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Synthesis of humic cationic polymer and the treatment of wastewater of oilfield

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ABSTRACT

Treating and reinjecting the wastewater of oilfield is a correct way to develop and use water resources at present. A novel-type humic cationic polymer was synthesized using humic acid (HA), dimethylamine (DMA), and epichlorohydrin (ECH) by aqueous solution polymerization. The optimal reaction conditions were determined. The reaction temperature was 65℃, the reaction time was 6.0 h, m (HA):m (ECH):m (DMA) = 1.0:13.9:15.0. The oil removal efficiency and viscosity reduction effects were investigated using the polymer-flooding wastewater of Daqing oilfield. The results showed that humic cationic polymer had good effect on viscosity reduction, polymer removal, and oil removal of the polymer-flooding wastewater. The wastewater after being treated can provide as reinjection water for chemical flooding, which also improve the utilization of the wastewater.

Keywords: Humic acid; Cationic polymer; Synthesis; Polymer-flooding wastewater

1. Introduction

Nowadays, many problems were encountered during the oilfield production processes, for example, the composition of the wastewater was very complex, which was produced by polymer flooding. Compared with the water flooding, polymer flooding had some difficulties such as higher oil content, higher solution viscosity, and serious emulsification problem [1–4]. Treating and reinjecting oilfield wastewater is a correct way to develop and use water resources at present. The keys of the solution polymer-flooding wastewater are to remove the residual polymers. The most useful solution is to use the cationic polymer as the water treatment agent which was added into the wastewater process of the polymer flooding. As one of the functional polymer materials, cationic polymers have been widely used in many fields [5–8]. Because the quaternary ammonium existed in the cationic polymers, they had good water solubility and strong flocculation ability. However, their production costs were relatively high [9].

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Humic acid (HA) comes from natural. So far all the structure of HA has been speculated. A typical humic substance was a mixture of many molecules; some are based on the matrix of the aromatic with phenolic and carboxylic substituents being connected together. A typical model of HA molecular structure was proposed by Stevenson [10], as shown in Fig. 1.

This is an organic macromolecule compound with many functions including hydrophilic, interfacial activities, cation-exchanging capacity, and adsorption dispersing ability. Phenolic and carboxylic groups were as the main functional groups, which can contribute to the surface charges and reactivities of humate substances. The adsorption capacity of HA is mainly created by the molecule which contains a large number of carboxyl and hydroxyl functional groups, especially to some polyvalent metal ions. It can be used in the process of wastewater treatments and wastewater containing heavy metal ions and various organic compounds [11,12]. During the present oilfield production process, HA is widely used as the drilling fluid additives, such as the fluid loss agent, the anti-swelling agent, the viscosity reduction agent, and so on. The synthetic cationic polymers with epichlorohydrin (ECH) and dimethylamine (DMA) have a high cationic degree structure characteristic and low molecular weight. They have a large number of hydroxyl groups. HA is a kind of non-specific molecular structure mixture which contains many reactive functional groups, such as carboxyl group, hydroxyl group, and phenolic hydroxyl group [13]. This provides a theoretical possibility to synthesize the cationic polymer from HA by grafting polymerization processes.

In this paper, a novel type of humic cationic polymer was synthesized by aqueous solution polymerization processes, being combined with both the advantages of HA and quaternary ammonium salt cationic polymer. This paper studied the effects of the reaction time, the reaction temperature, the mass ratio of reactants, and the dosage of crosslinking agents. The optimum reaction conditions were determined by the experiments. The efficiency of the viscosity reduction, the polymer removal, and oil removal were especially investigated to the polymer-flooding wastewater of Daqing oilfield.

2. Experimental

2.1. Reagents and instruments

HA, T.P., Hegang Crane Ka humic acid Co. Ltd, in China; ECH, A.R., Tianjin large alum chemical reagent factory in China; DMA, A.R., (30–33%) Shenyang east China reagent factory in China; ethylenediamine, A.R., Harbin chemical reagent factory in China; tetraphenylborate, C.P., Tianjin large alum chemical reagent factory in China; ethanol, A.R., Harbin chemical reagent factory in China; hydrochloric acid., A.R., Harbin chemical reagent factory in China; strong aqua (28%), A.R., Tianjin large alum chemical reagent factory in China; FLUKO high shear emulsifying machine; Brookfield DVII$^+$ viscometer (USA). DZF-6030A Vacuum drying oven, Shanghai Yiheng Technology Co. Ltd, China; DS-101S collection hot constant temperature heating magnetic stirrer, Gongyi City Instrument Co. Ltd, China.

2.2. Experimental process

HA and DMA were added according to the proportion *m* (HA):*m* (ECH):*m* (DMA) = 1.0:13.9:15, and stirred in a three-necked flask, which was placed in an ice water bath below 10.0℃ and equipped with a reflux condenser. ECH was added dropwisely in the

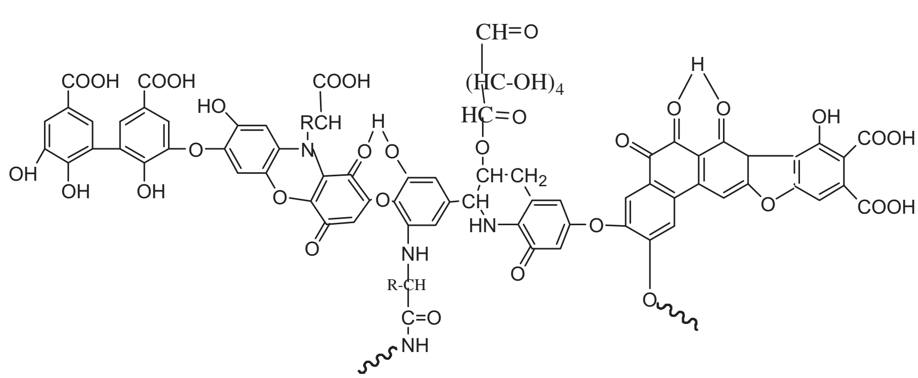

Fig. 1. A typical model of humic acid structure.

three-necked flask by a dropping funnel in 2.0 h. Then, the certain amount of ethylenediamine was added. The reaction temperature was raised to 65℃ and kept for 6 h until the viscosity of the reaction system was no longer increased. The final product was made after purified by ethanol, and dried under vacuum for 24 h at 65℃. The synthetic route of the product was shown in Fig. 2.

2.3. Cationic degree and apparent viscosity determination of the product

Cationic degree can describe the cationic performance of polymer. In this paper, the cationic degree of the product was determined by the method for sodium tetraphenylborate [14]. The cationic degree of the product was 4.6 mmol g^{-1}.

Because viscosity-average molecular weight is related to the intrinsic viscosity of the polymer, so the viscosity of the polymer is used to characterize the molecular weight of the polymer. The greater the viscosity is, the greater the molecular weight is. In this paper, the apparent viscosity of the product was determined by Brookfield viscosity to characterize the molecular weight and degree of polymerization of the product. The apparent viscosity of the product was 18.9 mPa s at 6.0 r/min, 20℃.

3. Results and discussions

3.1. Determination of optimal synthetic process

3.1.1. Effects of reaction time

The viscosity of reaction system increased obviously at the beginning of reaction at 2.0 h and remained stable after reacting for 6.0 h. This agreed with the characteristics that the polymerization conversion increased with the extension of reaction time [15]. Therefore, the optimal reaction time was determined at 6.0 h.

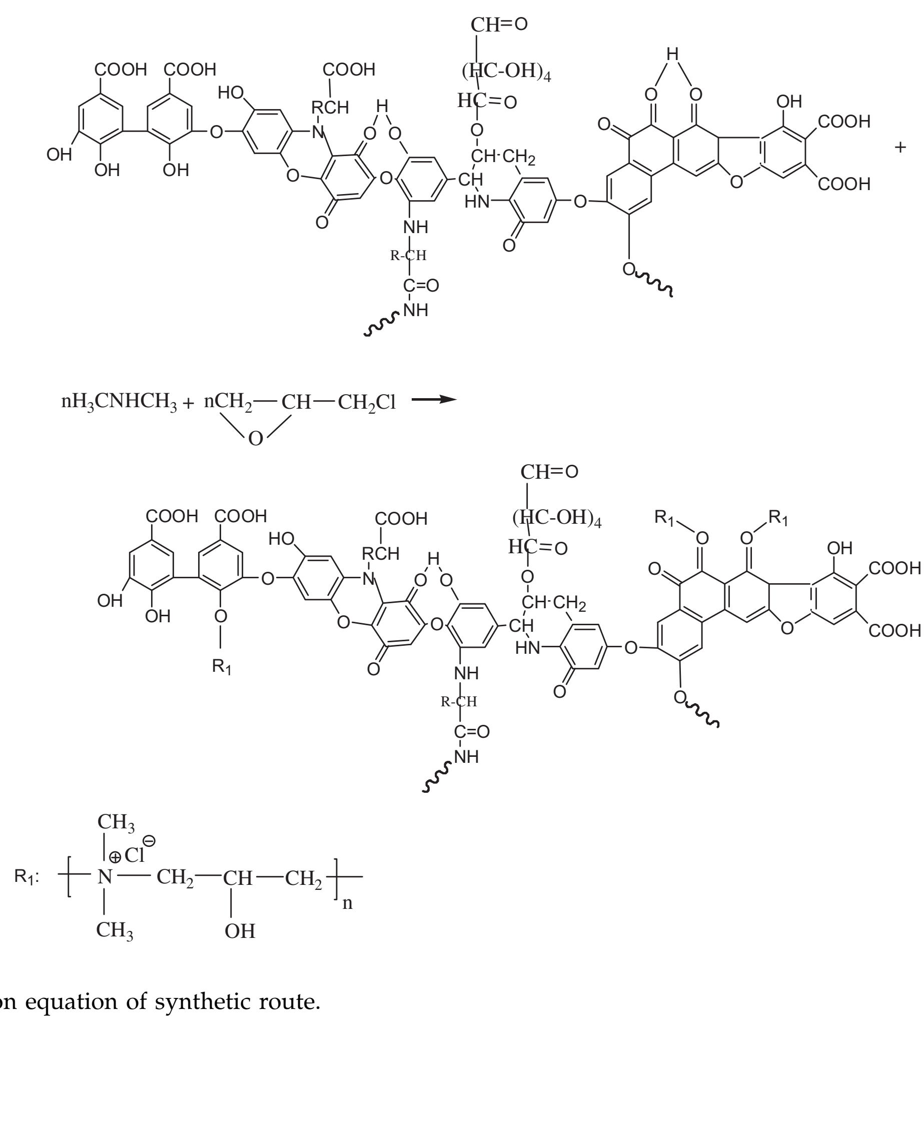

Fig. 2. The reaction equation of synthetic route.

3.1.2. Effects of the reaction temperature

As the reaction time was 6.0 h and *m* (HA):*m* (ECH):*m* (DMA) = 1.0:13.9:15.0, the relationship of the cationic degree and apparent viscosity of the product on different reaction temperatures were determined and shown in Fig. 3.

When the reaction temperature was less than 65.0℃, the higher reaction temperature led to the higher cationic degree and apparent viscosity of the product, the polymerization rate was increased accordingly. But when the reaction temperature was above 65.0℃, the higher temperature led to the smaller cationic degree and apparent viscosity of the product.

Because the higher temperature may initiate the homopolymerization of the ECH, the equivalent ratio of the ECH and DMA should be decreased during the quaternary ammonium reaction. The optimal reaction temperature was determined at 65.0℃.

3.1.3. Effect of the mass ratio of the materials

The cationic degree and apparent viscosity of the product were determined by changing the mass ratio of HA, ECH, and DMA at 65.0℃ in 6.0 h; the amount of ethylenediamine crosslinking agent dosage was 3% in all reactions, as shown in Fig. 4.

Fig. 4 showed both the cationic degree and apparent viscosity increased before *m* (HA):*m* (ECH):*m* (DMA) = 1.0:13.9:15.0; after that point, the viscosity increased slowly, but the cationic degree decreased gradually. So the optimal mass ratio of the materials was determined at *m* (HA):*m* (ECH):*m* (DMA) = 1.0:13.9:15.0.

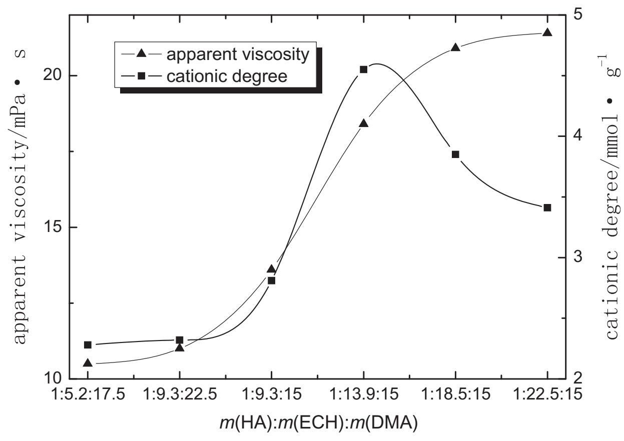

Fig. 4. Effect of the mass ratio of the materials on cationic degree and apparent viscosity.

3.1.4. Effect of ethylenediamine amount

The cationic degree and the apparent viscosity were measured by changing the amount of ethylenediamine (on the total mass ratio of ECH and DMA) at 65℃ in 6 h, the mass ratio of the materials was *m* (HA):*m* (ECH):*m* (DMA) = 1.0:13.9:15.0, and the results were shown in Fig. 5.

When the amount of the ethylenediamine was lower than 3%, the higher amount was, the higher cationic degree and apparent viscosity of the product was. But the amount of the ethylenediamine was above than 3%, the cationic degree fell quickly while the apparent viscosity increases rapidly. In this case, the polymerization reaction entered to the final stage prematurely. This suggests that the water solubility of the product is weakened. Accordingly, the optimal

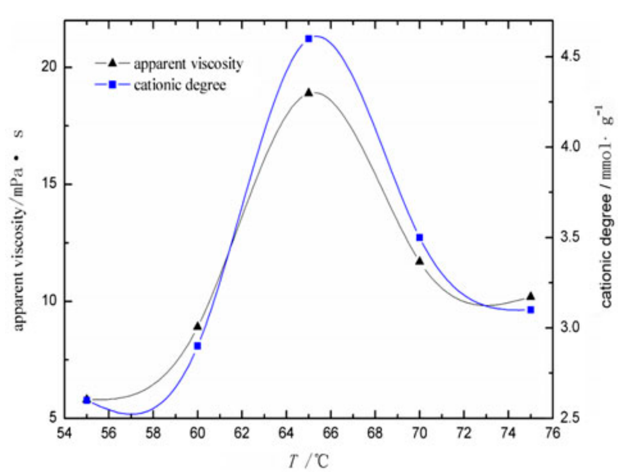

Fig. 3. Effects of temperature on the cationic degree and apparent viscosity.

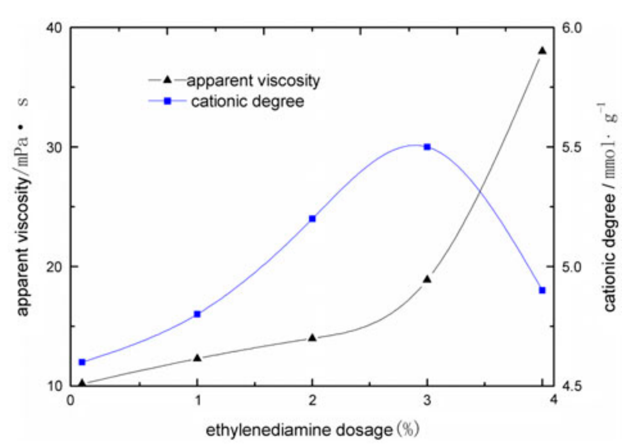

Fig. 5. Effect of ethylenediamine amount on viscosity and cationic degree.

Table 1
Effect of product dosage to the wastewater

Addition amount of the product (mg L^{-1})	0	150	175	200	225	250	275	300	325	350
Wastewater apparent viscosity (mPa s)	8.4	3.4	3.0	2.7	2.4	2.1	1.7	1.5	1.2	1.1
HPAM content in wastewater (mg L^{-1})	972	577	534	477	421	336	242	164	102	94
Oil content in wastewater (mg L^{-1})	1,040	533	490	440	402	367	328	289	264	247

amount of the crosslinking agent (ethylenediamine) was determined at 3%.

3.2. Properties of the product on the polymer-flooding wastewater treatment of Daqing oilfield

The polymer-flooding wastewater of Daqing Oilfield was being used in this paper, the oil content was 1,040 mg L^{-1}, the polymer content was 972 mg L^{-1}, the total salinity was 4,512 mg L^{-1}, pH value was 7.4, and the viscosity of the wastewater was 8.4 mPa s. The viscosity of the solution was determined using BROOK FIELD DVII^{+} viscometer at 6.0 r/min and 45.0℃.

According to the methods of SY/T 5281-2000 "Bottle test method for the demulsification performance of crude oil demulsifiers" [16], the amount of dehydration and the interfacial state were tested and recorded under different factors, then the dehydration rate was calculated.

3.2.1. Effect of the addition amount on the properties of the product

Different amounts of the product were added in the wastewater at 45.0℃. The effect of the product on the wastewater was studied. Wastewater viscosity, the oil content, and HPAM content were recorded. The results were given in Table 1. The zero dosage of product means that the wastewater without the addition of the product.

As shown in Table 1, with the increase in the amount of the product in the wastewater, the oil content and the HPAM content decreased gradually. The apparent viscosity of the wastewater decreased gradually too. As the addition amount reached to 325 mg L^{-1}, the HPAM content in the wastewater fell to about 102 mg L^{-1}. The oil content fell to 264 mg L^{-1} in the wastewater. In this moment, the rate of the polymer removal was 89.5% and the rate of the oil removal was 74.6%. The apparent viscosity decreased to 1.2 mPa s. Then, the amount of the product increased, and the apparent viscosity showed slight changes.

HPAM can hinder the aggregation of the oil droplets and form a viscoelasticity protective film, which is unfavorable to the oil–water separation. Within the certain range, as the polymer concentration increased, the oil content and the apparent viscosity in the wastewater increased too. Table 1 shows that the product had strong capability of the adsorption and coagulation. It could adsorb and agglomerate HPAM effectively, and also destroy the original interfacial film between the HPAM and oil droplets. The product can accelerate the flotation and agglomeration of the oil droplets. Thus, the content of oil and the polymer decreased in the wastewater. On the other hand, HA molecules had many active functional groups according to their molecular structure. The molecular weight of the product was increased after humic grafting polymerization, and the structure became more complex, as shown in Figs. 1 and 2, which can adsorb and capture certain polymers such as HPAM. The cationic HA owns large amounts of positive charges, and the HPAM molecules had negative charges, so they can attract each other to achieve the adsorption. These played an important role in promoting the oil–water separation of the wastewater.

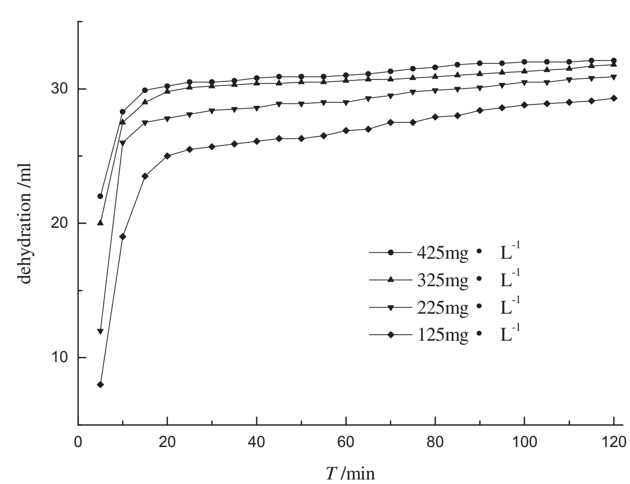

Fig. 6. Effect of product concentration on dehydration rate.

Table 2
Effect of the temperatures on the wastewater treatment

Temperature (°C)	Oil content (mg L^{-1})	Polymer content (mg L^{-1})	Apparent viscosity (mPa s)
25	562	330	2.9
30	517	273	2.6
35	459	217	2.2
40	361	158	1.7
45	236	89	1.1
50	221	84	1.1

3.2.2. Effect of the product concentration on the properties of the product

Products with different concentrations were added into 50-mL wastewater at 45.0°C. The effects of product concentration on dehydration rate were shown in Fig. 6.

As shown in Fig. 6, as the product concentration and time increased in 0–15 min, the amount of the dehydration increased quickly. The content of oil and polymer decreased rapidly in the wastewater, and the apparent viscosity decreased rapidly. As the product concentration was 325 mg L^{-1}, the dehydration amount was 30.2 mL, and the dehydration rate was 91.71%. The curve of the product concentration with 425 mg L^{-1} was almost the same with the curve of the product concentration with 325 mg L^{-1}. The dehydration rate tended to stable after 15 min.

3.2.3. Effect of the temperature on the properties of the product

As the product concentration was 325 mg L^{-1}, the effect of the temperatures on the wastewater was shown in Table 2.

In Table 2, as the temperature increased, the content of oil and polymer and the apparent viscosity decreased in the wastewater. Because the stability of the wastewater containing oil can be influenced greatly by the temperature, raising the temperature can not only reduce the interfacial tension of oil–water interface but also enhance the molecular thermal motion of oil droplets. This will weaken the emulsion membrane and accelerate the coalescence of oil droplets [17]. These are helpful to the oil–water separation of wastewater.

Above 50°C, the properties of the wastewater changed little. As the temperature increased higher in the wastewater, the diffusion of oil droplets was accelerated, and the adsorption on the interface of the oil droplets weakened. And also this reduced the oil surface electrostatic neutralization capacity while increased the electrostatic repulsive force between the oil droplets. These led to the reduction of the oil removal rate [18]. We observed as the temperature increased, the oil–water separation was accelerated, and the oil–water interface became clear. This showed that humic cationic polymer had good effects of demulsification.

4. Conclusions

Humic cationic polymer was synthesized using HA and DMA. The effect of the reaction time, the reaction temperature, the mass ratio of reactants, and the amount of crosslinking agents was investigated. The optimal reaction conditions were determined, the reaction temperature was 65°C, the reaction time was 6 h, *m* (HA):m (ECH):*m* (DMA) = 1.0:13.9:15.0. The effect of the product on the wastewater of Daqing oilfield was studied. Especially, the effect of different conditions, such as time, the temperature, and the amount of the product on the viscosity reduction, the polymer removal, and oil removal was tested. Results showed that the viscosity reduction, the polymer removal, and oil removal increased to a relatively high value in 15 min, 325 mg L^{-1} product concentration, and below 50°C. This showed that humic cationic polymer had good effects of the viscosity reduction, the polymer removal, and oil removal on the polymer-flooding wastewater of Daqing oilfield. Oil–water interface was clear. Treated oilfield wastewater can provide as the flooding reinjection water to improve the utilization of the wastewater.

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