

# Preparation of Chitosan-Based Flocculant for High Density Waste Drilling Mud Solid–Liquid Separation

Hong Zhu, Haiyun Sun, Fanghui Wang, Jing Zou, Jiantao Fan

State Key Laboratory of Organic–Inorganic Composites, Department of Organic Chemistry, School of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received 19 April 2011; accepted 21 August 2011

DOI 10.1002/app.36418

Published online 29 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** High performance flocculant was prepared by chitosan (CS), ethacryloyloxyethyl trimethyl ammonium chloride (DMC), and acrylamide (AM). The optimum preparation conditions were determined by orthogonal test of four factors and three levels. The different factors affecting the flocculating ability of the prepared flocculants for waste drilling mud were studied, and optimal synthesis conditions were established: polymerization temperature was 60, reaction time was 4 h, DMC was 3 mL,  $w(\text{AM}) : w(\text{CS})$  was 4, and the initiator was 0.4% of AM (wt %). The prepared CS–AM–DMC copolymer was char-

acterized by Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), and gel permeation chromatography (GPC). The results showed that AM, DMC were grafted to CS successfully. The solid–liquid separation properties were also investigated, and the prepared flocculant showed great advantages than commercial products for high density waste drilling mud use. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2646–2651, 2012

**Key words:** high density; waste drilling mud; chitosan grafted; AM; DMC; highly effective flocculant

## INTRODUCTION

Solid–Liquid separation has advantages of large capacity, easy operation, and less instrumental dependence. However, some unsolved problems such as the relative high solid moisture content (SMC) of the centrifuged product still restrict its application seriously.

Flocculants can be widely used for solid–liquid separation in many technical processes,<sup>1</sup> especially in oilfield.<sup>2</sup> Different systems of flocculant for oilfield including cationic flocculants,<sup>1,3</sup> anionic flocculants,<sup>4</sup> and nonionic flocculants<sup>5</sup> are developed rapidly. Starch derivative flocculant,<sup>6–8</sup> chitosan (CS) derivative flocculant,<sup>9</sup> and cellulose derivative flocculant<sup>10</sup> have attract researchers' most attentions over the last two decades. However, commercial flocculants are not applicable to oilfield sometimes, for their poor solubility in water, small molecular weight, low charge density, and high concentration.<sup>11</sup> Furthermore, many commercial flocculants are obtained from petroleum-based raw materials by

processing chemistry, which is not always environmentally friendly.<sup>12</sup>

In this work, we report a water-soluble cationic flocculant prepared by CS, ethacryloyloxyethyl trimethyl ammonium chloride (DMC), and acrylamide (AM). Flocculant studies showed its potential for waste drilling mud solid–liquid separation uses in oilfield.

## MATERIALS AND METHODS

### Chemicals

CS was supplied by Beijing Bohailitong Co., China. DMC (the concentration is 78 wt % in water) as the cationic reagent was bought from Le Tai Chemical Supermarket, Beijing, China. Acrylamide (AR), Cerium(IV) ammonium nitrate (CAN), and Acetic acid were analytic grade, supplied by Beijing Chemistry Reagent Co. and used without further purification.

Commercial flocculants, such as cationic polyacrylamide, anionic polyacrylamide, polymerization ferric sulfate (Fe), and polymerization aluminum sulfate (Al), were supplied by Shandong Taihe Water Treatment Co., Ltd., China.

High density waste drilling mud was collected from Shengli petroleum field. The basic characteristic of waste drilling fluid was list as follows (Table I).

The structural formula of DMC was as follows:



Correspondence to: H. Zhu (zhuho128@126.com).

Contract grant sponsor: National Key Technology R&D Program; contract grant number: 2008BAC43B02.

Contract grant sponsor: Fundamental Research Funds for the Central Universities.

**TABLE I**  
Basic Characteristic of Waste Drilling Fluid

Characteristic item	Value	Characteristic item	Value
Density (g/mL)	1.62	Oil content (%)	5.00
Solid content (%)	57.63	pH	11.64

### Preparation of CS-AM-DMC copolymer flocculant

General procedure: in a 250-mL 3-neck-round-bottom-flask, CS was suspended in H<sub>2</sub>O under N<sub>2</sub> atmosphere. A 2% of Acetic acid was added dropwise with stirring to make the mixture uniformity. The apparatus was then heated and added AM and DMC. After 0.5 h, CAN was added. The reaction was run at a constant temperature for several hours.

### Flocculent treatment

The flocculent treatment was conducted at room temperature (about 25°C). First, the prepared flocculant was added to waste drilling mud and stirred for an appropriate time. Then, the mixture was centrifuged at a speed of 3500 rpm for 10 min.

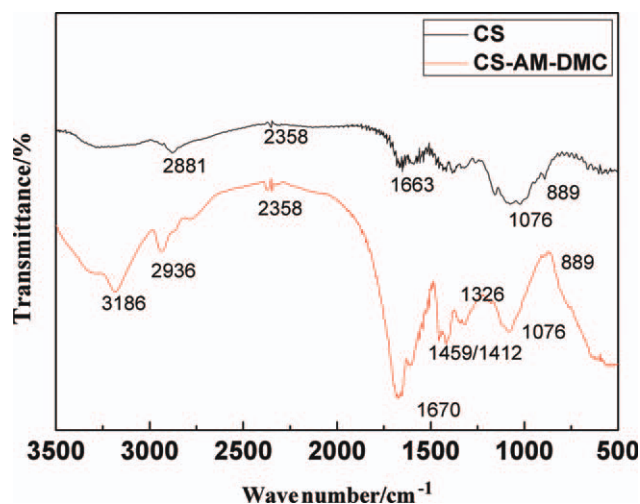
The solid moisture % was calculated according to the following equation:

$$\text{Solidmoisture}\% = \left(1 - \frac{m_2}{m_1}\right) \times 100$$

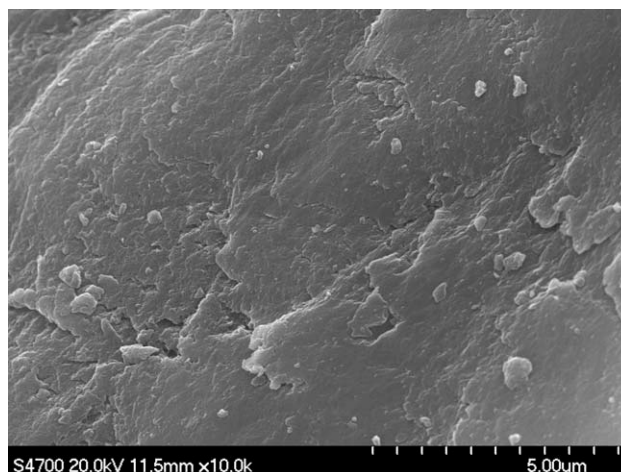
$m_1$  and  $m_2$  are the weight of the crude residue and the dried residue, respectively.

### Characterization

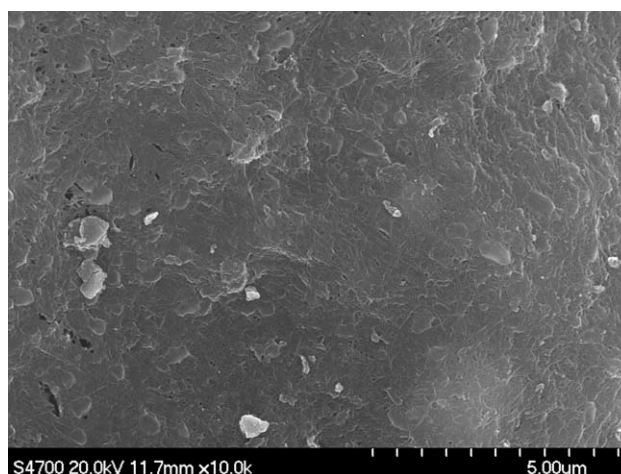
The CS-AM-DMC copolymer was using Fourier Transform Infrared spectrophotometer (FTIR). Potassium bromide pellet method was used for FTIR



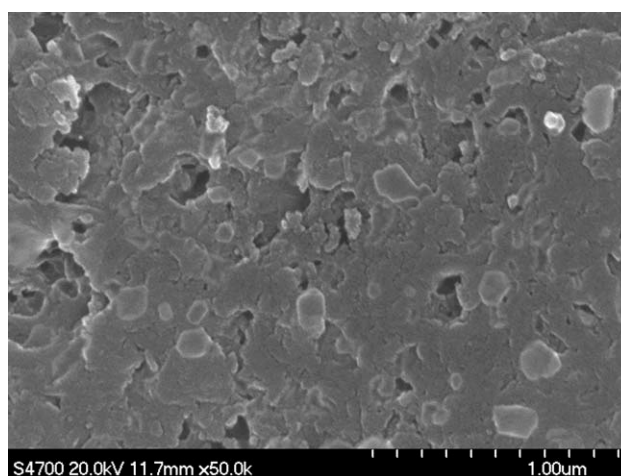
**Figure 1** FTIR spectrum of the CS-AM-DMC copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2** CS at 10k SEM.



**Figure 3** CS-AM-DMC at 10k SEM.



**Figure 4** CS-AM-DMC at 50k SEM.

TABLE II  
GPC Analysis of the Synthesized Polymer

Max.RT	Mp	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mn
10.45	1,483,115	495,096	1,051,367	1,456,394	980,227	2.124	2.942

study. The CS-AM-DMC's morphology was investigated by scanning electron microscopy (SEM) after the sample was sputtered with a thin layer of platinum. Molecular weight of the copolymer was measured by gel permeation chromatography (GPC).

#### FTIR

Figure 1 shows the FTIR spectrum of CS. The broad band at  $2881\text{ cm}^{-1}$  was due to the stretching mode of the Saturation C-H ( $\text{CH}_2, \text{CH}_3$ ). The  $-\text{NH}_2$  stretching vibration absorption peak appeared at  $1663\text{ cm}^{-1}$ . The band at  $1076\text{ cm}^{-1}$  was attributed to  $\text{CH}_2-\text{O}-\text{CH}_2$  stretching vibrations. The broad band at  $889\text{ cm}^{-1}$  was due to stretching vibration absorption peak of the backbone in CS Glucose ring.

The peak at  $3186\text{ cm}^{-1}$  showed the  $-\text{NH}_2$  stretching vibration in the copolymer, which did not exist in CS, obviously. The peak at  $1670\text{ cm}^{-1}$  was due to the bending vibration of  $-\text{NH}_2$ , and the band around  $1412\text{ cm}^{-1}$  was assigned to  $-\text{CH}_2$  stretching vibration. The band around  $1459\text{ cm}^{-1}$  and  $1326\text{ cm}^{-1}$  were assigned to  $-\text{CONH}$  the second as well as the third spectrum absorption peak. The  $-\text{CO}$  stretching vibration absorption peak appeared at  $1076\text{ cm}^{-1}$ , so there must have some structural units of AM and DMC remained in the CS-based cation copolymer flocculant.

#### Scanning electron microscopy

Figures 2–4 are SEM images of CS and the CS-AM-DMC copolymer, respectively. Figures 3 and 4 show that in transversal direction, CS-DMC-AM formed a reticulation structure, which was good for the solid

precipitate from the steady solid/liquid system. In longitudinal direction, the netlike structure could promote the absorbing and bridging performance as a flocculant for waste drilling fluid.

#### Gel permeation chromatography

The molecular weights and corresponding polydispersity index of the optimum CS-AM-DMC copolymer were determined (relative to polystyrene standard) by GPC in THF. The copolymer was precipitated with a solution of acetone/ethanol (1 : 1, v/v) and purified by HOAc/NaOAc (1 : 1, v/v). The results are shown in Table II and Figure 4.

## RESULTS AND DISCUSSIONS

### Preparation of CS-AM-DMC copolymer

#### Effect of dosage of initiator CAN

The reaction conditions were as follows: 1.5 g CS, 1.5 mL DMC, 4.5 g AM,  $\text{pH} = 6$ ,  $60^\circ\text{C}$ , and 3 h. The initiator CAN was 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, and 0.6% of AM (wt %), respectively. The flocculant experiment results are shown in Figures 5 and 6.

Figure 6 indicated that the SMC was the lowest (30.58%) when the dosage of CAN was 0.4% of AM. When the dosage of the CAN was under 0.4% of AM, there were not enough free radicals for the grafting reaction. When the dosage of the CAN was more than 0.4% of AM, the excessive free radicals increased the probability of the homopolymerization of AM and thus the probability of the chain-terminating step of the reaction. These result in low molecular weight

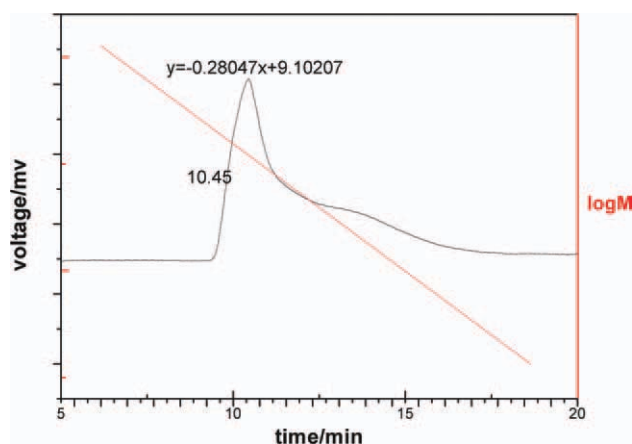


Figure 5 GPC analysis of the synthesized polymer.

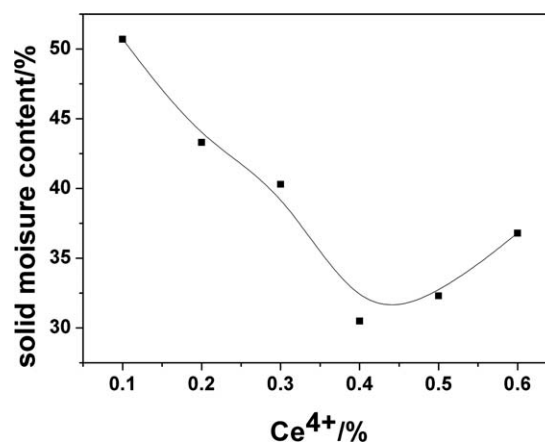


Figure 6 Effect of the Dosage of Initiator on Solid Moisture Content.

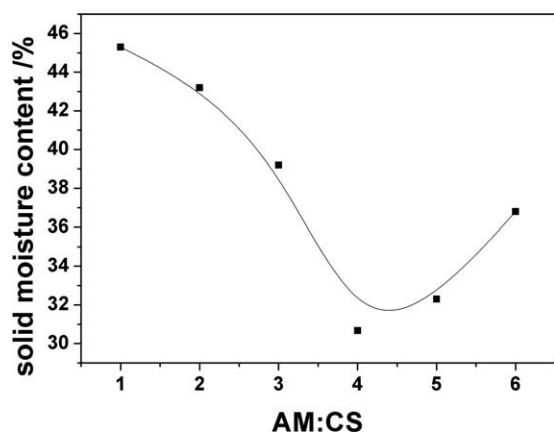


Figure 7 Effect of The Dosage of AM on Solid Moisture Content

copolymer, which would give poor flocculation activity because the flocculant could not attached closely with waste drilling mud.

Effect of dosage of acryl amide (AM)

The reaction conditions were as follows: 1.5 g CS, 1.5 mL DMC, pH = 6, 60°C, 3 h, CAN was 0.4% of AM (wt %), and AM was 1.5 g, 3.0 g, 4.5 g, 6.0 g, 7.5 g, and 9.0 g, respectively. The flocculent experiment results are shown in Figure 7.

Figure 7 indicated that the SMC was the lowest (30.63%) when the dosage of AM was four times of CS. When the ratio AM/CS was under 4, there was not enough AM grafted to CS. However, the excess AM would reduce the adhesion between the flocculant and waste drilling mud by the formation of low molecular weight side product of homopolymerized AM.

Effect of dosage of DMC

The reaction conditions were as follows: 1.5 g CS, 6 g AM, pH = 6, 60°C, 3 h, CAN was 0.4% of AM (wt

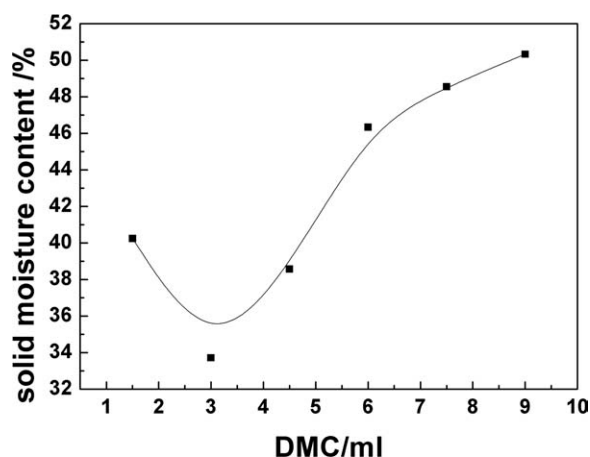


Figure 8 Effect of The Dosage of DMC on Solid Moisture Content.

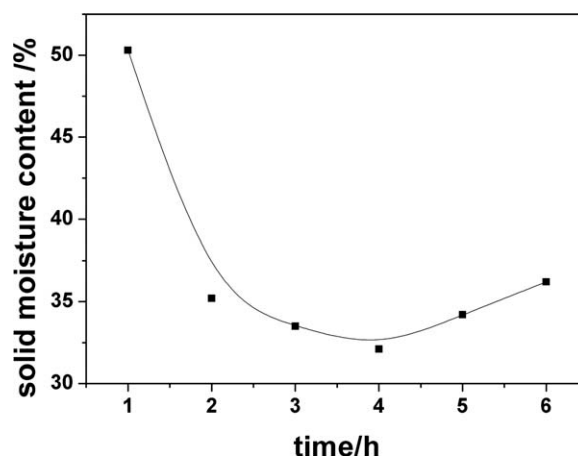


Figure 9 Effect of The Reaction Time on Solid Moisture Content.

%), and DMC was 1.5 mL, 3.0 mL, 4.5 mL, 6.0 mL, 7.5 mL, and 9.0 mL, respectively. The flocculent experiment results are shown in Figure 8.

Figure 8 indicated that the SMC was the lowest (33.67%) when the dosage of DMC was 3 mL. As a quaternary ammonium, small amount of DMC could neutralize negative charges the mud contains. However, the excess DMC would hydrolyze and participate in neither neutralization nor polymerization.

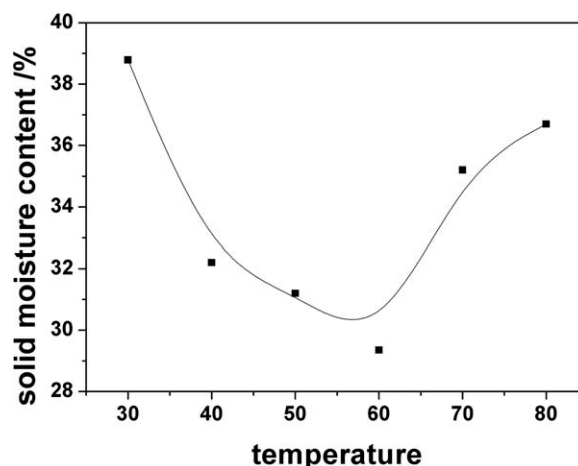


Figure 10 Effect of The Reaction Temperature on Solid Moisture Content [1 cationic polyacrylamide (CPAM) 2 anionic polyacrylamide (APAM) 3 polymerization Ferric sulphate (Fe) 4 polymerization Aluminum sulphate (Al) 5 CS-AM-DMC flocculant].

TABLE III  
The Orthogonal Experimental Design

Reaction condition	1	2	3
Reaction temperature (°C)	55	65	75
Dosage of DMC (mL)	2.5	3.5	4.5
Reaction time (h)	3.5	4.5	5.5
Dosage of AM (g)	5.5	6.5	7.5

TABLE IV  
The Orthogonal Experimental

Experiment number	Reaction temperature (A)	Dosage of DMC (B)	Reaction time (C)	Dosage of AM (D)	Solid moisture content (%)
1	1 (55°C)	1 (2.5 mL)	1 (3.5 h)	1 (5.5 g)	34.01500
2	1	2 (3.5 mL)	2 (4.5 h)	2 (6.5 g)	30.44000
3	1	3 (4.5 mL)	3 (5.5 h)	3 (7.5 g)	32.42000
4	2 (65°C)	1	2	3	31.33000
5	2	2	3	1	33.39000
6	2	3	1	2	33.29000
7	3 (75°C)	1	3	2	30.65000
8	3	2	1	3	30.41000
9	3	3	2	1	29.92000
I	32.2900%	32.0000%	34.0200%	32.4400%	—
II	32.1700%	31.4100%	30.5600%	31.4600%	—
III	30.3300%	31.8800%	32.1500%	31.3900%	—
R	0.006533	0.001967	0.011533	0.0035	—
Optimum			A <sub>3</sub> B <sub>2</sub> C <sub>2</sub> D <sub>3</sub>		

#### Effect of reaction time

The reaction conditions were as follows: 1.5 g CS, 3.0 mL DMC, 6 g AM, pH = 6, 60°C, CAN was 0.4% of AM (wt %), the reaction time was 1 h, 2 h, 3 h, 4 h, 5 h, and 6 h, respectively. The flocculent experiment results are shown in Figure 9.

Figure 9 indicated that the SMC was the lowest (32.12%) when the optimum reaction time was 4 h. At the beginning of the reaction, there were more active centers for grafting, and the molecular weight was increasing with time. After the completion of the reaction, the excess active centers encouraged the formation of the low molecular weight byproduct, which would widen the molecular weight distribution and thus decreased the flocculation activity.

#### Effect of reaction temperature

To investigate the temperature effect on the CS-AM-DMC copolymer composition, a series of experiments were carried out. The reaction condi-

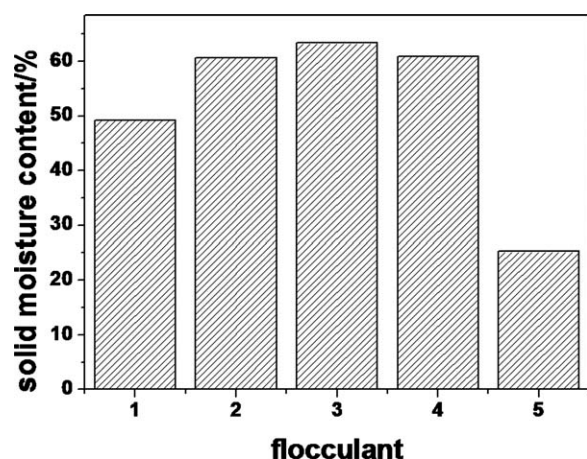


Figure 11 Comparison of flocculants.

tions were as follows: 1.5 g CS, 3.0 mL DMC, 6 g AM, pH = 6, 4 h, and CAN was 0.4% of AM (wt %), the reaction temperature was 30°C, 40°C, 50°C, 60°C, 70°C, and 80°C, respectively. The flocculent experiment results are shown in Figure 10.

Low temperature helped to carry out the grafting reaction smoothly. But high temperature could increase the probability of collision of the active centers, leading to chain termination. So the optimum reaction temperature was 60°C, and the corresponding SMC was 29.30%.

#### Orthogonal experimental design for optimum synthesis

Simply assembled of all the optimum conditions could not get the best condition. An orthogonal experimental design was used to determine the optimum conditions for CS-AM-DMC preparation. Table III shows the orthogonal experimental design.

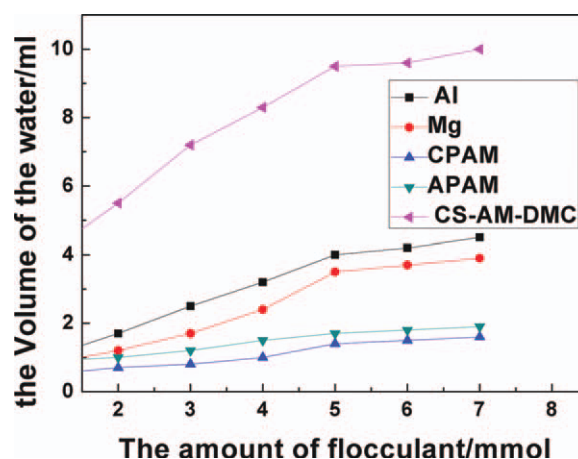


Figure 12 The amount of flocculant (mmol) and the relationship with the flocculation.

Table IV shows the optimum condition and the effect of the each factor.

The best flocculent property was obtained by using the optimum condition  $A_3B_2C_2D_3$ , which SMC was 25.23%.

#### Comparison of the flocculent property between commercial and prepared flocculants

Figure 11 showed that compared with the commercial flocculants, the prepared flocculant did better in waste drilling mud system.

Figure 12 showed that the amount of flocculant (m mol) and the relationship with the flocculation.

#### CONCLUSIONS

CS-AM-DMC copolymer flocculant was successfully prepared, and the optimum preparation conditions were investigated. Flocculent experiment showed that SMC of the mud reduced from 57.63% to 25.23% by using the optimum flocculant. The results indicated that the prepared CS-AM-DMC copoly-

mer flocculant had higher flocculent property than commercial products in waste drilling mud system.

#### References

1. Schwarz, S.; Jaeger, W.; Paulke, B.-R.; Bratskaya, S.; Smolka, N.; Bohrisch, J. *J Chem* 2007, 111, 8649.
2. Wang, F. H.; Zou, J.; Zhu, H.; Han, K. F.; Fan, J. T. *J Environ Prot* 2010, 1, 179.
3. You, L. J.; Lu, F. F.; Li, D.; Qiao, Z. M.; Yin, Y. P. *J Hazard Mater* 2009, 172, 38.
4. Beltrań-Heredia, J.; Sańchez-Martuń, J.; Solera-Hernańdez, C. *Ind Eng Chem Res* 2009, 48, 5085.
5. Li, Q.; Yue, Q. Y.; Sun, H. J.; Su, Y.; Gao, B. Y. *J Environ Manage* 2010, 91, 1601.
6. Chen, Y. X.; Liu, S. Y.; Wang, G. Y. *Chem Eng J* 2007, 133, 325.
7. Wei, Y.; Cheng, P.; Zheng, H. *Carbohydr Polym* 2008, 74, 673.
8. Bratskaya, S.; Schwarz, S.; Liebert, T.; Heinze, T. *Colloids Surf A: Physicochem Eng Aspects* 2005, 254, 75.
9. You, L. J.; Lu, F. F.; Zhong, D. L.; Qiao, M.; Yin, Y. P. *J Hazard Mater* 2009, 172, 38.
10. Hebeish, A.; Higazy, A.; El-Shafei, A.; Sharaf, S. *Carbohydr Polym* 2010, 1, 60.
11. Richard, J.; John, J.; Sylvester, N. D. *Ind Eng Chem Res* 1983, 22, 473.
12. Dragan, E. S.; Mihai, M. *Appl Mater Interfaces* 2009, 1, 1231.