NaOH/urea aqueous solutions successfully. AMC contains acylamino and carboxyl groups simultaneously, which is similar with the structure of HPAM. In this study, we obtained a series of AMC samples with various degree of hydrolysis (DH) value by controlling the hydrolysis of acylamino groups in alkaline medium successfully. The structure and solution properties of AMC were characterized. Moreover, AMC were studied as flocculants in colloid particles separation. $Fe(OH)_3$ was selected as a model colloid particle. We suppose to develop a novel water treatment agent with high flocculation efficiency, non-toxicity as well as biodegradability.

2. Experimental

2.1. Materials

The cellulose (cotton linter pulp) was supplied by Hubei Chemical Fiber Group Ltd. (Xiangfan, China), and the viscosity-average molecular weight (M_η) of the cellulose was determined by viscometry in cadoxen (Brown & Wiskstön, 1965) to be 10.3×10^4 g/mol. Acrylamide and other reagents were of analytical grade and were used without further purification.

2.2. Synthesis and hydrolysis of AMC

AMC-0 sample was prepared according to our previous work (Song et al., 2009; Song et al., 2008). Briefly, cellulose was dissolved in NaOH/urea aqueous solutions to obtain a transparent solution (4 wt%), then a certain amount of acrylamide aqueous solution was added drop-wise into the cellulose solution, and the mixture was stirred for 6 h at 25 °C. The reaction product was neutralized to weak alkaline with acetic acid, dialyzed and freeze-dried to obtain AMC-0 derivative.

NaOH aqueous solution (4 M, 100 mL) was added into AMC-0 aqueous solution (2 wt%, 100 g), and the mixture was stirred at 25 °C for 1, 2, 6, and 12 h, respectively. The hydrolysis products were neutralized to weak alkaline with acetic acid, dialyzed and freeze-dried, coded as AMC-1, AMC-2, AMC-6, and AMC-12, respectively.

2.3. Characterization of AMC

FT-IR spectra of AMC samples were performed with a Nicolet 170SX Fourier transform infrared spectrometer. The test specimens were prepared by the KBr-disk method. ^{13}C NMR measurements of AMC samples in D_2O at 25 °C were carried on a Varian INOVA-600 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe at ambient temperature, and the sample concentration was about 3.5 wt%. The chemical shifts were referenced to the signals of D_2O and tetramethylsilane (TMS). Nitrogen contents (N %) of AMC samples were measured with an elemental analyzer (CHN-O-Rapid, Foss Hera us GmbH, Hanau, Germany).

The zeta potential of AMC samples in distilled water ($c_{polymer} = 1$ mg/mL) was performed on a Malvern Zetasizer (Malvern Instruments, UK) at 25 ± 0.1 °C. The viscosity of AMC samples was measured at 25 ± 0.1 °C with an Ubbelodhe capillary viscometer. The kinetic energy correction was always negligible. The intrinsic viscosity ($[\eta]$) of AMC in water was obtained by Fuoss–Strauss equation (Fuoss & Strauss, 1948). Huggins equation was used to estimate $[\eta]$ of AMC in 0.15 M NaCl aqueous solution (Huggins, 1942).

2.4. Flocculation of ferric hydroxide ($Fe(OH)_3$) colloid

Saturated ferric chloride solution was added drop-wise into boiling water to obtain the $Fe(OH)_3$ colloid. 10–400 μL of AMC aqueous solution (1.0 wt%) was added into 7 mL of $Fe(OH)_3$ colloid, respectively. Then the mixture was vortexed for 30 s and allowed to stand for 30 min at room temperature. The transmittance of clarified layer was measured before flocculation and after flocculation at the end of the settling period with a spectrophotometer (UV-160A, Shimadzu, Japan) at 500 nm, respectively. Distilled water served as a reference.

Table 1
Hydrolysis conditions and results of AMC samples.

Sample	Time (h)	N %	Degree of substitution[a]			DH_N [b] (%)	DH_{NMR} [c] (%)
			DS_{Total}	$DS_{Acylamino}$	$DS_{Carboxyl}$		
AMC-0	0	3.529	0.67	0.54	0.13	20.0	20.0
AMC-1	1	2.647	0.67	0.41	0.26	39.1	36.0
AMC-2	2	2.159	0.67	0.34	0.34	50.0	51.7
AMC-6	6	1.617	0.67	0.25	0.42	62.2	62.1
AMC-12	12	0	0.67	0	0.67	100	100

[a] calculated from nitrogen content and ^{13}C NMR.
[b] calculated from $DS_{Carboxyl}/DS_{Total}$.
[c] determined by ^{13}C NMR of the AMC samples.

3. Results and discussion

3.1. Alkaline hydrolysis of AMC

The hydrolysis reaction conditions and results of AMC samples are summarized in Table 1. The hydrolysis reaction time was kept for 0, 1, 2, 6, and 12 h, respectively. At the same time, the N content of AMC sample was 3.529%, 2.647%, 2.159%, 1.617%, and 0, respectively. It can be seen that with increasing of the hydrolysis reaction time, the N content of AMC decreased gradually, which corresponded to the gradual hydrolysis of AMC in NaOH aqueous solution (Scheme 1). When the hydrolysis time increased up to 12 h, the N content of AMC-12 reduced to 0, meaning that the acylamino groups of AMC had been hydrolyzed to be carboxyl groups completely.

It is well known that the alkaline hydrolysis of PAM could not proceed completely. Especially under mild alkaline conditions, the hydrolysis of PAM almost ceases near 40–50% conversion attributing to the pronounced retardation. The retardation is usually interpreted in terms of the nearest neighbor effect due to the electrostatic repulsion between –COO$^-$ groups formed and the electrostatic field of remote units (Kudryavtsev, Litmanovich, & Platé, 1998). However in contrast, in our study herein, the alkaline hydrolysis of AMC was not retarded apparently in comparison with that of PAM. We speculate that the saccharide ring chains of AMC (Scheme 1) may play an important role in the hydrolysis to weaken the nearest neighbor effect and result in the complete hydrolysis of acylamino groups.

3.2. Structure analysis

Fig. 1 displays the FT-IR spectra of the AMC samples. The peak at 1670 cm^{-1} of the spectra represents acylamino (–CONH$_2$) groups. The peak at 1570 cm^{-1} observed was due to the asymmetrical stretching of carboxyl (–COO$^-$) groups (Song et al., 2008). Comparing the relative intensity at 1570 cm^{-1} and 1670 cm^{-1}, we can see that the intensity at 1570 cm^{-1} apparently increased from AMC-0 to AMC-12 gradually, while intensity at 1670 cm^{-1} apparently decreased simultaneously, indicating an increase in the hydrolysis of acylamino groups. The FT-IR spectra also clarified the hydrolysis of acylamino groups.

The ^{13}C NMR spectra of AMC samples in D$_2$O at 25 °C are shown in Fig. 2. The peaks at about 177.5 and 180 ppm corresponded to the carbon signal of carbonyl groups in acylamino (C-9) and carboxyl (C-9′) groups, respectively (Song et al., 2008). The peak at 36 ppm was assigned to methylene carbon connected to acylamino groups (C-8). The signal of methylene carbon connected to carboxyl groups (C-8′) appeared at 38 ppm. The peaks attributed to other methylene carbon (C-7 and C-7′) of the substituents were overlapped by the chemical shift of cellulose AGU signals between 60 and 103 ppm. The DH value of AMC samples ($DS_{Carboxyl}/DS_{Total}$) could be obtained according to the peak intensity of the two carbonyl peaks (C-9 and C-9′) or the methylene peaks that connected to carbonyl groups (C-8 and C-8′). The results (DH_{NMR}, obtained according to NMR) are summarized in Table 1. Obviously, with increasing of the hydrolysis reaction time, the peak intensity of C-9′ and C-8′ increased, while those of C-9 and C-8 decreased. Especially when the hydrolysis time increased to 12 h, the peak of C-9 and C-8 disappeared, suggesting the acylamino groups of AMC-12 had been hydrolyzed completely to carboxyl groups.

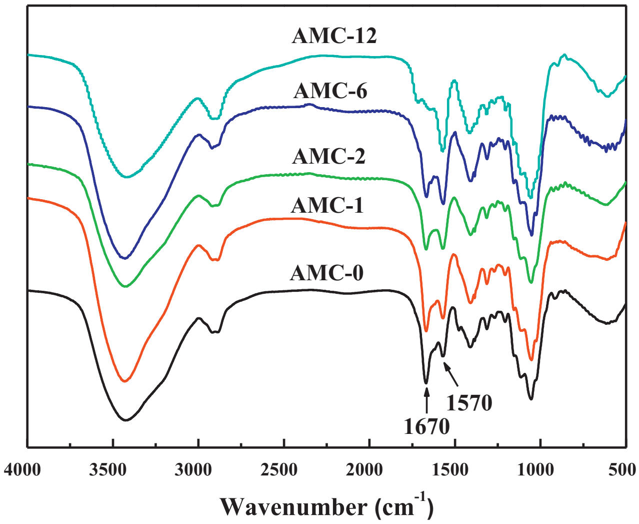


Fig. 1. FT-IR spectra of AMC samples.

The degree of substituent (DS) value of AMC samples can be calculated from the N content as following:

$$N\,\% = \frac{1400\,x}{(162 + 71\,x + 94\,y)}$$

where, x is the DS of acylamino groups ($DS_{Acylamino}$), y is the DS of carboxyl groups ($DS_{Carboxyl}$). As for AMC-0, the molar ratio of x to y could be determined to be 4 by ^{13}C NMR spectra. Therefore, according to the N content (3.529 wt%) listed in Table 1 and the molar ratio of x to y, $DS_{Acylamino}$, $DS_{Carboxyl}$, and DS_{Total} could be calculated to be 0.54, 0.13, and 0.67, respectively. For AMC-1–AMC-12, the sum of x and y was 0.67, $DS_{Acylamino}$ and $DS_{Carboxyl}$ could be calculated according to the N content. The DH value of all AMC samples (DH_N, obtained according to N content) could be obtained and summarized in Table 1. The results revealed that AMC samples with DH value of 20–100% could be obtained by controlling the hydrolysis reaction time. Obviously, with increasing of the hydrolysis reaction time, the DH value increased. When the hydrolysis time increased to 12 h, the DH value increased up to 100%.

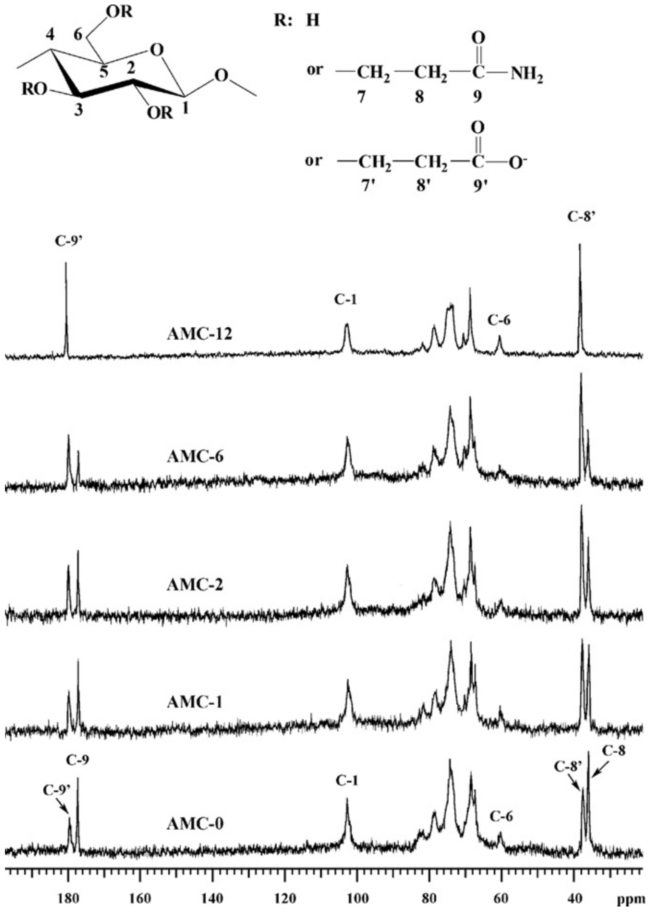


Fig. 2. ^{13}C NMR spectra of AMC in D_2O at 25 °C.

3.3. *Physicochemical properties of AMC aqueous solution*

The zeta potential of AMC samples with difference DH values in distilled water is shown in Fig. 3. Obviously, with DH value increased from 20% to 100% gradually, the content of carboxyl groups ($-COO^-$) increased, therefore the zeta potential of AMC samples decreased gradually from −25.0 to −46.6 mV. The result agreed well with those from NMR spectra, FT-IR spectra, and elemental analysis.

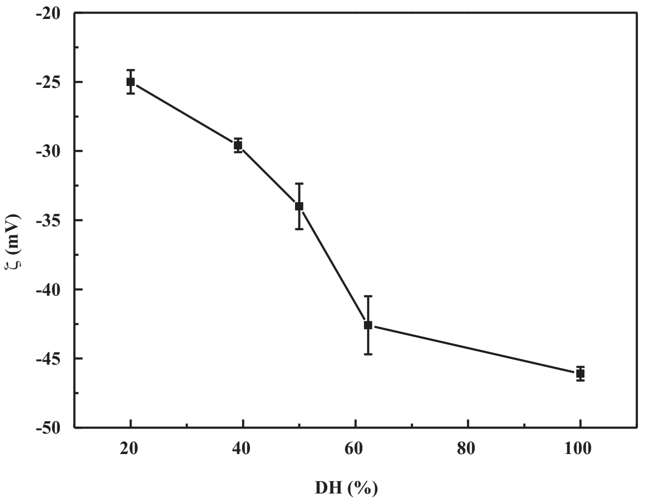


Fig. 3. Zeta potential of AMC samples. Data are shown as mean ± SD (n = 3).

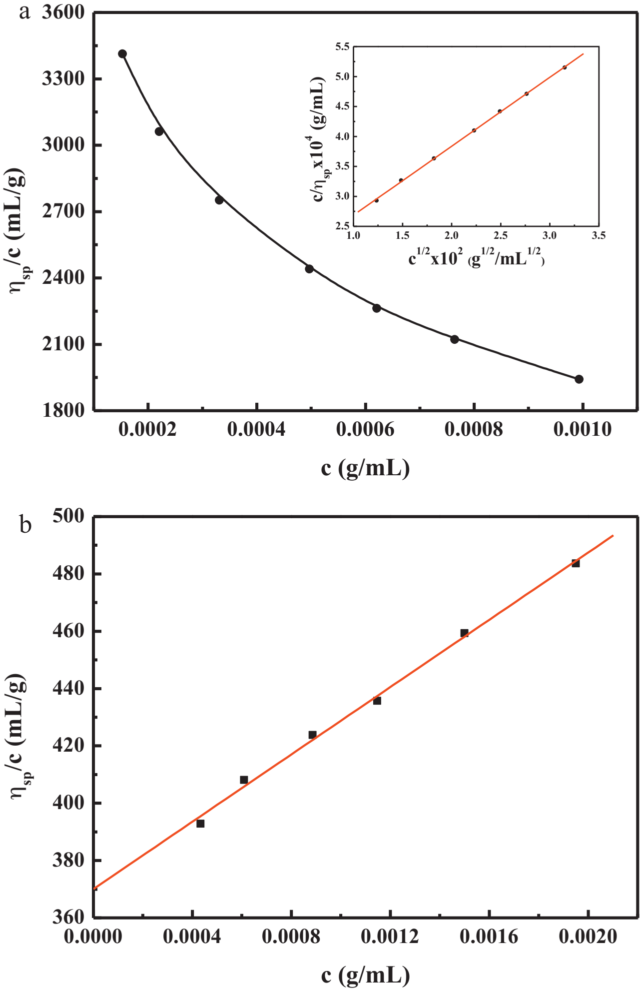


Fig. 4. Dependence of the reduced viscosity (η_{sp}/c) on concentration for the AMC-6 sample (a) in pure water and (b) in 0.15 M NaCl aqueous solutions at 25 °C. Inset of (a) is the dependence of c/η_{sp} on $c^{1/2}$.

The reduced viscosity (η_{sp}/c) of AMC-6 in pure water at 25 °C is displayed in Fig. 4a. In the absence of salt, the reduced viscosity of AMC displays a typical electrostatic repulsion effect as a result of the expanded polyelectrolyte chains and chain–chain repulsion, which remarkably increases with the decreasing of the polymer concentration. Then the intrinsic viscosity ([η]) of AMC in the absence of salt can be estimated from Fuoss equation (Fuoss & Strauss, 1948):

$$\frac{c}{\eta_{sp}} = \frac{(1 + Ac^{1/2})}{[\eta]}$$

where A is a constant, to account for the interactions of polyelectrolyte. Intrinsic viscosity ([η]) is a measure of hydrodynamic volume of macromolecules. It is generally accepted that macromolecule conformation and molecular weight play a fundamental role, through their relationships with the molecular dimensions and shapes, in determining the value of [η]. Therefore, the [η] values could reflect the expanded extent of the polymer chain (Lapasin & Pricl, 1995; Michell, 1979). In this study, [η] values of AMC samples ranged in 4793–6605 mL/g (see Fig. 5), which suggested AMC had extended chain conformation in water attributing to the electrostatic repulsion of the polyelectrolyte solutions and the stiffness of cellulose backbone (Song et al., 2009). Comparing the [η] values of AMC samples, it can be seen that with DH value increased, the content of carboxyl groups increased, therefore the electrostatic

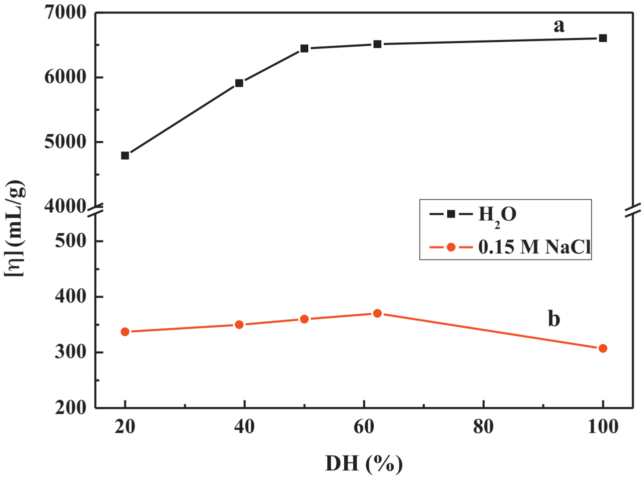


Fig. 5. [η] of AMC in water (a, data estimated from Fuoss equation) and in 0.15 M NaCl aqueous solutions (b, data estimated from Huggins equation).

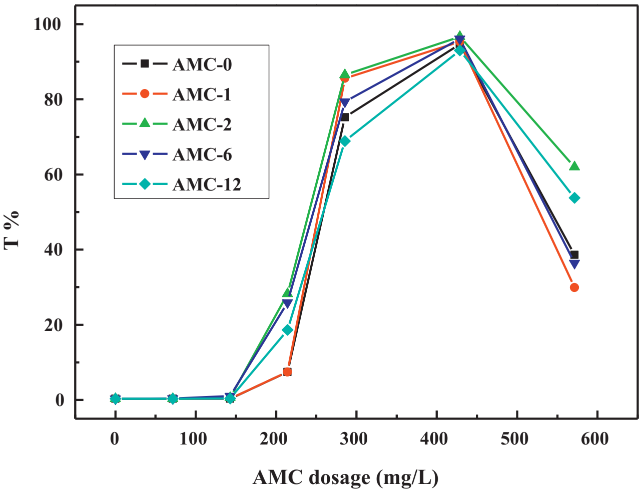


Fig. 6. Flocculation performance of AMC sample in the $Fe(OH)_3$ colloid.

repulsion interaction increased, the chain conformation became more extended, which resulted the increasing of [η] value. The electrostatic repulsion interactions could be screened with the addition of NaCl, leading to the normally viscosity behavior of AMC solutions like to neutral polymers (see Fig. 4b). Then Huggins equation (Huggins, 1942) can be used to estimate the intrinsic viscosity of AMC in presence of NaCl. As shown in Fig. 5, the [η] values of AMC in 0.15 M NaCl aqueous solutions are ranged from 307 to 370 mL/g, much lower than that obtained in water.

3.4. Flocculation of $Fe(OH)_3$ colloid

The flocculation of AMC samples to $Fe(OH)_3$ colloid are illustrated in Fig. 6. It can be seen that AMC samples with different DH values were effective flocculants to $Fe(OH)_3$ colloid, and the maximum transmittance value could reach up to nearly 100%. The flocculants dosage rising to the maximum transmittance value is considered as an optimal dosage value. Initially in this study, with the increase of AMC sample dosage up to the optimal dosage, the transmittance of clarified layer is gradually increased and then followed by a decreasing trend with further increases in dosage level. These are typical curves of the flocculation system controlled by the charge neutralization mechanism (Szyguła, Guibal, Palacín, Ruiz, & Sastre, 2009). The introducing of charged carboxyl groups in AMC can enhance the flocculation efficiency of AMC by the charge neutralization. The cationic $Fe(OH)_3$ colloid particles are electrostatically attracted by the carboxyl groups of AMC. This reaction neutralizes the cationic charges of $Fe(OH)_3$ colloid particles, then the colloid particles can bind together and settle. When the carboxyl groups had completely neutralized the cationic charges (at the optimal flocculant dosage), the transmittance reached its maximum. However, when the optimal dosage range is exceeded, stabilization takes place by the electrostatic repulsion among the $Fe(OH)_3$ colloid particles already bound with AMC and the transmittance decreased again, which is the well-known phenomenon in flocculation (Song et al., 2010).

The mechanism of the $Fe(OH)_3$ colloid flocculation with AMC may be explained by a combination of charge neutralization and polymers bridging. Charge neutralization is the main driving force in flocculation of $Fe(OH)_3$ colloid. However, contribution of bridging cannot be neglected. AMC molecule contains acylamino ($-CONH_2$) and carboxyl ($-COO^-$) groups simultaneously. The bridging takes place easily by adsorption of an AMC molecule at more than one site on a $Fe(OH)_3$ colloid particle or at sites on different $Fe(OH)_3$ colloid particles, due to electrostatic interaction with carboxyl groups and hydrogen bonding with acylamino groups (Boltoa & Gregory, 2007; Pal, Mal, & Singh, 2005). Absorbed AMC polymers tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends also dangle and get adsorbed on the surface of another particle forming a bridge between particles (Wei, Cheng, & Zheng, 2008). For effective bridging occur, the chain conformation of polymer chains should be extended enough to extent from one particle surface to another (Song et al., 2010). In this study, as mentioned above, the AMC molecules have the extended conformation in aqueous solution attributing to the charge repulsion produced by the carboxyl groups, which facilitates polymer bridging of the primary amide functional groups ($-CONH_2$) (Mpofu, Addai-Mensah, & Ralston, 2004; Rivas & Maureira, 2008). By the combination of charge neutralization and polymers bridging, AMC samples are effective flocculants for $Fe(OH)_3$ colloid. Considering the non-toxicity and biodegradability, AMC could be considered as promising flocculants with excellent flocculation properties.

4. Conclusion

Based on the Michael addition and saponification reactions, a series of AMC samples with DH value ranging from 20% to 100% were obtained. The results revealed that the DH value of AMC could be controlled by adjusting the hydrolysis reaction condition. With increasing of the hydrolysis reaction time, the DH value increased, as well as the carboxyl group content and the intrinsic viscosity value. The DH value increased up to 100% when the hydrolysis time increased to 12 h. The flocculation results proved that, by the combination of charge neutralization and polymers bridging, AMC samples are effective flocculants for $Fe(OH)_3$ colloid. This study demonstrated that the alkaline hydrolysis of AMC could be controlled, and AMC could be potentially used as novel efficient, non-toxic and biodegradable flocculants in the water treatment field.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (973 Program, 2010CB732203), the National Natural Science Foundation of China (50973085), the Fundamental Research Funds for the Central Universities (2081005), and the Foundation of Key Laboratory of Cellulose and Lignocellulosic Chemistry, Chinese Academy of Sciences, China.

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