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A Water-soluble Antimicrobial Acrylamide Copolymer Containing Sulfitobetaine for Enhanced Oil Recovery

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Here we report a novel acrylamide copolymer with antimicrobial property as enhanced oil recovery chemical. The copolymer was synthesized using acrylamide (AM), acrylic acid (AA) and 2-((2-(acryloyloxy)ethyl)dimethylammonio)ethyl sulfite (ADMES) via oxidation-reduction initiation system. Subsequently, the copolymer AM/AA/ADMES was evaluated and characterized on several aspects such as IR, ^{1}H NMR, intrinsic viscosity and dissolubility. And the AM/AA/ADMES solution exerted remarkable thickening ability, salt tolerance abilitiy and viscoelasticity. In addition, the rheological properties, temperature resistance ability and long-term stability of AM/AA/ADMES were systematically investigated in the presence of sulfate-reducing bacteria and the relatively low viscosity loss could be obtained comparing with partially hydrolyzed polyacrylamide. On the basic of core flooding experiments, AM/AA/ADMES was exhibited a valuable prospect that was 10.5 of resistance factor, 4.6 of residual resistance factor and up to 11.0% of enhanced oil recovery.

Introduction

Currently, enhanced oil recovery (EOR) technology by means of polymer flooding has been getting more attention by many countries.[1-3] And the oil field experiments applying polymer flooding to enhance crude oil recovery in the main oil regions of many countries, such as Daqing oilfield (China), North Burbank oilfield (America) and Sanand oilfield (India), have obtained some achievements.[4-7] Nevertheless, new problems arise with the use of polymers in high-temperature and high-salinity reservoirs.[8] Hydrolysis, degradation, and the coil of molecular chain in brine of the commonly used polymers, such as partially hydrolyzed polyacrylamide (HPAM), result in reducing oil recovery efficiency.[8,9] Therefore, many different water-soluble polymers are synthesized and studied, which contributes significantly to providing theoretical foundation for application of these polymers utilized in EOR.[10]

Most research in water-soluble polymers for EOR has focused on water-soluble polymers containing hydrophobic,[11,12] rigid ring,[13,14] zwitterionic groups and so on. The introduction of these special functional groups benefits the improvement of the performances on thickening ability, temperature resistance, salt tolerance and anti-shear property.[8] Recently, polymers containing zwitterionic groups have been most extensively studied due to their special solution properties, outstanding antimicrobial properties, as well as providing the capability of further function.[15-19] Polyampholytes that were synthesized via conventional free radical polymerization were first reported in 1950s.[20-23] Later, McCormick et al. demonstrated that the polyampholytes displayed a higher intrinsic viscosity than HPAM at higher ionic strength, which was explained by a probable result of the inherent bulkiness of the polymer unit that restricted the rotational freedom of the polymer chain.[24,25] Thus, polyampholytes are used for many technology processes such as EOR, papermaking, water treatment, biomedical technology, and so on.[26-29]

Meanwhile, polymers containing zwitterionic groups, such as sulfobetaine, phosphobetaine and carboxybetaine have been the subject of considerable interest and extensive research in resisting bacterial growth in aqueous solution as well as on the surface.[30-33] As we know, polymers for enhanced oil recovery were dissolved in oilfield water where a large group of sulfate-reducing bacteria (SRB) grow. SRB are a large group of anaerobic microorganisms that obtain their energy for growth using sulfate as a terminal electron acceptor.[34-37] SRB have been recognized as the most important contributors to microbiological induced corrosion (MIC) leading to severe industrial problems.[38,39] For example, SRB can cause pipeline corrosion and oil well perforation, promote the growth and reproduction of other types of bacteria, and produce large amount of sticky mud blocking pipeline.[40] In addition, the presence of SRB could cause degradation of HPAM, which has significant influence on recovery efficiency. Currently, bactericide commonly used is non-oxidizing bactericide dosing dodecyl dimethyl benzyl ammonium chloride (1227), but the resistance arises after long-term using. Ma and Guan et al. synthesized bactericide containing sulfitobetaine groups, which exhibited excellent bactericidal efficiency.[41,42]

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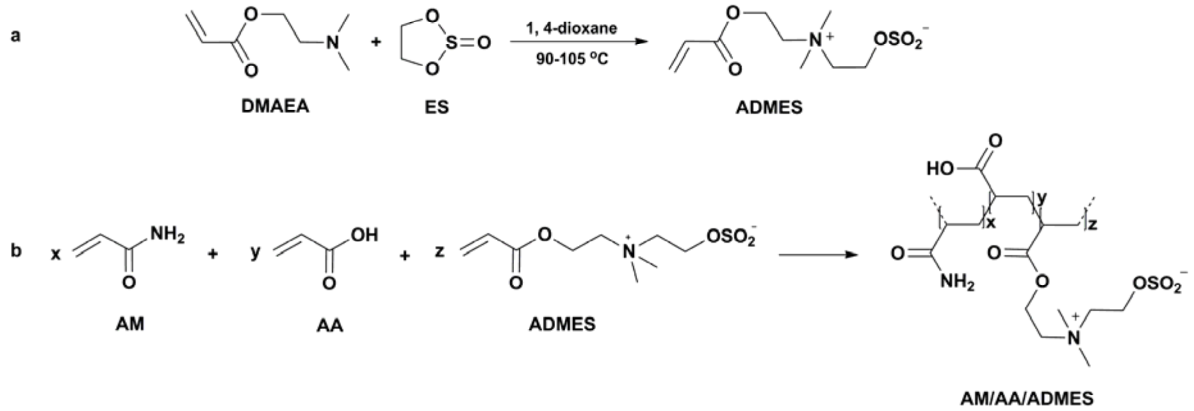

Scheme 1 The synthesis routes of ADMES (a) and AM/AA/ADMES (b).

On the basis of these findings and research, development of antimicrobial polymer is critical for polymer flooding. In this paper, a novel antimicrobial sulfitobetaine-based acrylamide copolymer AM/AA/ADMES was synthesized by copolymerization of acrylamide (AM), acrylic acid (AA), and 2-((2-(acryloyloxy)ethyl) dimethylammonio)ethyl sulfite (ADMES) as EOR chemical. The thickening property and salt tolerance ability of AM/AA/ADMES were investigated in deionized water. In addition, the loss in apparent viscosity of AM/AA/ADMES and HPAM was studied in the presence of SRB under different conditions, such as varying copolymers concentration, different pH, changing temperature and predetermined testing time. In order to obtain the rheological properties of the copolymers, shear resistance ability and viscoelasticity were researched in the presence of SRB, which provides a theoretical perspective for EOR ability of the copolymers. Then, mobility control ability and EOR ability of AM/AA/ADMES were investigated by core flooding experiments, and the copolymer AM/AA/ADMES was expected to have remarkable ability to enhance oil recovery in high-temperature and high-salinity reservoirs.

Experimental

Materials

Acrylamide (AM), acrylic acid (AA), $NaHSO_3$, $(NH_4)_2S_2O_8$, NaOH, NaCl, $MgCl_2·6H_2O$, $CaCl_2$, thionyl chloride ($SOCl_2$), ethylene glycol, ethanol and 1, 4-dioxane were purchased from Chendu Kelong Chemical Reagent Company (Sichuan, China). 2-(Dimethylamino)ethyl acrylate (DMAEA) was purchased from Shanghai Jingchun Scientifical Co., Ltd. Theviscosity-average molecular weight of partially hydrolyzed polyacrylamide (HPAM, Daqing Refining and Chemical Company) was $8.0×10^6$. Ethylene sulfite (ES) was synthesized according to the reported method.[43]

Synthesis of compound ADMES

2-((2-(acryloyloxy)ethyl)dimethylammonio)ethyl sulfite (ADMES) was synthesized referring to the reported methods as shown in Scheme 1a.[43] Briefly, DMAEA was dissolved in 1, 4-dioxane and excess ES was added slowly at 90 - 105 °C. Reaction of DMAEA and ES was carried out under reflux for 2 h and TLC analysis using petroleum ether/ethyl acetate mixture (1:3 v/v) confirmed product purity. After the reaction was ended, reaction product was allowed to cool at room temperature and concentrated on a rotary evaporator. The final product was further purified by the recrystrllization method with acetonitrile. The white powdery solid ADMES were obtained. ADMES: ^1H NMR (400 MHz, D_2O, δ): 3.16 (*m*, 10H, $–C(O)OCH_2CH_2N^+(C\boldsymbol{H}_3)C\boldsymbol{H}_2–$), 3.54 (*t*, *J*=5.0 Hz, 2H, $–C(O)OCH_2C\boldsymbol{H}_2–$), 4.01 (*t*, *J*=2.4 Hz, 10H, $–CH_2C\boldsymbol{H}_2–OSO_2^-$), 4.54 (*t*, *J*=2.3 Hz, 2H, $–C(O)OC\boldsymbol{H}_2CH_2–$), 5.71 (*m*, 1H, $\boldsymbol{H}(H)C{=}CH–$), 5.96 (*m*, 1H, $CH_2{=}C\boldsymbol{H}–$), 6.37 (*m*, 1H, $H(\boldsymbol{H})C{=}CH–$). ^{13}C NMR (100 MHz, D_2O, δ): 52.07, 55.37, 58.56, 63.32, 66.21, 127.38, 131.94, 172.60.

Synthesis of AM/AA/ADMES

AM/AA/ADMES was synthesized via the aqueous solution copolymerization, and the synthesis route was shown in Scheme 1b. A certain amount of AM, AA and ADMES was dissolved in deionized water in 100 mL three neck round-bottom flask under a nitrogen atmosphere. The pH value of the reaction was adjusted by adding NaOH and the solution was kept in a water bath heater at a constant temperature. And then, the indicated loading of the initiator [$n((NH_4)_2S_2O_8)$: $n(NaHSO_3)$ = 1: 1] was added slowly into the copolymerization system. After that, the copolymerization was carried out at indicated temperature under a nitrogen atmosphere for 8 - 10 h. The final product was precipitated with ethanol and

Table 1 Copolymerization conditions of AM/AA/ADMES

Copolymer	pH	Initiator (wt%)	Temperature (°C)	Concentration (wt%)	Monomer (wt%)		
					AM	AA	ADMES
AM/AA/ADMES	8	0.2	35	20	50	48	2

dried overnight at 45 °C in a vacuum oven to obtain the corresponding copolymer AM/AA/ADMES. The copolymerization conditions were presented in Table 1 and the optimum of copolymerization conditions was seen in Supplementary Information.

Characterization

IR. The IR spectra of the samples was measured with KBr pellets using a WQF-520A IR Spectrophotometer (Beijing Reili Analytical Instrument Company) in the optical range of 4500 - 400 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}.

^{1}HNMR. The ^1H NMR spectra of the monomer ADMES and copolymer AM/AA/ADMES were recorded on a BRUKER AM 400 MHz Nuclear Magnetic Resonance Spectometer (Bruker Co., Switzerland) in D_2O.

Intrinicviscosity measurement. All solutions were prepared by dissolving a certain amount of copolymers in brine (1 mol/L NaCl), and the polymer concentration (C= 1.0, 0.67, 0.50, 0.33 and 0.25 mg/L) was adjusted by adding salt solution to the flask in a constant temperature bath at 30 °C. The specific viscosity (η_{sp}) was calculated by the following equation 1. And then the [η] of AM/AA/ADMES was the y-axis intercept of η_{sp}/C versus C relationship lineaccording to equation 2.

$$\eta_{\mathrm{sp}} = \frac{t - t_0}{t_0} \qquad (1)$$

$$[\eta] = \lim_{C \to 0} \eta_{\mathrm{sp}} / C \qquad (2)$$

where η_{sp} is the specific viscosity of polymer; t_0 is flux time of 1 mol/L NaCl brine, s; and t is flux time of polymer brine solution, s.

It was clear to see from the Fig. S1 (see Supplementary Information) that the intrinsic viscosity ([η]) of copolymer AM/AA/ADMES was 1162 mL/g.

Cultivation of SRB

Seed SRB bacteria were isolated from oilfield injection water collected from Tuha oil field in China. The culture was prepared with 4.0 mL sodium lactate, 1.0 g yeast extract, 0.5 g K_2HPO_4 in 1.0 L simulated formation water with total dissolved solid (TDS) of 9753 mg/L (Table 2). The culture solution was autoclaved at 121 °C for 30 min before use. SRB were cultivated in ready-prepared cultures on a shaking platform at 120 rpm for 7 days at 30 °C. SRB were counted by the most probable number (MPN) method.

Antimicrobial activity test

The monomer ADMES and 1227 (40 mg/L) were added into the medium containing SRB, respectively. The medium solution was incubated for 24 h at 30 °C. The medium without fungicide (blank sample) was placed at less than 5 °C for 24 h. Then SRB were counted by MPN method. The antibacterial rate (AR) is calculated with the following equation 3.

$$AR = (1 - N_1 / N_0) \times 100\% \qquad (3)$$

where N_1 was the colony forming units at 30 °C; N_0 was the colony forming units at less than 5 °C.

Water solubility test

The dissolution behaviour of the copolymer (16-20 meshes) was studied by measured the conductivity of the polymer solution at different time by DDS-11A conductivity meter (Shanghai Rex Xinjing instruments Co. Ltd, China). The relationship curve between electrical conductivity and dissolution time of the polymer solution was measured at 30 °C in order to study the water solubility of the copolymer.

Thickening ability and salt tolerance test

The thickening ability of the copolymer was explored by measurement of the apparent viscosity at different concentrations of polymers solution, and the salt tolerance of 2000 mg/L copolymer solution was investigated by NaCl, $CaCl_2$, and $MgCl_2$ with different concentrations. The apparent viscosity of the polymers solution was measured at 30 °C using Brookfield DV-Ⅲ Programmable Rheometer (Brookfield Co., America) with a 00# (6 rpm) or 62# (18.8 rpm) rotor.

Concentration test

To investigate the effect of the copolymer concentration, SRB were seeded into 100 mL culture solution with different amount of copolymer. And the culture (3.0×10^3 CFU/mL SRB) was incubated for 7 days at 30 °C. Then theapparent viscosity of the culture solution with different concentration copolymer was measured at 30 °C using Brookfield DV-Ⅲ Programmable Rheometer (Brookfield Co., America) with a 00# (6 rpm) or 62# (18.8 rpm) rotor.

pH test

To assess the effect of pH, the cultures with 2000 mg/L copolymer and SRB (3.0×10^3 CFU/mL) at different pH were cultivated at 30 °C for 7 days. Then the culture solution was measured at 30 °C to obtain the apparent viscosity.

Temperature test

To evaluate the effect of SRB at different temperature on apparent viscosity, the cultures with 2000 mg/L copolymer and SRB (3.0×10^3 CFU/mL) were incubated at different temperature for 7 days, and then the apparent viscosity of the copolymer was determined by HAAKE MARS Ⅲ Rheometer (Haake Technik Co., Germany) at shear rate of 7.34 s^{-1}.

Rheology experiments and viscoelasticity

SRB (3.0×10^3 CFU/mL) in the culture solution with 2000 mg/L

Table 2 Ions composition of TDS

Inorganic ions	Na^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Cl^-	TDS
Content (mg/L)	3452	165	260	69	305	15	5487	9753

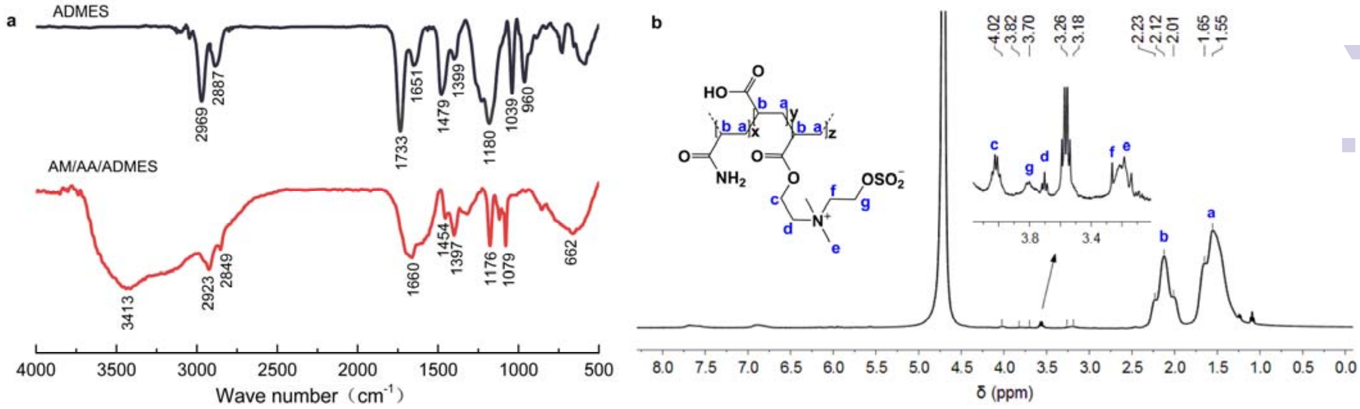

Fig. 1 (a) IR spectra of ADMES and AM/AA/ADMES, (b) ^{1}H NMR spectra of AM/AA/ADMES.

copolymer were incubated at 30 °C for 7 days. The apparent viscosity was measured by HAAKE MARS Ⅲ Rheometer (Haake Technik Co., Germany) to in the range of 7.34 to 1000 s^{-1} shear rates at 30 °C. And the elastic modulus (G’) and viscous modulus (G”) were determined by HAAKE MARS Ⅲ Rheometer to obtain the viscoelasticity property of the copolymer.

Long-term stability

SRB (3.0×10^3 CFU/mL) in the culture with 2000 mg/L copolymer were cultivated at 60 °C in condition of seal for 30 days to obtain the long-term stability behavior. The apparent viscosity of the copolymer was measured at different time using Brookfield DV-Ⅲ Programmable Rheometer (Brookfield Co., America) with a $00^{\#}$(6 rpm) or $62^{\#}$ (18.8 rpm) rotor.

Mobility control ability test

The mobility control ability of the polymer solutions was characterized by the resistance factor (RF) and the residual resistance factor (RRF).[44] The core used in the core flooding tests was stainless steel (500 mm in length and 25 mm in inner diameter) and packed with quartz sand (80-100 mesh, porosity: 22.8%, penetration: 820×10^{-3} μm^2). The sand was washed with 18% hydrochloric acid solution and then with a massive amount of water until the pH value reached 7. The copolymer solution was dissolved in simulated formation water with TDS of 9753 mg/L (Table 2). The brine and polymers solutions prepared with the brine were injected at 2.0 mL/min by the ISCO 260D syringe pump and the injection pressure was recorded by a pressure sensor. Experiments were carried out at 85 °C. The RF was defined by the following equation 4, and the RRF is calculated with the following equation 5:

$$RF = \frac{P_p / Q_p}{P_{ws} / Q_{ws}} \tag{4}$$

$$RRF = \frac{P_{wf} / Q_{wf}}{P_{ws} / Q_{ws}} \tag{5}$$

where P_p is stable pressure when injecting polymer solution, MPa; Q_p is injecting rate when injecting polymer solution, mL/min; P_{ws} is stable pressure when saturating water, MPa; and Q_{ws} is injecting rate when saturating water, mL/min; P_{wf} is stable pressure when water flooding, MPa; and Q_{wf} is injecting rate when water flooding, mL/min.

Enhanced oil recovery test

The EOR ability of these polymers solution (2000 mg/L) prepared with simulated formation water (Table 2) was studied. Each polymer flooding test was preceded by water flooding and followed by subsequent water flooding at 85 °C. The water flooding was conducted with brine at 3 mL/min until the water content exceeded 98%. The polymer flooding and subsequent water flooding were conducted at 1 mL/min. The value for enhanced oil recovery (EOR) was determined by the following equation 6:

$$EOR = H_1 - H_2 \tag{6}$$

where H_1 is the oil recovery of polymer flooding and H_2 is the oil recovery of water flooding.

Results and discussion

IR

IR spectra of ADMES and AM/AA/ADMES were shown in Fig. 1a. The IR spectra of ADMES exhibited the following characteristic peaks. The peaks at 2969 cm^{-1} and 2887 cm^{-1} was due to the stretching vibration of C-H in the methyl and methylene groups. The peak at 1733 cm^{-1} was assigned to stretching vibration of C=O. The characteristic absorption peak at 1651 cm^{-1} was the result of the stretching vibration of C=C. In addition, the peaks at 1479 cm^{-1} and 1399 cm^{-1} were the bending vibration peaks of C-H. The characteristic peaks at 1180 cm^{-1} and 1039 cm^{-1} indicated the presence of S=O. The IR spectra of AM/AA/ADMES presented the expected characteristic peaks. The peak at 3413 cm^{-1} was attributed to the stretching vibration peak of N-H. 2923 cm^{-1} and 2849 cm^{-1} was assigned to the stretching vibration of C-H of methyl and methylene. The peak at 1660 cm^{-1} was the characteristic peaks of C=O. And the characteristic absorption peaks at 1176 cm^{-1} and 1079 cm^{-1} corresponded to the stretching vibration of S=O. As expected, the IR spectra indicated the successful copolymerization of AM, AA and ADMES.

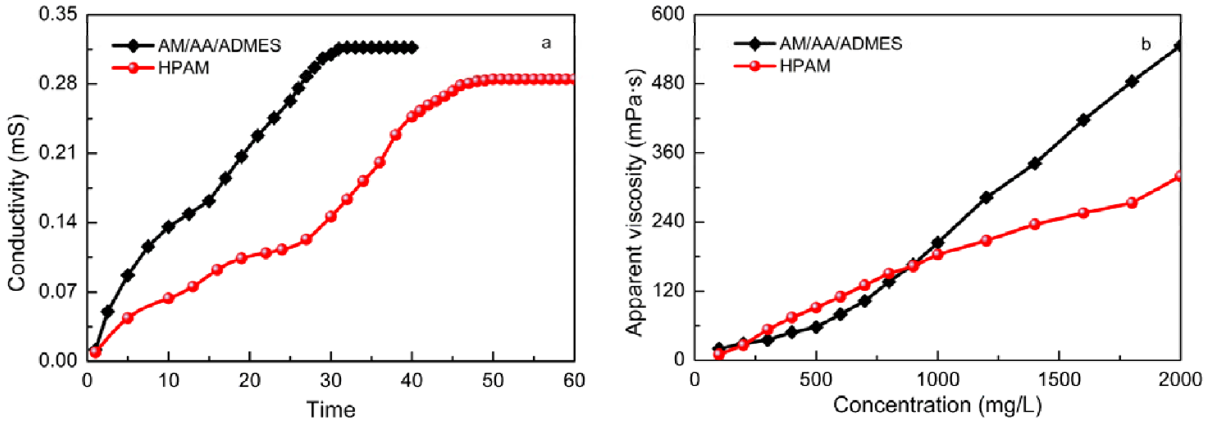

Fig. 2 (a) Dissolution time of AM/AA/ADMES and HPAM, (b) Thickening ability of AM/AA/ADMES and HPAM.

^{1}H NMR

The ^{1}H NMR spectra of AM/AA/ADMES was displayed in Fig. 1b. In the ^{1}H NMR spectra of the copolymer AM/AA/ADMES, the chemical shift at 1.55-1.65 ppm was assigned to the signal of protons of -C$\boldsymbol{H}_2$- groups in the polymeric main chain. The signal of protons at 2.01-2.23 ppm was due to -C$\boldsymbol{H}$- groups in the polymeric main chain. In the expanded region, The peak at 3.14-3.18 ppm was related to the signal of protons of -CH$_2$-N$^+$(C$\boldsymbol{H}_3$)$_2$-CH$_2$-OSO$_2^-$ groups of the ADMES functional monomer in the copolymer. The relevant signal of protons with -N$^+$(CH$_3$)$_2$C$\boldsymbol{H}_2$-CH$_2$-OSO$_2^-$ groups in the copolymer appeared at 3.26 ppm. The signal at 3.68-3.70 ppm indicated the existence of -COO-CH$_2$-C$\boldsymbol{H}_2$-N$^+$(CH$_3$)$_2$CH$_2$- groups. The chemical shift of protons at 3.80 ppm was due to -C$\boldsymbol{H}_2$-OSO$_2^-$ groups of the ADMES functional monomer in the copolymer. The signal of protons at 4.01-4.02 ppm showed the presence of -COO-C$\boldsymbol{H}_2$- groups. Therefore, the structure of the copolymer AM/AA/ADMES was consistent with the original design by ^{1}HNMR analysis.

Antimicrobial activity of monomer ADMES

The antimicrobial activity results were shown in Table 3. The antibacterial rate of ADMES (92.5%) was lower than that of 1227 (99.9%). The result showed that ADMES exerted obvious antimicrobialactivity. The introduction of ADMES could contribute to resistance of degradation of the copolymer by SRB, which was due to that the adhesion of cationic charge groups to the microbe cell resulted in the death of microbes.[45]

Water solubility

The dissolution behaviour of the polymer was studied using conductometric technique. The polymer solution possessed certain power of conduct electricity when polymer containing ion groups was dissolved in deionized water.[46] The results were illustrated in Fig. 2a. The conductivity of these polymer solutions was small in the early stage, and then with time increasing, the conductivity of the polymer increased due to the increasing of the dissolved quantity. Finally the conductivity tended to be constant and the conductivity of the polymer AM/AA/ADMES and HPAM when they were dissolved completely in deionized water was 0.317 mS and 0.285 mS, respectively. The dissolving time of AM/AA/ADMES was 32 min, which was shorter than that of HPAM (50 min).

Thickening ability

To investigate the relationship between the apparent viscosity and concentration, the apparent viscosity as a function of concentrati in deionized water was determined for the polymers AM/AA/ADMES and HPAM as shown in Fig. 2b. For AM/AA/ADMES, as the concentration increased, a dramatic increase in the apparent viscosity was observed. The apparent viscosity of 546.5 mPa·s cou have been obtained under the concentration of AM/AA/ADMES solution with 2000 mg/L, while the apparent viscosity of 2000 mg/L HPAM solution was 320.2 mPa·s. The electrostatic attraction between the different polymer molecular chains was able to contribute to that the apparent viscosity of AM/AA/ADMES was higher than that of HPAM. In comparison with HPAM, the copolymer AM/AA/ADMES showed better thickening ability.

Salt resistance

The influence of salt on the copolymer AM/AA/ADMES and HPAM solution (2000 mg/L) was measured under different salts concentration. Then the change trend of the apparent viscosity to salt concentration was shown in Fig. 3. It was obvious that the apparent viscosity of copolymer solution decreased with the increase of salt concentration. At first stage, a large decreasein the apparent viscosity was observed. The influence, the reduction of intramolecular electrostatic repulsion with the addition of salt, resulted in the weakening of shrinkage degree of the polymer chain. The addition of small molecular electrolyte can weaken intra-anionic electrostatic repulsion, which led to the coil of the polymer

Table 3 Antimicrobial activity of monomer ADMES

Compound [a]	Colony forming union (CFU/mL)[b]	Antibacterial rate (%)
Blank sample	1.0×10^3	-
ADMES	7.5×10^1	92.5
1227	0.4×10^0	99.9

[a] Cultivation conditions: reagent dosages = 40 mg/L, time = 24 h.

[b] Colony forming union was measured after 24 h.

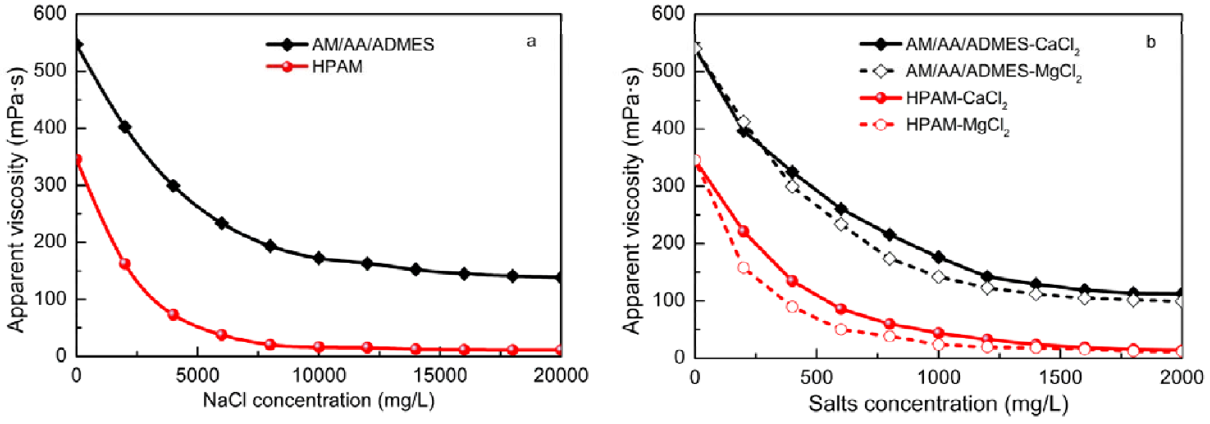

Fig. 3 Salt resistance of AM/AA/ADMES and HPAM, (a) effect of NaCl, (b) effect of $CaCl_2$ and $MgCl_2$.

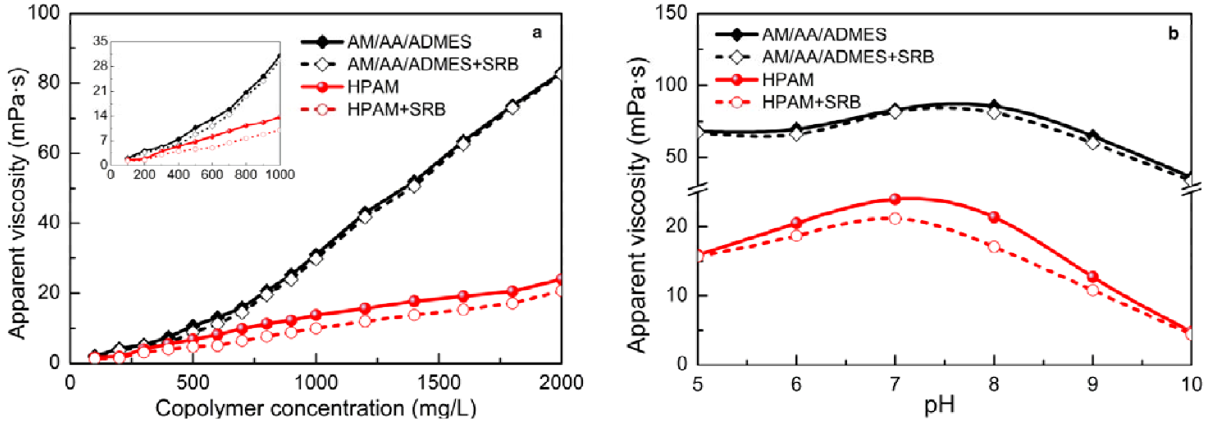

Fig. 4 (a) Effect of concentration and SRB on apparent viscosity of AM/AA/ADMES and HPAM solution, (b) Effect of pH and SRB on apparent viscosity of AM/AA/ADMES and HPAM solution.

molecular chain. As the salt concentration was further increased, a slight decrease in solution apparent viscosity was observed. For the copolymer AM/AA/ADMES, the viscosity retention rate of 25.3% (Fig. 3a), 20.9% and 18.4% (Fig. 3b) could be obtained under the concentration of 20 000 mg/L NaCl, 2 000 mg/L $CaCl_2$ and 2000 mg/L $MgCl_2$, respectively. In coparision with HPAM, AM/AA/ADMES possessed better salt resistance, which might be due to that the interaction between zwitterionic groups and salts could weaken influence of salts on shrinkage degree of the copolymer chain.

Effect of concentration and SRB

The effect of SRB on apparent viscosity of the copolymer solution with different concentration solution was also investigated. When the copolymer solution was seeded by SRB, the apparent viscosity of the copolymer solution displayed a declining trend. SRB could use the copolymer as the sole carbon source to grow, which promoted the copolymer degradation leading to the decreasing viscosity.[47] As shown in Fig. 4a, the apparent viscosity of HPAM reduced obviously under the concentration from 300 to 1000 mg/L because SRB were suitable to grow under these concentrations. The decreased viscosity loss was attributed to the reduced growth of SRB with the increase of concentration.[48] The obtained maximum loss in apparent viscosity was up to 30.9% at 500 mg/L. On the contrary, the changes in apparent viscosity of AM/AA/ADMES solution were extremely small. The only viscosity loss of 13.2% was obtained under the concentration of 400 mg/L and the AM/AA/ADMES solution with 2000 mg/L had little loss of the apparent viscosity. The extraordinary antibacterial property was ascribed to the presence of the betaine groups in the copolymer.[30]

Effect of pH and SRB

The effect of pH on apparent viscosity of 2000 mg/L copolymer solution was studied to obtain the results shown in Fig. 4b. HPAM and AM/AA/ADMES were insoluble under the condition of the relatively low pH due to the uncharged nature.[49] As the pH changed to 5 from 8, the degree of ionization of the carboxylic acid in the polymer was reduced. The extension of polymer chain was limited which caused the low apparent viscosity. With further increasing of pH, a sharp decrease was observed in apparent viscosity of two polymers. At relatively high pH, the intermolecular repulsion led to reduction in apparent viscosity with increasing of ionic strength.

As shown in Fig. 4b, the loss of the apparent viscosity was relatively less under the acidic or alkaline condition because the copolymer solutions at pH of 7 and 8 were suitable for growth of SRB.

Nevertheless, AM/AA/ADMES solution at pH of 7 had little loss of the apparent viscosity, which was ascribed to the excellent antibacterial ability of AM/AA/ADMES.[30]

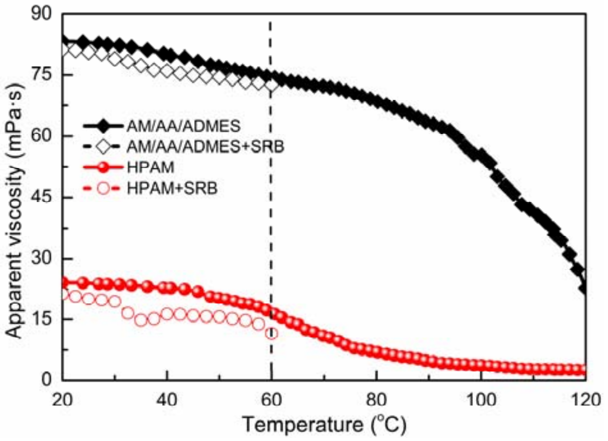

Fig. 5 Effect of temperature and SRB on apparent viscosity of AM/AA/ADMES and HPAM.

Effect of temperature and SRB

The effect of temperature on apparent viscosity of AM/AA/ADMES and HPAM solutions has been investigated from 20 to 120 °C at 7.34 s^{-1}, and the results were shown in Fig. 5. It was clear that the apparent viscosity of the copolymer decreased marginally under the temperature of 20 to 100 °C and decreased significantly within the range of 100 to 120 °C. The obtained viscosity retention rate of AM/AA/ADMES was up to 27.3% at 120 °C, which was much better than HPAM (retention rate 9.5%).

The investigation of the effect of SRB on apparent viscosity from 20 to 60 °C was displayed in Fig. 5. The apparent viscosity of two copolymers have both decreased comparing with the copolymers solution without been seeded with SRB at the same temperature. The HPAM solution displayed relatively great loss of 35.7% in apparent viscosity at 35 °C, while the change in apparent viscosity for AM/AA/ADMES was not obvious. The loss in apparent viscosity reached maximum that was only up to 4.7%. The obtained small changes in apparent viscosity were attributed to the antibacterial property of AM/AA/ADMES.

Effect of shear rate

The shear resistance ability of the polymers was investigated, and the results were shown in Fig. 6. It could be seen that the apparent viscosity of copolymer solution decreased sharply under a shear rate of 7.3 - 200 s^{-1} and slightly reduced under a higher shear rate of 500 - 1000 s^{-1}, suggesting a slight shear-thinning behavior. Compared with the polymer HPAM (viscosity retention rate: 3.3%), the copolymer AM/AA/ADMES had better viscosity retention rate (6.7%) at 1000 s^{-1}. The results indicated that the copolymer AM/AA/ADMES possessed good shear resistance ability.

When SRB were seeded into the copolymers solutions, the loss rate in apparent viscosity of AM/AA/ADMES solution was relatively low at the same shear rate comparing with HPAMsolution. It was obvious that the apparent viscosity of HPAM solution exhibited a sharp reduction as a result of degradation by SRB. A lower loss rate (18.3%) in apparent viscosity of AM/AA/ADMES was observ[illegible] comparing with HPAM (27.1%) under the shear rate of 200 s^{-1}.

Viscoelasticity

The viscoelasticity behavior of AM/AA/ADMES and HPAM is quite important for EOR as displayed in Fig. 6. It was obvious that both elastic modulus (G') and viscous modulus (G") of AM/AA/ADMES were higher than that of HPAM. This phenomenon indicated that the better viscoelasticity for AM/AA/ADMES could be obtained under concentration of 2000 mg/L. And the frequency of flow in the elasticity domination state was lower than that of HPAM. At relatively high frequency, G' of AM/AA/ADMES was obviously larger than G", which showed that AM/AA/ADMES had better elasticity. And the viscoelasticity of AM/AA/ADMES solution with being seeded by SRB was visibly superior to that of HPAM solution containing SRB. Therefore, the increasing elasticity could contribute to improve the microscopic swept efficiency of displacing fluid, which could be favorable to enhance oil recovery.

Long-term stability

The long-term stability is also important for the polymer for EOR due to long-term flow of displacing fluid in the formation. The apparent viscosity was measured at different time after aging at indicate temperature as shown in Fig. 7. The viscosity retention rate of 2000 mg/L AM/AA/ADMES solution could reach 81.1% after

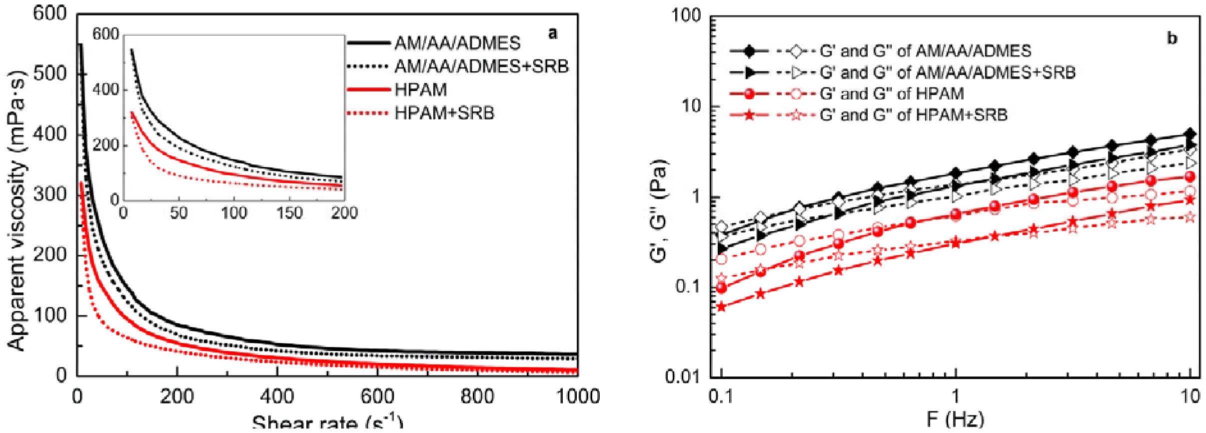

Fig. 6 Effect of shear rate on apparent viscosity of AM/AA/ADMES and HPAM solution. Viscoelasticity curves of AM/AA/ADMES and HPAM solution.

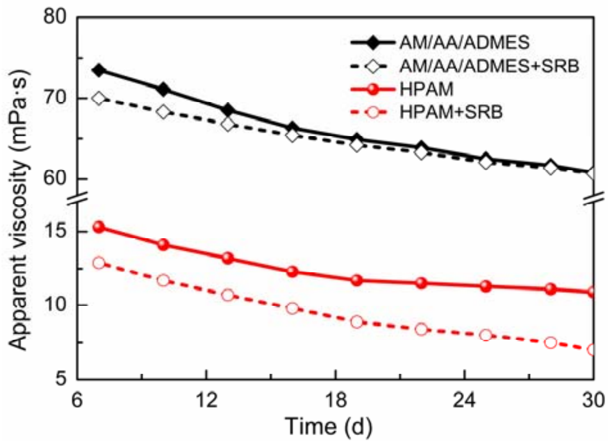

Fig. 7 The long-term stability of AM/AA/ADMES and HPAM solution.

aged 30 days, while the viscosity retention rate of HPAM was 71.8%. After the solution being seeded with SRB was aged, HPAM solution exerted larger loss rate in apparent viscosity. The viscosity loss rate increased with each passing day and the loss rate was 36.1% after being aged 30 days comparing with HPAM solution without being seeded with SRB. The phenomenon might be due to that the growth of SRB could promote degradation of HPAM.[47] While AM/AA/ADMES solution being seeded with SRB displayed higher retention rate, which was ascribed to the excellent antibacterial ability of AM/AA/ADMES. After being aged 30 days, comparing with the solution without being seeded with SRB, AM/AA/ADMES solution had little loss in apparent viscosity.

Mobility control ability

The flow characteristic curves of AM/AA/ADMES and HPAM in porous media was shown in Fig. 8a. The stable injection pressure of three stages was recorded in Table 4. Compared with HPAM (9.38 and 2.95) solution, the AM/AA/ADMES solution could establish much higher RF (15.30) and RRF (5.37) under the same conditions. The results indicated that AM/AA/ADMES solution had a stronger mobility control ability that was favourable to enhance oil recovery.

EOR ability

The core flooding test results for enhanced oil recovery of the copolymer AM/AA/ADMES and HPAM were illustrated in Fig. 8b. Compared with water flooding, the copolymer AM/AA/ADMES solution could enhance the oil recovery significantly up to 11.0%, which might be explained by the excellent mobility control ability. Therefore a conclusion could be obtained that the ability of the copolymer AM/AA/ADMES for enhanced oil recovery was better than that of HPAM (5.5%).

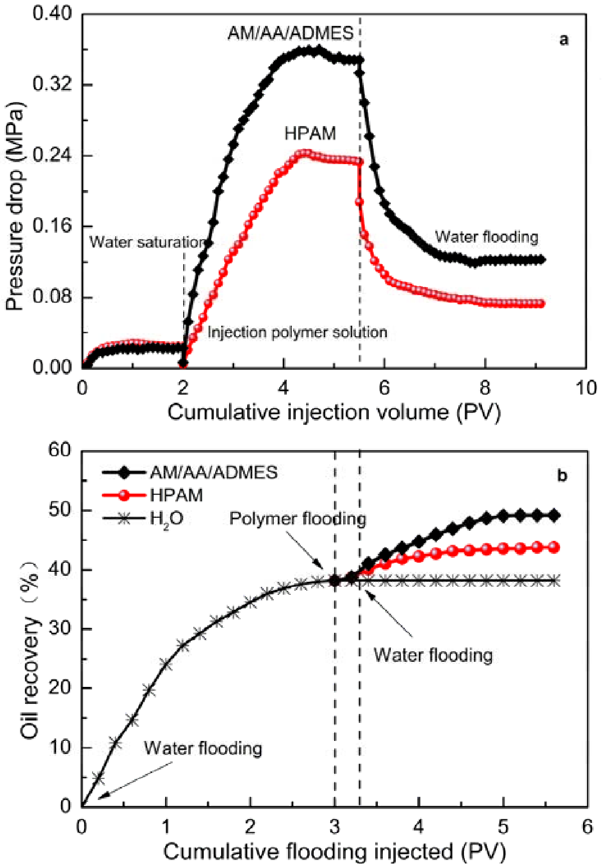

Fig. 8 (a) Flow characteristic curves of HPAM and AM/AA/ADMES solution, (b) EOR ability for AM/AA/ADMES and HPAM.

Conclusions

In this paper, a novel copolymer AM/AA/ADMES was synthesized as EOR chemical. The rheological properties and stability of AM/AA/ADMES solution were investigated. Then the copolymer AM/AA/ADMES solution under concentration of 2000 mg/L could significantly increase apparent viscosity up to 546.5 mPa·s. Meanwhile, the copolymer AM/AA/ADMES had excellent performances on antimicrobial ability, temperature resistance, salt tolerance, long-term stability, shear resistance and viscoelasticity. And the higher recovery efficiency of 11.0% could be obtained in comparison with HPAM (5.5%). So AM/AA/ADMES had certain potential application for enhancing oil recovery. And the further investigation on the applications of other similar copolymer for EOR chemical is in progress.

Table 4 The *RF* and *RRF* of AM/AA/ADMES and HPAM

Polymer	Water saturation pressure (10^{-3} MPa)	Polymer solution pressure (10^{-3} MPa)	Water flooding pressure (10^{-3} MPa)	*RF*	*RRF*
AM/AA/ADMES	22.76	340.20	122.25	15.30	5.37
HPAM	24.81	232.74	73.15	9.38	2.95

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Graphical abstract

Water-soluble Antimicrobial Acrylamide Copolymer Containing Sulfitobetaine for Enhanced Oil Recovery

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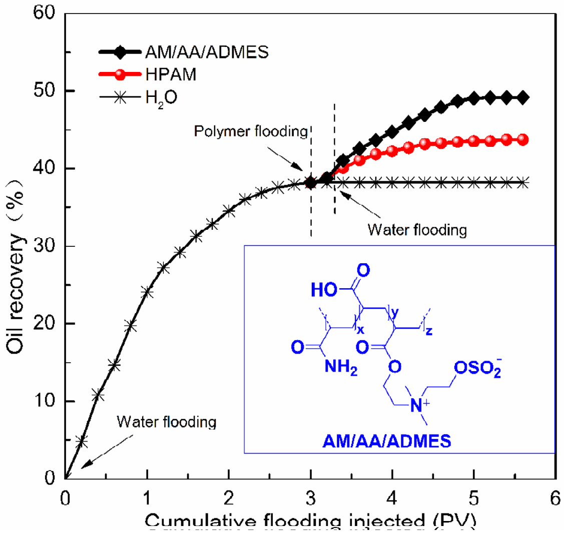

Here, an antimicrobial acrylamide copolymer containing sulfitobetaine was synthesized for enhanced oil recovery. We systematically investigated the thickening ability, temperature resistance, rheological properties and long-term stability of the copolymer dissolved in brine. And the low loss in apparent viscosity indicated that the copolymer possessed antimicrobial ability to resist the degradation by sulfate-reducing bacteria. In addition, 11.0% of enhanced oil recovery in the core flooding experiments could be obtained, which demonstrated that the copolymer had remarkable prospect for enhanced oil recovery.