Carbohydrate Polymers 80 (2010) 467–473

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Preparation and application of a new cationic starch ether – Starch–methylene dimethylamine hydrochloride

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ARTICLE INFO

Article history:
Received 10 October 2009
Received in revised form 1 December 2009
Accepted 3 December 2009
Available online 6 December 2009

Keywords:
Cationic starch
Etherification
Mannich reaction
Hydroxymethyl dimethylamine hydrochloride
NMR
Flocculation

ABSTRACT

A new cationic starch ether – starch–methylene dimethylamine hydrochloride (SMMAHC) was synthesized by the reaction of corn starch with cationic reagent hydroxymethyl dimethylamine hydrochloride (HMMAHC) using dry process according to Mannich reaction. Reaction parameters (temperature, time, molar ratio of HMMAHC to anhydrous glucose unit (AGU) of starch, and content of HMMAHC) and their effects on the degree of substitution (DS) and reaction efficiency (RE) had been investigated. Under the optimal reaction conditions, SMMAHC with high DS of 0.79% and RE of 96.3% was obtained. The structures of SMMAHC were characterized by ^{13}C-NMR and DEPT-135 spectroscopy. SMMAHC was used as flocculant to treat dyestuff (reactive brilliant red KE-3B) wastewater. The effects of DS and pH on the flocculation were studied and the dyestuff flocculation value reached a maximum of 209 mg/g.

1. Introduction

Cationic starches (CS) are widely used as additives in papermaking, wastewater treatment, textile, oilfield drilling and cosmetic industry because of their relatively low price, excellent properties and biodegradability (Granö, Yli-Kauhaluoma, Suortti, Käki, & Nurmi, 2000; Pal, Mal, & Singh, 2005; Zhang, 2001). Cationic starches can be classified into etherified starch (Khalil & Aly, 2001; Wei, Cheng, & Zheng, 2008), esterified starch (Auzély-Velty & Rinaudo, 2003) and graft copolymerized starch (Bruzzano, Sieverling, Wieland, & Jaeger, 2005; Gruber, & Bothor, 1998; Lu, Lin, & Yao, 2004) according to different chemical bonds formed between starch and cationic agents. As ether bond is more stable than ester bond and etherification is easier than graft copolymerization, etherified cationic starch has been paid much more attention in applications. Different methods for preparation of etherified cationic starch have been described. Solvent-free etherification processes, so-called dry cationization of starch, were applied owing to the advantages of non-solvent condition and high efficiency (Ju, Zhang, & Yang, 2000; Khalil & Farag, 1998; Xing, Zhang, Ju, & Yang, 2006; Zhang, Zhang, Ju, & Yang, 2007).

Etherified cationic starch is usually prepared by reaction of etherifying agent with hydroxyl groups in AGU of starch. Commercially important etherified cationic starches are the quaternary ammonium and tertiary amine starch ethers (Solarek, 1986). 3-Chloro-2-hydroxypropyltrimethylammonium chloride (Xu, Wei, Feng, Wang, & Li, 2004) and 2,3-epoxypropyltrimethylammonium chloride were the most widely used quaternary ammonium etherifying agents (Heinze, Haack, & Rensing, 2004). 2-Chloroethyl diethylamine, 3-chloro, 2-hydroxy propyl diethylamine, 2-chlorotriethylamine hydrochloride and N-(2-chloroethyl) diisopropylammonium chloride (Bohrisch & Zimmermann, 2007; Chan, 1994; El-Alfy, Samaha, & Tera, 1991; Khalil & Aly, 2004) were widely used as etherifying agents to synthesize tertiary amino cationic starch ethers. However, the usage of these agents consumes a large amount of alkaline agents to activate the hydroxyl groups of starch or to neutralize the acid yielded in the reaction, furthermore, the prices of those etherifying agents are relatively high. It was reported that Mannich reagent hydroxymethyl dimethylamine hydrochloride can be prepared from dimethylamine, formaldehyde and hydrochloric acid (Alexander & Underhill, 1949; Lieberman & Wagner, 1949; Pelton, 1984). HMMAHC could be used as a good cationic reagent by reason of its advantages, such as low-cost, simple preparation process, simple structure and high electrophilic reactivity. To the best of our knowledge there has been no report of preparation of cationic starch by using HMMAHC as cationic etherifying reagent.

Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein (Mishra, Bajpai, & Pandey, 2006). Reactive dyestuffs, which contain a large number of hydrophilic sulpho groups, were difficult to be precipitated from the liquors even though after being hydrolyzed. As starch derivative, cationic starch bearing a cationic moiety *N*-(3-chloro-2-

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doi:10.1016/j.carbpol.2009.12.002

hydroxypropyl)-trimethyl ammonium chloride was the conventionally flocculant for treatment of the reactive dyestuffs effluent (Klimaviciute, Riauka, & Zemaitaitis, 2007). However, as mentioned above, the preparation process of this quaternary ammonium cationic starch would cause environment pollution and its cost is relatively high.

Therefore, the purposes of this paper are to synthesize new tertiary amino starch ether – starch–methylene dimethylamine hydrochloride by the reaction of corn starch with cationic reagent HMMAHC using dry method and to investigate its flocculation characteristics.

2. Materials and methods

2.1. Materials

The materials and reagents used in this study were purchased from the following companies: food-grade corn starch (12% moisture) from HuangLong Food Company (Changchun, PR China); dimethylamine from Tianjin Fuchen Chemical Reagent Factory (Tianjin, PR China); formaldehyde from Shenyang Shenlian Reagent Factory (Shenyang, PR China); hydrochloric acid from Xinguang Chemical Reagent Factory (Peking, PR China); all other chemicals were supplied by Tianjin Plant of Agents (Tianjin, PR China). The concentration of dimethylamine and formaldehyde and hydrochloric acid solution are 33%, 37–40%, 36–38% (w/w), respectively. All of the reagents are of analytical grade. The starch was dried at 105 °C under vacuum to constant weight before use.

2.2. Methods

2.2.1. Preparation and purification of hydroxymethyl dimethylamine hydrochloride

The reactions were carried out in a 250 ml three-necked round-bottom flask equipped with stirrer, thermometer and drop funnel. Formaldehyde (0.5 mol) solution was added into the flask under stirring, then dimethylamine (0.5 mol) solution was added dropwise in 30 min, the hydroxymethylation was carried out; hydrochloric acid (0.425–0.5 mol) was then added dropwise in 30 min to generate HMMAHC ($HO—CH2—N(CH_3)_2{\cdot}HCl$), then the mixture was stirred for another 30 min to ensure complete reactions. During the reactions, the system temperature was kept within 5–10 °C. Different amounts of side product of dimethylamine hydrochloride (MAHC) ($HN(CH_3)_2{\cdot}HCl$) would be generated. Unreacted dimethylamine and formaldehyde were removed using rotary vacuum evaporator until the weight was constant, only the non-volatile compounds of HMMAHC and MAHC were left in the mixture.

2.2.2. Preparation of starch–methylene dimethylamine hydrochloride

Starch–methylene dimethylamine hydrochloride was prepared by dry method. Starch was well-mixed with HMMAHC and some water, and then the water of the mixture was removed using rotary vacuum evaporator at 60 °C until a constant weight was obtained. The reaction was carried out in a vacuum oven for hours at high temperature. After being cooled to room temperature, the products were Soxlet-extracted with ethanol for 24 h. Thin layer chromatography showed that unreacted HMMAHC and side products were removed completely.

2.3. Measurements

2.3.1. Content of HMMAHC M_{HMMAHC}% and MAHC M_{MAHC}%

Content of HMMAHC was determined by measuring the amount of hydroxyl groups of the compound (Pesez & Bartos, 1974), orange complex compound was formed when HMMAHC reacted with ammonium ceric nitrate as the following equation:

$$\mathrm{HO{-}CH_2{-}N(CH_3)_2\cdot HCl + (NH_4)_2Ce(NO_3)_6} \\ \rightarrow \mathrm{(NH_4)_2Ce(O{-}CH_2{-}N(CH_3)_2\cdot HCl)(NO_3)_5 + HNO_3}$$

The amount of HMMAHC could be calculated using the standard curve of pure HMMAHC.

Content of HMMAHC M_{HMMAHC}% was calculated as follows:

$$M_{\mathrm{HMMAHC}} = \frac{N}{H} \times 100$$

Content of MAHC M_{MAHC}% was counted by subtracting the amount of HMMAHC from hydrochloric acid as follows:

$$M_{\mathrm{MAHC}} = \frac{H - N}{H} \times 100$$

where N is molar quantity of HMMAHC, H is the molar quantity of hydrochloric acid to prepare samples.

2.3.2. Measurements of the nitrogen content of the starch derivative

The extent of amination was traced by determining the nitrogen content (*%N*) using the semimicro *Kjedahl* method (Vogel, 1975). The degree of substitution which is the number of substituted hydroxyl groups per AGU in the starch polymer was calculated following the equation:

$$\mathrm{DS} = \frac{162 \times \%N}{1400 - 93.5 \times \%N}$$

The reaction efficiency was calculated as follows:

$$\mathrm{RE}\% = \frac{\mathrm{DS}}{n(\mathrm{HMMAHC})/n(\mathrm{AGU})} \times 100\%$$

where n(HMMAHC) is the molar quantity of hydroxymethyl dimethylamine hydrochloride, n(AGU) is the molar quantity of anhydrous glucose units in starch.

2.3.3. ^{13}C-NMR and DEPT-135

Standard ^{13}C-NMR and DEPT-135 were recorded on a Nuclear Magnetic Resonance Spectrometer (Varian INOVA 400M NMR, America) after the sample was dissolved in D_2O and measured in deuterium oxide at 300 K.

2.3.4. Flocculation of dyestuff hydrolysate liquors

Two hundred milliliters of dyestuff hydrolysate solution (reactive brilliant red KE-3B, 0.1 g/L hydrolysate) containing other necessary substances (e.g. hydrochloride acid or sodium hydroxide for the adjustment of the pH value) was prepared. After the addition of the cationic starch, the solution was immediately stirred at a constant speed of 120 r/min for 1 min, followed by a slow agitation at 40 rpm for 20 min (this period named flocculating time). The flocs were then allowed to settle down for 15 min (sedimentation time). At the end of the settling period, the solution was filtered and the transmittance of filtrate was measured using a UV/vis spectrometer (hp 8453) at 542 nm.

3. Results and discussion

The reactions for preparation of starch–methylene dimethylamine hydrochloride and decomposition of cationic starch are shown in Fig. 1. Etherifying reagent HMMAHC was prepared from hydroxymethyl dimethylamine (**a**) in strong acid medium, and it would be converted into dimethylamino carbonium salt intermediate (**b**) and methylene iminium salt intermediate (**c**) (reactions 1) according to Mannich reaction (Arend, Westermann, & Risch, 1998; Hellmann & Optiz, 1959). Intermediates **b** and **c** could exist

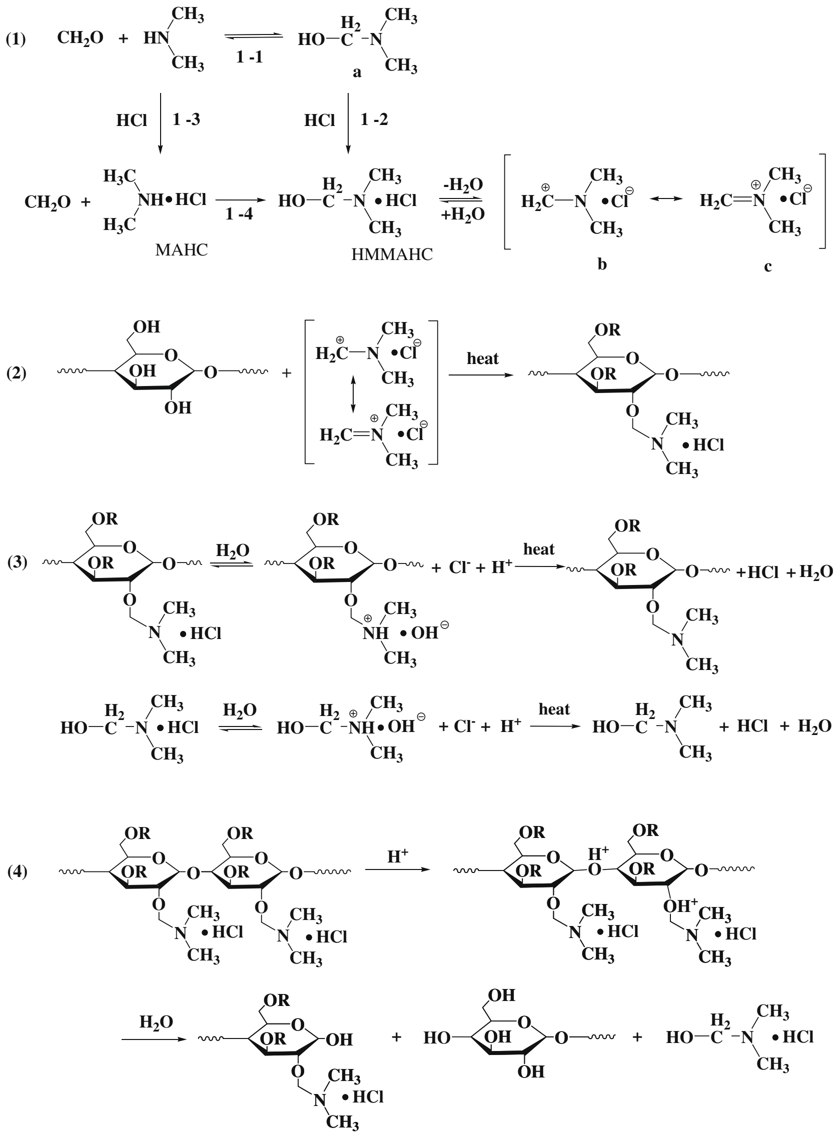

Fig. 1. Scheme of formation of etherifying reagent and cationic starch and decomposition of cationic starch (R = H or cationic group according to DS).

under non-water condition. And because of the strong positive centers, the electrophilic intermediates (**b** and **c**) were activated to attack the groups with activated hydrogen. During the preparation of cationic starch at high temperature, HMMAHC lost water molecules, the generated intermediates **b** and **c** would react with starch (reaction 2). Methylene dimethylamine hydrochloride (MMAHC) groups on cationic starch and HMMAHC would be hydrolyzed and decomposed (reaction 3). The prepared SMMAHC would be degraded (reaction 4) by the generated proton under the condition of high temperature.

The existence of water favored the side reaction. Hence water should be prevented in the etherification process and dry method was recommended for the reaction. In this study, the preparation of SMMAHC was carried out under different conditions. According to reactions 1 and 2, reaction temperature and the content of HMMAHC would have significant impact on the etherification, therefore, the influences of temperature, time, molar ratio of HMMAHC to starch, and content of HMMAHC on DS and RE were taken into account. And before the preparation of cationic starch, the influences of different molar quantities of hydrochloric acid on the contents of HMMAHC and MAHC in etherifying reagent were taken into consideration.

3.1. Influences of different molar quantities of HCl on the contents of HMMAHC and MAHC in etherifying reagent

As shown in reactions 1 (Fig. 1), during the preparation of HMMAHC (reaction 1-2), MAHC would be generated (reaction 1-3) because it was a balance system composed of hydroxymethyl dimethylamine (**a**), formaldehyde and dimethylamine (reaction 1-1).

Table 1 showed the effects on the contents of HMMAHC and MAHC when the molar ratios of hydrochloric acid to hydroxymethyl dimethylamine (**a**) solution were different (courting as 100% of the generation of hydroxymethyl dimethylamine in reaction 1-1). As can be seen, with the molar ratio of hydrochloric acid to hydroxymethyl dimethylamine (**a**) increased, the content of generated hydrochloride (HMMAHC + MAHC) equivalently increased; however, with the content of HMMAHC increased, the content of MAHC decreased. It could be explained that the alkalinity of $HO{-}CH_2{-}N(CH_3)_2$ was stronger than $HN(CH_3)_2$ due to more alkyl groups on hydroxymethyl dimethylamine, and MAHC could convert to HMMAHC (reaction 1-4) at low pH (Le, Jones, Bickelhaupt, & Wolf, 1989). Therefore, more HMMAHC was generated, and HMMAHC was more stable than MAHC.

Table 1
Influence of different molar quantity of HCl to the contents of HMMAHC M_{HMMAHC}% and MAHC M_{MAHC}%.

Sample number	Molar ratio of HCl/**a**	Content of hydrochloride (HMMAHC + MAHC) [%] before purification	Content of HMMAHC M_{HMMAHC} [%] after purification	Content of MAHC M_{MAHC} [%] after purification
I	0/100	–	–	–
II	85.4/100	85.4	93.0	7.0
III	96.5/100	96.5	99.6	0.4
IV	100/100	100	100	0

3.2. Influences of temperature and time and molar ratio of HMMAHC to starch for preparation of cationic starch

According to reactions 1 and 2, higher temperature was favorable to generate more intermediates **b** and **c** and increase DS when the intermediates reacted with starch, so etherification temperature was raised from 80 °C to 150 °C. As can be seen from Table 2 (when the molar ratio of HMMAHC to AGU was 0.6), DS and RE were 0 at 80 °C, which indicated the temperature was not high enough to trigger the reaction, only when it got to 100 °C, etherification began to take place, DS and RE increased by prolonging the reaction time. However, when the temperature got to 120 °C, DS and RE got to their maxima and then reduced with the extension of reaction time, it could not increase DS and RE any longer, when the temperature got to 140 °C, DS and RE reduced to small values and the cationic starch products began to degrade. When it got to 150 °C, cationic starch products were degraded distinctly.

The reason for this phenomenon was that the ammonium salts were easily to thermally decompose (Olszak-Humienik, 2001). During the etherification, a small quantity of generated water would make MMAHC groups on cationic starch and HMMAHC hydrolyze and then thermally decompose (reaction 3), when the temperature was above 120 °C, because of long time heating (more than 4 h), a small quantity of the generated protons became activated and began to play the role of free acid, α-D-(1 → 4), α-D-(1 → 6) glucosidyl bonds in starch chains and the generated ether bonds could be easily broken in acidic condition, DS and RE were reduced, side reaction 4 took place.

In addition, the thermogravimetric analysis (TGA) curve showed the weight loss of native starch and cationic starch. In Fig. 2, the weight of native starch (a) lost sharply when it got to 300 °C, which indicated it was the decomposition temperature of native starch; as for the cationic starch product (b), its weight began to lose dramatically at 150 °C, which interpreted the rapid decomposition of the cationic starch at that temperature. The TGA curve demonstrated the upper limit temperature of the etherification.

As stated above, much higher temperature went against the raising of DS due to the occurrence of side reactions 3 and 4, thus, in order to remove the generated water molecule, facilitate reactions 1 and 2 and avoid side reactions 3 and 4, temperature of 100 °C was suitable.

At the selected reaction temperature of 100 °C, when the molar ratio was 0.6, the effect of reaction time on DS and RE was studied (in Table 2). The results showed when the reaction time was prolonged, DS and RE increased and after the duration of 20 h they got to 0.53% and 88.3%, respectively, but the growth slowed down after the reaction time was more than 16 h. Therefore, in order to prepare cationic starch with higher DS and RE, the reaction time should not be less than 16 h.

The effects of different molar ratios of HMMAHC to starch were investigated under the conditions of 100 °C, 16 h (in Table 2), when molar ratio was raised from 0.40 to 0.82, RE increased from 72.5% to 96.3% and DS increased from 0.29 to 0.79, however, when the molar ratio rose to 1.00, DS rose a little, whereas RE reduced sharply. Generally, when the molar ratio of HMMAHC to AGU was increased, the ratio of free hydroxyl groups of starch to etherified agent would decline, RE would show a downward trend, however, in the course of etherification, RE showed an increased trend first and then decreased. The rise of RE might result from the damage of crystallinity of starch during reaction and the increasing diffusion rate of etherifying reagent due to the generated water, those reasons make more free hydroxyl groups take part in the reaction. The viscous state of cationic starch with high DS verified that explanation. When the molar ratio was more than 0.82, the proportion of free hydroxyl groups decreased and RE were reduced. In

Table 2
Influence of different reaction conditions on DS and RE of starch–methylene dimethylamine hydrochloride.

Reaction conditions[a]			Starch–methylene dimethylamine hydrochloride	
Temperature (°C)	Time (h)	Molar ratio HMMAHC/AGU	DS	RE (%)
80	10	0.60	0	0
100	8	0.60	0.01	1.1
100	12	0.60	0.20	33.3
100	16	0.40	0.29	72.5
100	16	0.60	0.52	86.7
100	16	0.80	0.76	95.0
100	16	0.82	0.79	96.3
100	16	0.84	0.80	95.2
100	16	1.00	0.83	83.0
100	20	0.60	0.53	88.3
120	2	0.60	0.04	15.9
120	4	0.60	0.19	31.7
120	8	0.60	0.15	25.0
140	1	0.60	0.02	3.3
140	2	0.60	0.03	5.0
140	3	0.60	0.02	3.3
150	1	0.60	–	–

[a] Content of HMMAHC in etherifying reagent was 100%.

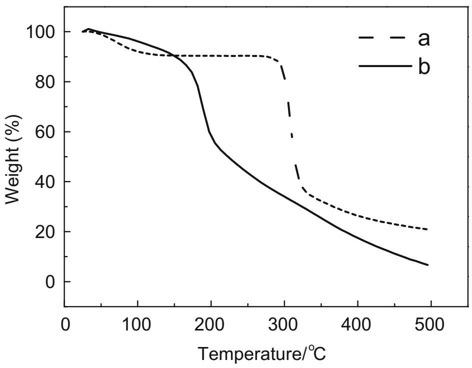

Fig. 2. Thermogravimetric analysis of native starch (a) and cationic starch (b, DS = 0.46).

consideration of the values of RE and DS, the molar ratio of 0.82 was the optimal ratio.

In summary, three advantages of dry method were concluded for this reaction:

(1) Dry method shook off the shackles of boiling point of solvent, at the temperature of 100 °C, reactions 1 took place and activated intermediates **b** and **c** were generated.
(2) Only under the condition of non-water, could intermediates **b** and **c** be steadily formed, could their reactions with starch take place.
(3) When dry method was used in the process of etherification, the damage which would take place in acid solution would be avoided.

3.3. Influence of content of HMMAHC/MAHC in the etherifying agent for preparation of cationic starch

During the preparation of cationic starch, etherifying agents containing different contents of HMMAHC/MAHC (Table 1, HMMAHC% + MAHC% = 100%) had a great effect on the RE. Three groups of columns in Fig. 3 showed that RE increased when the content of MAHC in raw materials decreased (II, III, IV). When the content of MAHC was 0% and reaction time was 16 h (column c in the group IV), RE got to 96.3%. The descending trends of groups (IV, III, II) indicated that RE was reduced when the existence of MAHC increased. The reason was that, as mentioned above, the electron density on nitrogen of MAHC was lower than that of HMMAHC, and compared to one proton on nitrogen of HMMAHC, there were two protons on nitrogen of MAHC, the protons on nitrogen of MAHC were more activated than that on HMMAHC, so MAHC was thermally labile and it was easy to release proton to destroy the ether bonds (side reaction 4). Blank experiment verified that the cationic starch samples with pure MAHC were seriously degraded under the conditions of 100 °C and 12 h. It could be proved that MAHC and HMMAHC were both potential acids, compared with HMMAHC (it was easy to make the protons on nitrogen of HMMAHC and MMAC group of CS more active at the temperature of more than 120 °C), MAHC was more unstable and it would release proton to destroy ether bond at the optimum etherification temperature of 100 °C. Therefore, the existence of MAHC had an impact on RE, the lower the content of MAHC (the higher the content of HMMAHC) was, the lower the probability of side reaction 4 occurred and the higher RE was.

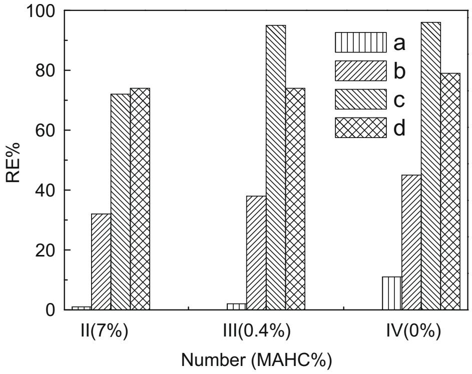

Fig. 3. Effect of the content of MAHC on RE at different time of 8 h (a), 12 h (b), 16 h (c) and 20 h (d), $n_{\mathrm{HMMAHC}}:n_{\mathrm{starch}} = 0.82:1$, 100 °C.

According to the study of the factors (temperature, time, molar ratio of HMMAHC to starch and content of HMMAHC in etherifying reagent) which had significant impact on DS and RE of the cationic starch, the conclusions were as follows: when the reaction temperature was conducive to generating intermediates **b** and **c**, DS and RE of CS could be increased remarkably; when reaction 4 was avoided effectively under the optimum conditions, RE could get to its maximum.

3.4. Characterization of cationic starch

The prepared cationic starch was characterized by DEPT-135 spectra. The peaks of the CH_2-groups at C6 and C7 had negative intensities and can be distinguished from the CH-groups easily (Fig. 4A). The signals of the raw material HMMAHC appeared at 81.9 and 34.8 ppm were assigned to C7 and C8, respectively, and C8 showed an intense signal. The signal of C7 in MMAHC group of CS product was 93.5 ppm. Comparison of signals of C7 in raw material HMMAHC and MMAHC group on CS product showed that the later shifted 11.6 ppm to the low field. This was in accordance with the calculated result based on Lindeman and Adams formula (Lindeman & Adams, 1971), when the substituted group connected to methylene was changed from —OH to —OR (R = AGU group), chemical shift of carbon on methylene would move about 10 ppm to low field. Chemical shifts of C7 had corroborated the occurrence of etherification.

Standard ^{13}C-NMR spectra were measured in deuterium oxide at 300 K. In Fig. 4B, a representative ^{13}C-NMR spectrum of a prepared starch–methylene dimethylamine hydrochloride (DS = 0.79) was shown. The resonances of unmodified AGU skeleton were determined from 60 ppm to 80 ppm for C2—C6, 99.9 ppm for C1. The introduction of the MMAHC moieties at 2-position and 6-position of starch resulted in three new peaks at 97.9 ppm, 80.2 ppm and 67.9 ppm for C1′, $C2_S$ and $C6_S$, respectively. Free hydroxyl groups at position 2 in AGU were active, and the steric hindrance of C6 position was smaller, so etherification took place at those two positions in AGU. As shown in detail in Fig. 4C, both peaks $C2_S$ and $C6_S$ became more intense with increasing DS, indicating that substitutions occurred at C2 position and C6 position simultaneously.

Based on DEPT-135 and ^{13}C-NMR spectra of the cationic starch, the changes in chemical shift of C7 and the splitting of the signals for C1, C2 and C6 gave strong evidence for the occurrence of etherification and that the substitutions occurred at both 2-position and 6-position.

3.5. Flocculation performance

The prepared cationic starch was used as flocculant to treat dyestuff (reactive brilliant red KE-3B) wastewater. The effects of DS and pH on the flocculation of dyestuff were shown in Fig. 5. It was apparent from the curves that the flocculation values increased with the increasing DS of CS, which revealed that the nitrogen was the essential element and played an important role in dyestuff flocculation process. When the pH increased from 1 to 8, the dyestuff flocculation

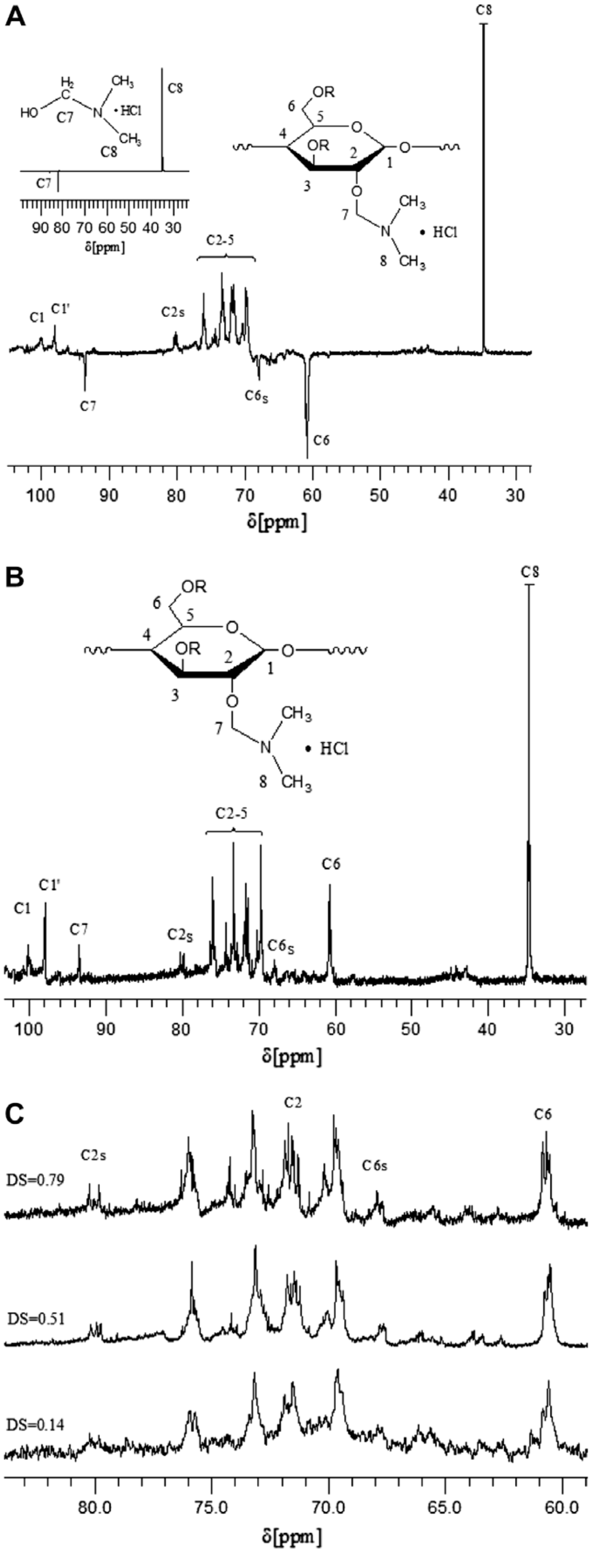

Fig. 4. DEPT-135 spectrum of HMMAHC and cationic starch (A, DS = 0.51), ^{13}C-NMR spectrum of cationic starch derivatives (B, DS = 0.79) and the changes of adsorption peaks intensity in detail (C) measured in D_2O at 60 °C (R = H or cationic group according to DS).

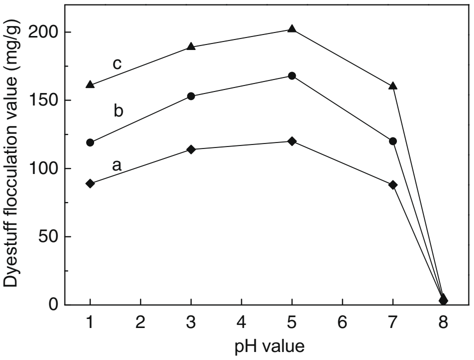

Fig. 5. Effect of DS and pH on the flocculation of dyestuff (a, DS = 0.36; b, DS = 0.51; c, DS = 0.72).

values reached to their maxima and then decreased, the appropriate pH range was 3–5, and at pH 5, the dyestuff flocculation value of cationic starch (DS = 0.72, curve **c**) got to its maximum of 209 mg/g. It was interesting since, at pH 8, the flocculation almost did not take place. This phenomenon could be explained as follows: in alkaline medium, the tertiary amino cationic group of CS was neutralized and then it lost the anion adsorption capacity. For this reason, the flocculation process of this tertiary amino cationic starch would be reversible and the flocculated dyestuff could be stripped from CS, after that, the CS would be reusable for further flocculation. It is obvious that SMMAHC can be used as a potentially effective flocculant to treat anionic dyestuffs wastewater. Further research to fully investigate other flocculation properties such as the reuse of CS is under way in our lab.

4. Conclusions

A new cationic starch ether – starch–methylene dimethylamine hydrochloride with high degree of substitution was prepared by using hydroxymethyl dimethylamine hydrochloride as etherifying reagent. It was concluded that dry method was feasible for this etherification; at the selected temperature of 100 °C, intermediates **b** and **c** could be generated and the etherification took place; DS and RE were influenced by higher temperatures (>120 °C) and the existence of dimethylamine hydrochloride; less content of dimethylamine hydrochloride in etherifying reagent make DS and RE be less affected. Under the optimum conditions of 100 °C, 16 h and molar ratio $n_{\mathrm{HMMAHC}}:n_{\mathrm{starch}} = 0.82:1$, cationic starch with high DS of 0.79 and RE of 96.3% was obtained. Flocculation experiment of anionic dyestuff (reactive brilliant red KE-3B) wastewater showed that, at pH 5, the flocculation value of cationic starch (DS = 0.72) reached its maximum of 209 mg/g. This work provides a simple and easy way to prepare tertiary amine etherified cationic starch, and the prepared cationic starch can be used as a potentially effective flocculant.

Acknowledgements

We are grateful to The National High Technology Research and Development Program of China (863 Program, No. 2006AA06Z317) for financial support of this research, and the program for Chang Jiang scholars and Innovative Research Team in the University (IRT0711).

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