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β-Cyclodextrin modified anionic and cationic acrylamide polymers for enhancing oil recovery

Changjun Zou[a,*], Pinwen Zhao[a], Ju Ge[a], Ying Lei[b], Pingya Luo[c]

[a] *School of Chemistry and Chemical Engineering, Southwest Petroleum University, No. 8 Xindu Road, Chengdu 610500, PR China*
[b] *Natural Gas Purification Plant, Oil and Gas Field Southwest Branch of CNPC, Suining 629000, PR China*
[c] *State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, PR China*

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ABSTRACT

Both of acrylamide and allyl-β-cyclodextrin are utilized to react with acrylic acid and dimethyl diallyl ammonium chloride respectively to synthesize the novel anionic acrylamide polymer and cationic acrylamide polymer by redox free-radical copolymerization. The structures of copolymers are characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. Subsequently, the copolymers are evaluated on several aspects such as optimum polymerization conditions, intrinsic viscosity, interfacial tension and stability experiments. It is found that the anionic and cationic acrylamide polymers containing cyclodextrin moieties show better performances on interfacial tension, salt resistance, temperature tolerance, viscosification property and shear resistance than that of polyacrylamide. By the comprehensive comparison and analysis, the anionic polymer is more conductive to decrease the interfacial tension for the tertiary oil recovery process, while the cationic polymer is more suitable for enhancing oil recovery in high-temperature and high-mineralization oilfield.

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six to eight glucose units linked by 1,4-α-glucosidic bonds forming a torus-shaped ring structure (Del Valle, 2004; Douhal, 2004; Lebrilla, 2001; Loftsson & Duchêne, 2007; Saenger et al., 1998), wherein the β-cyclodextrin (β-CD) containing seven glucose units has been widely used in organic chemistry and polymer chemistry (Ding, Li, Jia, Deng, & Yang, 2011; Liu, Yu, Zhang, Guo, & Liu, 2008; Ritter & Tabatabai, 2002). The primary hydroxyl groups and the secondary hydroxyl groups in β-CD form a complex network of intramolecular hydrogen bonds to give a polar hydrophilic outer shell and a relatively hydrophobic cavity (Li & Purdy, 1992), thus β-CD can generate host/guest inclusion complexes by inclusion with suitable hydrophobic molecules (Deng, He, Wu, & Yang, 2008; Klink & Ritter, 2008; Koontz & Marcy, 2003; Li & Loh, 2008). Meanwhile, β-CD has also been widely used for the preparation of hydrogels and nanogels (Daoud-Mahammed et al., 2008; Wang et al., 2007). However, despite the enormous applications of β-CD mentioned above, no report has been found yet in literature to be focused on using β-CD moieties for the preparation of chemical flooding in tertiary oil recovery.

In recent years, the ultrahigh molecular weight polyacrylamide (PAM) is being paid more attention because of its good capability of thickening, flocculation and rheological behavior (Barari, Abdollahi, & Hemmati, 2011; Caulfield, Qiao, & Solomon, 2002; Huang, Lipp, & Farinato, 2001). This kind of polymer is widely used in all fields of national economy, especially in oil industry, water treatment and papermaking industry (Chelaru, Diaconu, & Simionescu, 1998; Jha, Agrawal, Mishra, & Rai, 2001; Lu, Liu, & Sun, 2002; Siyam, 2001). However, non-ionic or anionic or cationic type PAM series reveal many weaknesses in practical application, such as weak improvement of oil-water-rock interfacial tension, low salt resistance and degradation and so on (Vinu & Madras, 2008; Y. Wang et al., 2003; Zhou et al., 2010). Therefore, introducing functional groups to modify PAM has become the research focus of domestic and foreign workers (Lu, Yao, Lin, Cao, & Chen, 2003; Shashkina et al., 2003).

In this study, we synthesize the novel anionic and cationic polymers—P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC). Because of the special β-CD cavity structure, the polymer host has good weak inclusion relations with surfactant to form the host/guest systems. Host–guest theory considers that host molecules can not only identify but also selectively assemble and release guest molecules (Griessl, Lackinger, Edelwirth, Hietschold, & Heckl, 2002; Messner, Kurkov, Jansook, & Loftsson, 2010; Schneider, 1991). So the surfactant can be easily recognized by oil phase molecules on the interface between displacing fluid and oil phase. Since the cavity of polymer is oleophylic, it is more

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[*] Corresponding author. Tel.: +86 02883037327; fax: +86 02883037305.
E-mail address: changjunzou@126.com (C. Zou).

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likely to be stimulated by oil molecules, and releases surfactant. Thereby the interfacial tension among oil, water and rock reduces. In addition, owing to the bulky rigid β-CD structure, P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) can effectively resist the high temperature of strata and the shearing effect of clay. We believe that the present anionic and cationic acrylamide polymers will be of great importance for enhancing oil recovery, and other more potential applications can also be expected from them.

In this paper, the novelty of the present work is that the cyclodextrin moiety containing torus-shaped ring structures and the special property of "hydrophilic outer and hydrophobic cavity" has been introduced into the acrylamide polymers in order to improve the stability in high-temperature, high-mineralization and high-shear oilfield conditions to achieve the purpose of enhanced oil recovery.

2. Experimental

2.1. Materials

In this paper, β-CD, acrylamide (AM), sodium acrylate (NaAA), dimethyl diallyl ammonium chloride (DMDAAC), ethylenediaminetetraacetic acid disodium (EDTA), potassium persulfate, sodium bisulfite, cetyltrimethylammonium chloride, ethanol, dimethyl sulfoxide (DMSO), sodium hydroxide, acetone and allyl bromide were analytical reagent grade. All of them were purchased from the Kelong Chemical Reagent Factory (Chengdu, China). The viscosity-average molecular weight of polyacrylamide (Kelong, Chengdu) was 1.2×10^6 g/mol, and allyl-β-cyclodextrin (A-β-CD) was prepared in laboratory.

2.2. Synthesis of A-β-CD

A certain amount of β-CD was placed in a beaker, and completely dissolved by the addition of an appropriate amount of DMSO. Then sufficient sodium hydroxide as a catalyst was added into the beaker, which was put on a magnetic stirrer to mix approximately 1 h. After that, a certain amount of allyl bromide was slowly dropped into the beaker in the ice water bath (0–10 °C). The reaction was ended until appearing massive yellow precipitate. The solvent was removed by vacuum filtration, and then a white powder was obtained after washing with a large amount of acetone. Because of high hygroscopicity, the product shall be kept under the sealed condition.

2.3. Synthesis of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC)

The copolymerization was the typical redox free-radical polymerization, which could be divided into the elementary reactions of chain initiation, chain growth and chain termination, and might even be accompanied by the chain transfer reaction. The prepared solution with some monomer feed ratio of AM/A-β-CD/NaAA or AM/A-β-CD/DMDAAC was added in the assigned 250 ml beaker, and the beakers were stirred on a six joint magnetic stirrer. Then a certain number of EDTA, potassium persulfate and sodium bisulfite was respectively added in. After evenly mixed, the beakers were put into a thermostat to start the polymerization. Then, transparent gelatinous materials were obtained after 4–6 h, which shall be washed for several times with ethanol until precipitating white block solids. The solids were further dried in an oven at 50 °C for 48 h. The synthetic process of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were shown in Fig. 1. Furthermore, to obtain the optimum polymerization conditions, the effects of different factors on the apparent viscosity were investigated by the means of single variable method in the copolymerization process.

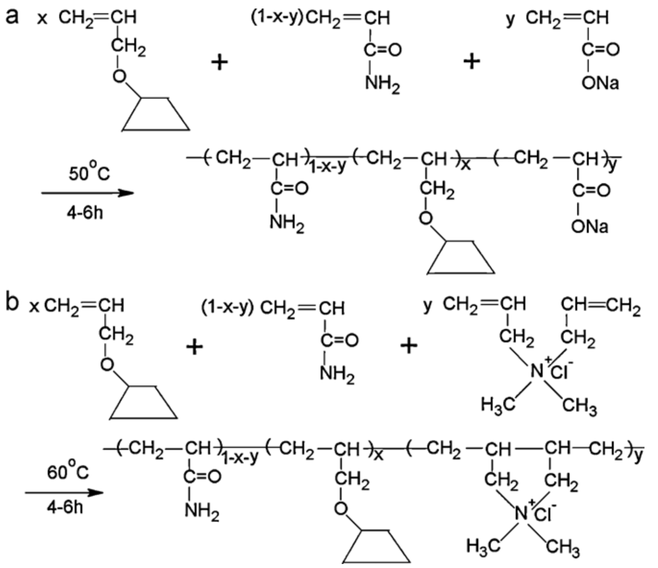

Fig. 1. The synthetic processes of copolymers, (a) P(AM/A-β-CD/NaAA), reaction conditions: AM:A-β-CD:NaAA = 70:5:25; pH 8.0; time = 4–6 h; temperature = 50 °C; (b) P(AM/A-β-CD/DMDAAC), reaction conditions: AM:A-β-CD:DMDAAC = 85:5:10; pH 8.0; time = 4–6 h; temperature = 60 °C.

2.4. Characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were recorded on a Nicolet Nexus 470 spectrometer (on KBr tablets) in the optical range of 400–4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}.

The surface morphologies of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were observed by the scanning electron microscope (SEM; PHLIPS-XL30, Holland).

2.5. Intrinsic viscosity of polymers

The NaCl solution of 1.0 mol/L was prepared as the solvent. The Ubbelohde capillary viscometer was utilized to measure the relative, specific and reduced viscosity of the polymer solutions from the flow times of solutions (Zeynali, Rabii, & Baharvand, 2004). The viscosity measurements were carried out at a constant temperature of 30 °C. The solution temperature was controlled by a thermostat in a circulating bath and monitored by a thermometer. The stopwatch with a resolution of 0.1 s was used to measure the flow times. To obtain the intrinsic viscosity, the following equations were necessary.

$$\eta_r = \frac{t}{t_0} \tag{1}$$

$$\eta_{sp} = \eta_r - 1 \tag{2}$$

$$\frac{\eta_{sp}}{C} = [\eta] + k_H[\eta]^2 C \tag{3}$$

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} \tag{4}$$

where t was the flow time for sample solution (s), t_0 was the flow time for 1.0 mol/L NaCl solution (s), C was the initial concentration of sample solution (g/mL), η_r was the relative viscosity, η_{sp} was the specific viscosity, $[\eta]$ was the intrinsic viscosity (mL/g), and k_H was the Huggins coefficient.

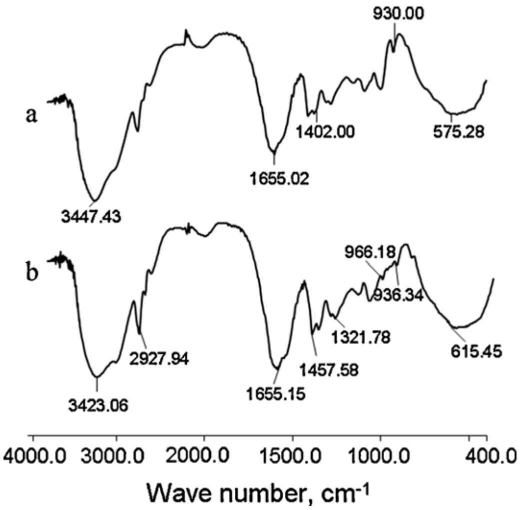

Fig. 2. The FT-IR spectra of polymers, (a) P(AM/A-β-CD/NaAA), polymerization conditions: AM:A-β-CD:NaAA = 70:5:25; pH 8.0; time = 4.8 h; temperature = 50 °C; (b) P(AM/A-β-CD/DMDAAC), polymerization conditions: AM:A-β-CD:DMDAAC = 85:5:10; pH 8.0; time = 5.6 h; temperature = 60 °C.

2.6. *Interfacial tension experiments*

In order to have a clear understanding for the process of enhancing oil recovery, the interaction between polymer and surfactant was researched. Interfacial tension experiments of the mixed system of polymer and surfactant were carried out. The interfacial tensions of the mixtures were measured through ring-detachment method using the ZL-3000 automated tensiometer with a precision of ±0.1 mN/m. The tensiometer was adjusted through ultra pure water at room temperature.

2.7. *Stability experiments*

In this paper, the properties of PAM, P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) solutions were evaluated through stability experiments of salt resistance, temperature tolerance, viscosification property and shear resistance. The performance comparisons among the three polymers were carried out by investigating the variations of apparent viscosity with mineralization and temperature. Viscosity measurement was performed with the NDJ-8S viscometer. The measurement error was 5%, and the rotor speed was 60 rpm. The viscometer was adjusted by standard silicon oil at room temperature.

3. Results and discussion

3.1. *Characterization of polymers*

3.1.1. *Structures of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC)*

The chemical structures of the P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) respectively prepared by optimum conditions were determined by Fourier transform infrared spectrometer. The FT-IR spectra were shown in Fig. 2.

It could be seen from Fig. 2a that strong absorption peaks were observed at 3447.43 cm^{-1} and 1655.02 cm^{-1}, which were attributed to the stretching vibrations of N–H and C=O in –CONH$_2$ group, respectively. 1402.00 cm^{-1} was associated with the –COO^{-} group. It could be inferred that the polymer contained the structures of AM and NaAA. Furthermore, the peaks at 930.00 cm^{-1} and 575.28 cm^{-1} corresponded to the skeleton vibrations of allyl-β-cyclodextrin, which indicated that the structure of A-β-CD was well maintained in the anionic acrylamide polymer.

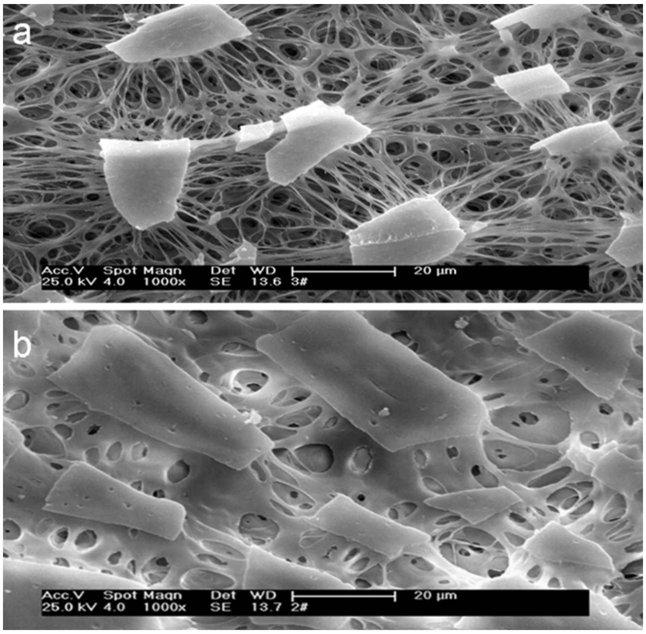

Fig. 3. The SEM images of polymers, (a) P(AM/A-β-CD/NaAA), polymerization conditions: AM:A-β-CD:NaAA = 70:5:25; pH 8.0; time = 4.8 h; temperature = 50 °C; (b) P(AM/A-β-CD/DMDAAC), polymerization conditions: AM:A-β-CD:DMDAAC = 85:5:10; pH 8.0; time = 5.6 h; temperature = 60 °C.

The typical absorption peaks of AM and A-β-CD were present in Fig. 2b. Besides, it was noticeable that new absorptions were found in Fig. 2b. The stretching vibration peak at 2927.94 cm^{-1} was associated with C–H bond of methyl and methylene in DMDAAC, and 1457.58 cm^{-1} was assigned to the bending vibration absorption peak of double methyl bonded with N^{+} (Jia & Zhang, 2010). The bands at 1321.78 cm^{-1} and 966.18 cm^{-1} were respectively attributed to the symmetric bending vibration peak for methyl and the stretching vibration absorption peak for quaternary ammonium (–(CH$_2$)N(CH$_3$)$_2$Cl) (J.X. Wang et al., 2003). Thus, a conclusion could be reached that cationic acrylamide polymer contained the structures of AM, A-β-CD and DMDAAC.

3.1.2. *Surface morphologies of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC)*

The scanning electron microscopy images of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were shown in Fig. 3, which indicated that the anionic and cationic polymers were typical gel-network structures. The reasons could be that several hydroxyl groups of β-CD were replaced by allyl groups, and then polymerization of A-β-CD with AM and NaAA or DMDAAC formed the supramolecular chain aggregates; on the other hand, the intermolecular or intramolecular association and cross-linking reaction between gels led to a formation of three-dimensional network structure, and the incorporation of the bulky cyclodextrin molecules caused a large number of cavities inside the network. By the comparison between Fig. 3a and b, it could be seen that P(AM/A-β-CD/NaAA) owned the better three-dimensional net microstructure. Namely, under the same conditions, the structure of anionic polymer was more conductive to include oil reservoir molecule.

3.2. *Optimum polymerization conditions*

To obtain the optimum polymerization conditions, we investigated the effects of temperature, pH, total content of monomers

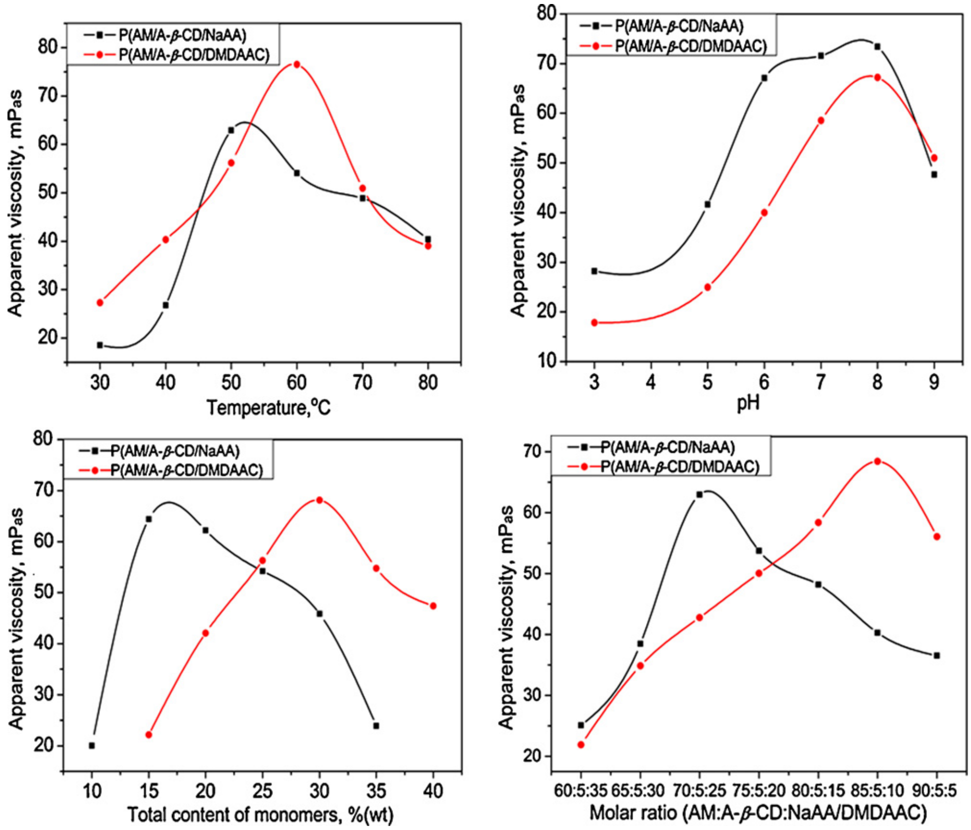

Fig. 4. The effects of temperature, pH, total content of monomers and molar ratio of monomers on apparent viscosity.

as well molar ratio of monomers on the apparent viscosity of the polymers by the single variable method under the experimental conditions. Firstly, keeping the content of potassium persulfate 0.05 wt%, sodium bisulfite 0.1 wt% and EDTA 0.05 wt%, and then ensuring the temperature, reaction time, monomer feed ratio and total content of monomers as fixed values, the pH of the system was changed to investigate the influence of pH on the polymerization. Based on the above approach, the effects of other factors on the polymerization were studied. The results were shown in Fig. 4.

It could be seen from Fig. 4 that the preparation conditions of anionic and cationic polymers were very different. As the initial temperature was too low, the activity of the initiator was so little that the required activation energy could not be reached. When the temperature rose to an excess, the initiator brought about a large number of free radicals so that the chain termination rate constant increased much more than the chain growth rate constant in the system, which led to the apparent viscosity of the polymer decrease at last. The maxima at 50 °C for P(AM/A-β-CD/NaAA) and at 60 °C for P(AM/A-β-CD/DMDAAC) were probably the results of the minima of chain transfer rates under the experimental conditions. So, the optimum initial temperature of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) was 50 °C and 60 °C, respectively. The initial temperature shall be as low as possible under a sufficient free radical concentration in the polymerization reaction system, which was good for enhancing average molecular weight of polymer and lowering production costs.

In the polymerization process, pH value had an important influence on the property of the copolymer. Under the acidic conditions, free radicals generated by the initiator would attack C–H radicals on the tertiary carbon, resulting in the cross-linking between carbon bonds. Meanwhile, the polymerization was prone to bring to the intramolecular and intermolecular imidization reactions to form the branches and cross-linking products. When the pH value was more than 10, the hydrolysis reaction of acrylamide was more likely to take place. Therefore, it was conducive to obtain the high molecular weight polymer under the slight alkaline condition of pH value at 8.0.

As the polymerization reaction rate was proportional to the total monomer concentration, when the concentration was much low, the polymerization rate was very little. Moreover, the increase of cage effect of solvent led to the decrease of the initiator efficiency and the decline of the conversion rate. Therefore, the viscosity of polymer was remarkably low. With the increase content of monomers, polymerization rate became rapidly, and the final monomer conversion also rose. However, when the content of monomers continued to increase to an excess, the reaction released too much heat to distribute, which resulted in the increasing chance of chain transfer reaction and the decrease of the polymer molecular weight. So, the optimum total content of monomers for P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) was 17.5 wt% and 30 wt%, respectively.

In the experiment, AM, A-β-CD and NaAA/DMDAAC were respectively acted as the main monomer, functional monomer and hydrophilic monomer. The content of A-β-CD was kept a constant, and the proportion of AM and NaAA/DMDAAC was changed. On the one hand, the charge density of polymer increased due to the addition of NaAA/DMDAAC monomer, which increased the electrostatic repulsion of charged groups. Therefore, the polymer chains were more extended, and the effective volume of polymer increased. On the other hand, the repulsion of polymer molecules circumvented the relative movement of molecules, which increased the viscosity of polymer. However, with the increase of NaAA/DMDAAC to an excess, owing to the lower reactivity of NaAA/DMDAAC molecules, the monomer conversion ratio reduced leading to the decrease of the apparent viscosity. In addition, the small viscosity at low content of NaAA/DMDAAC was probably the result of the

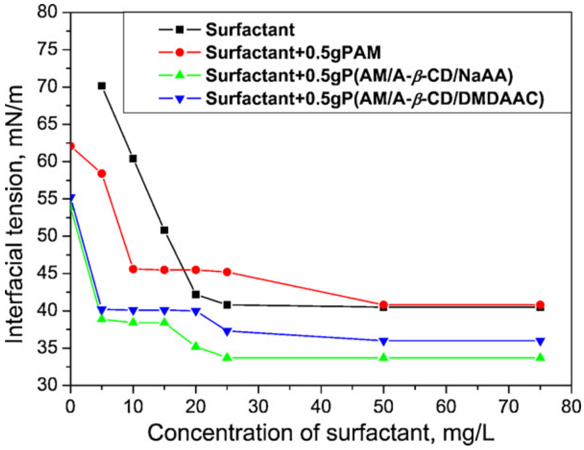

Fig. 5. The interfacial tensions between polymers and surfactant.

cross-linking reaction of acrylamide. So the optimum monomer feed ratio of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) was 70:5:25 and 85:5:10, respectively.

In addition, we investigated the influence of reaction time on the apparent viscosity of polymers. The apparent viscosities of anionic and cationic polymers first increased with the rising reaction time, and then respectively kept stable values after 4.8 h and 5.6 h. By purification and drying, the mass ratios of final product and original total monomers were calculated. Then, the final conversion rates of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were obtained, which were 82.7% and 78.8%, respectively.

3.3. *Measurement of intrinsic viscosity*

In this paper, the 1.0 mol/L NaCl solution and the polymer sample solutions were repeatedly measured for three times, and the difference among each time was not more than 0.2 s. The final flow times were determined by the arithmetic mean values.

By plotting the reduced viscosity (η_{sp}/c) of polymer solutions against concentration, extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity $[\eta]$ was determined. The intrinsic viscosity of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were 412.3 mL/g and 635.8 mL/g, respectively.

It could be seen that the intrinsic viscosity of P(AM/A-β-CD/DMDAAC) was larger than that of P(AM/A-β-CD/NaAA) under the same conditions. Namely, the cationic polymer owned a greater degree of polymerization, which was probably caused by the higher cross-link degree. In addition, the different size and shape of the dissolved polymer as well as the nature of polymer solution had a very important influence on the intrinsic viscosity. The more the intrinsic viscosity, the higher the thickening degree, and the better advantage for enhancing oil recovery.

3.4. *Interfacial tension experiments*

The aqueous solutions with the same quality of PAM, P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were respectively prepared to 2.0 g/L. Then the equivalent cetyltrimethyl ammonium chloride acted as a surfactant was added in each polymer solution. The interfacial tensions of pure surfactant solution and the mixed solutions were measured at 25 °C, and the results were shown in Fig. 5.

As shown in Fig. 5, there were big turning points in the interfacial tension curves with the increasing surfactant concentration. Namely, the addition of polymer could affect the process of the interfacial tension reduction of surfactant solution. Compared with the pure surfactant solution, there was equilibrium interfacial tension in the mixed solution during the appropriate surfactant concentration, and finally reached to a lower value. Additionally, it could be known that the decreasing order of the final interfacial tension was the mixture of surfactant and PAM, the pure surfactant, the mixture of surfactant and P(AM/A-β-CD/DMDAAC), the mixture of surfactant and P(AM/A-β-CD/NaAA). So it could be indicated that P(AM/A-β-CD/NaAA) had a better performance for the decrease of interfacial tension. These phenomena could be understood as below. There existed a starting point for the surfactant associating to the polymer in the critical concentration, and the surfactant could not improve the surfactant activity during the process, then the equilibrium interfacial tensions emerged. Owing to the selectivity and self-assembly of β-CD cavity, the equilibrium interfacial tension of the mixture of ion polymer and surfactant was lower than that of PAM mixture. With the saturation of the association process, the surfactant activity increased, and the interfacial tension decreased again. The difference of the final interfacial tension for P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) was probably attributed to the intramolecular or intermolecular cross-link degree, and the molecular association of cationic polymer also might be a factor.

3.5. *Stability experiments*

3.5.1. *Salt resistance of polymers*

The aqueous solutions of P(AM/A-β-CD/NaAA), P(AM/A-β-CD/DMDAAC) and PAM were respectively prepared with deionized water, and then the salt solutions of the three polymers were prepared with NaCl, $CaCl_2$ and $MgCl_2$. The concentrations of all the solutions were 2.0 g/L. The total salinity of each salt solution was 1.6×10^5 mg/L, and each salt solution contained 2000 mg/L Ca^{2+}, 1000 mg/L Mg^{2+}, and the rests were Na^+ and Cl^-. The apparent viscosities were measured at 25 °C, and then the viscosity retention rate of each polymer solution was calculated. The results were that the viscosity retention rate of PAM, P(AM/A-β-CD/NaAA), and P(AM/A-β-CD/DMDAAC) was 22.72%, 45.64%, and 65.95%, respectively.

It could be seen that the apparent viscosities of polymers would decrease in the salinity of 1.6×10^5 mg/L, and the viscosity retention rates of anionic and cationic polymers were higher than that of PAM. Moreover, the viscosity retention rate of cationic polymer was approximately 1.5 times as large as anionic polymer. These behaviors could be understood as below. Charge neutralization would occur between Ca^{2+}, Mg^{2+} and $-COO^-$, and even led to precipitate, which reduced the viscosities of anionic polymer. However, the addition of divalent metal cations increased the polarity of cationic polymer, and the synergy effect between metal cations and quaternary ammonium ion also strengthened the electrostatic repulsion of macromolecule chains. These behaviors circumvented chains curl in the high salinity condition, and maintained the viscosity of cationic polymer. Therefore, it was known that A-β-CD acting as a salt insensitive functional monomer increased the salt resistance of polymers, and the salt resistance of P(AM/A-β-CD/DMDAAC) was better than that of P(AM/A-β-CD/NaAA).

3.5.2. *Temperature tolerance of polymers*

Under the conditions that the concentration of polymer solution was 3.0 g/L and the total salinity was 1.6×10^5 mg/L, the effect of temperature on the apparent viscosity of polymer salt solution was investigated. The viscosities of PAM, P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were measured at different temperatures. The results were illustrated in Fig. 6.

It could be seen that the apparent viscosities of polymer salt solutions decreased with the increasing temperature, but the decreasing rates were obviously different. The apparent viscosity of PAM started to decrease sharply at 30 °C, while that of anionic

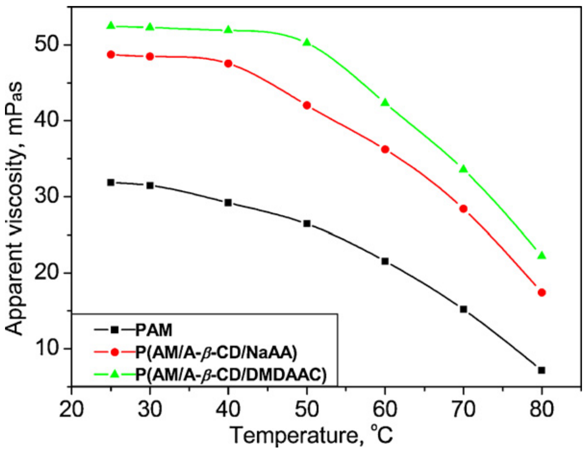

Fig. 6. The comparison of temperature tolerance among polymers.

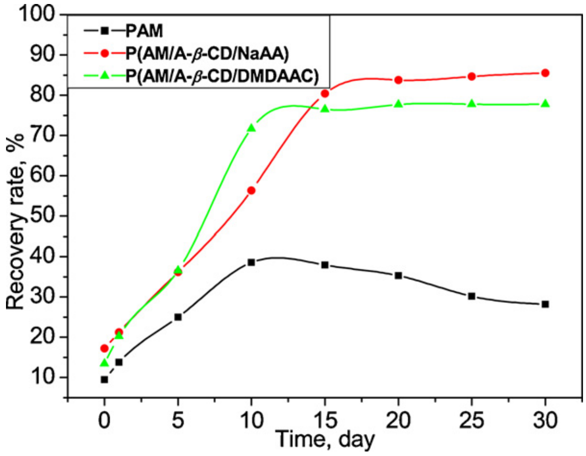

Fig. 8. The comparison of shear resistance among polymers.

and cationic polymers were 40 °C and 50 °C, respectively. Furthermore, at the same temperature the apparent viscosity decreasing order was P(AM/A-β-CD/DMDAAC), P(AM/A-β-CD/NaAA), PAM. The reason was that A-β-CD owned a torus-shaped ring structure increasing the rigidity of the polymer chains. Moreover, the structure had a synergy effect with internal 5-membered ring of cationic polymer. These meant P(AM/A-β-CD/DMDAAC) had a stronger ability to maintain its structure at high temperature.

3.5.3. *Viscosification properties of polymers*

The aqueous solutions of P(AM/A-β-CD/NaAA), P(AM/A-β-CD/DMDAAC) and PAM were prepared with different concentrations. Then the viscosification property of each polymer solution was investigated at room temperature, and the results were shown in Fig. 7.

It was clear from Fig. 7 that the apparent viscosities of polymer solutions increased with the rising concentrations, and the viscosities of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were larger than that of PAM at the same condition. When the concentration of ion polymer was over 1500 mg/L, the viscosity increased significantly. The reasons were as follows. There were lots of groups containing charges in the polymer macromolecule chain, and the intramolecular repulsion as well as the hydration of polar groups kept macromolecule main chain in loose stretching. When the concentration reached to a certain degree, the space network structures formed in the polymer. Then the hydrodynamic volume rose, and viscosification property increased. However, because of the large steric hindrance, the viscosification property of cationic polymer was relatively smaller. Besides, the sudden increase of viscosity for anionic polymer at 2500 mg/L was probably attributed to the intermolecular association.

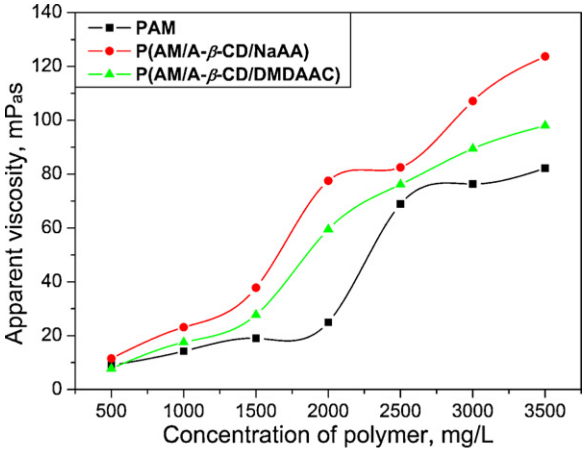

Fig. 7. The comparison of viscosification property among polymers.

3.5.4. *Shear resistance of polymers*

Under the conditions that the concentration of polymer solution was 3.0 g/L and the temperature was 25 °C, polymer solutions were stirred for 30 min in the high shear rate of 100 s^{-1}. The effects of mechanical degradation on PAM, P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) aqueous solutions were investigated. The apparent viscosities of polymers were measured at the different time, and then the shear resistance recovery rates were calculated. The results were illustrated in Fig. 8.

As shown in Fig. 8, the shear resistance recovery rates of anionic and cationic polymers first increased and finally maintained stable with the rising time. However, there existed an interesting phenomenon in PAM due to its viscosity first increased and then decreased with the rising time. On the one hand, the bulky β-CD moieties made the polymer macromolecule keep the rigidity. On the other hand, owing to the effects of electrostatic forces, hydrogen bonding and van der Waals forces, the physical association was generated in polymer molecules, which had a certain degree of strength but was reversible. In addition, the decreasing viscosity of PAM might be resulted from the generation of the hydrolysis process. Therefore, a conclusion could be obtained that the shear resistances of P(AM/A-β-CD/NaAA) and P(AM/A-β-CD/DMDAAC) were better than that of PAM.

4. Conclusions

In the paper, to introduce the inclusion function of β-cyclodextrin into acrylamide polymers, the novel anionic and cationic polymers were synthesized by aqueous free-radical copolymerization. Furthermore, FI-IR and SEM characterizations confirmed the synthetic products contained the structures of AM, A-β-CD and NaAA or DMDAAC. Through the experiments of interfacial tension and stability, it was found that the introduction of β-cyclodextrin moieties could effectively compensate the weakness of PAM to improve the performance; on the other hand, it added new features to enhance the application fields in oilfield. P(AM/A-β-CD/NaAA) was suited to decrease the interfacial tension for the tertiary oil recovery process, while P(AM/A-β-CD/DMDAAC) had the wider potential application for enhancing oil recovery in high-temperature and high-mineralization oilfield.

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