Preparation and Solution Properties of Zwitterionic Polyacrylamide for Enhancing Oil Recovery

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Article

Preparation and Solution Properties of Zwitterionic Polyacrylamide for Enhancing Oil Recovery

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Abstract

The viscosity stability of the polymer solution is one of the challenges in enhancing oil recovery and zwitterionic copolymer presents excellent viscosity stability and emulsification performance, enabling effective control the oil/water interface mobility and enhancing oil recovery. Herein, a zwitterionic copolymer (P(AM/AMBS/MAPTAC)) containing sulfonic acid group and quaternary amine group was synthesized by segmentation initiation with AM, AMBS and MAPTAC as monomers. The chemical structure of P(AM/AMBS/MAPTAC) was confirmed by FTIR and ^{1}H NMR. The M_w value of (P(AM/AMBS/MAPTAC)) was 9.91×10^6, and the apparent viscosity of the solution of 2000 mg/L solution was 24.92 mP·s at 60 ℃ in the 5000 mg/L salt solution. P(AM/AMBS/MAPTAC) with the sulfonic acid group and the quaternary amine group exhibits outstanding salt tolerance and shear resistance. When the salinity was 10000 mg/L and the shear rate was 300 s^{-1}, the apparent viscosity and the viscosity reduction rates for the P(AM/AMBS/MAPTAC) solution were 23.45 mP·s and 69.23 %, respectively. Moreover, P(AM/AMBS/MAPTAC) exhibited higher emulsion property and higher oil-water interface thickness than HPAM and SPAM because of the synergistic effect of sulfonic acid and quaternary amine groups in the P(AM/AMBS/MAPTAC) molecule. The polymer flooding and the alkali-surfactant-polymer flooding formed by P(AM/AMBS/MAPTAC) had high chemical oil recovery and the oil displacement efficiency was higher than HPAM and SPAM in the polymer flooding and the alkali-surfactant-polymer flooding systems.

Keywords: zwitterionic copolymer; polyacrylamide; segmentation initiation; enhance oil recovery

1. Introduction

Polymer flooding has been used as an enhanced oil recovery (EOR) technique for a long time in many countries, and partially hydrolyzed polyacrylamide (HPAM) is a widely used polymer in polymer flooding due to its cost-effectiveness, good viscosity and physicochemical properties [1,2]. However, there are many drawbacks in the practical use of HPAM to a high temperature and high-salinity reservoir [3]. Increasing reservoir temperature leads to the breakdown of the molecular chain of HPAM, as well as the significant reduction of the solution viscosity. The thickening capability of HPAM in high-salt conditions is also decreased significantly [4], especially

with the presence of Ca^{2+} and Mg^{2+}. Many reports identified that introduction of the functional groups into the polyacrylamide backbone was favorable to improve temperature-tolerance and salt-tolerance of the polymers and these polymers were used in harsh reservoir condition replacing HPAM [5–10]. Zhang [5] synthesized a terpolymer by introducing a cationic monomers during the polymerization process of acrylamide and acrylic acid and the synthesized cationic hydrophobically

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modified polyacrylamide had good viscosity stability in the solution of 2000 mg/L at above 60 ℃. Yang prepared a active amphiphilic polymer with hydrophobic monomer (C16DMAAC), acrylamide and acrylic acid as comonomers, and the active amphiphilic polymer represented excellent viscoelasticity with enhanced aging stability and shear resistance [9]. Moreover, the injection of the active amphiphilic polymer effectivity raised the recovery of heavy oil Wu synthesized a salt-induced tackifying polymer (PAMNS) for enhancing oil recovery in high salinity reserviors, and PAMNS domenstrated superior performance in polymer flooding experiments under salinity ranges from 50000 mg/L to 200000 mg/L[10]. Li [11] synthesized a kind of water-soluble sulfonate copolymer (SPAM) using acrylamide (AM), 2-(dimethylamino) ethyl methacrylate (DMAEMA) and 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propane sulfonic acid (AMPS) as monomers, and SPAM had good temperature-tolerance and salt-tolerance. However, the viscosity stability of the polymer solution and the emulsification were poor, and the the reports of the synthesis and the oil displacement performance about the zwitterionic polyacrylamide with good temperature and salt resistance performance were relatively little so far.

Based on our previous work [11], a zwitterionic polyacrylamide P(AM/AMBS/MAPTAC) was synthesized by segmentation initiation with 2,2'-azobis[2-methylpropionamidine] dihydrochloride and redox initiation system and the effects of the copolymeric monomers and polymeric parameters on the weight average molecular weight (M_w) and the solution viscosity were investigated in this work. The effects of temperature and salinity on the viscosity of the P(AM/AMBS/MAPTAC) solution were probed to investigate the viscosity stability under high temperature and high salinity. The emulsification and the oil displacement performance for P(AM/AMBS/MAPTAC) in polymer flooding and the alkali-surfactant-polymer flooding were evaluated, and were compared with the commonly used partially hydrolyzed polyacrylamide (HPAM) and the sulfonate copolymer (SPAM) synthesized in our previous work [11]. The zwitterionic polyacrylamide could be a promising alternative of the widely used HPAM in chemical flooding.

2. Experimental

2.1. Materials and Instruments

Acrylic acid (AA), acrylamide (AM), 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propane sulfonic acid (AMPS), 2-acrylamide ethyl-4-methylbutanesulfonic acid (AMBS), 2-(dimethylamino) ethyl methacrylate (DMAEMA), 2'-azobis[2-methylpropionamidine] dihydrochloride (AIBA), ammonium persulphate (APS), N,N,N',N'-tetramethylethylenediamine (TEMED), sodium formaldehyde sulfoxylate (HMSNa), sodium formaldehyde sulfoxylate, acrylic acid (AA), dimethylaminopropyl methacrylamide (DMAPMA), (3-acrylamidopropyl)trimethylammonium chloride (DAC), (3-acrylamidopropyl) trimethylammonium chloride (MAPTAC) were purchased from Sigma-Aldrich Reagents Ltd. Sodium chloride (NaCl), sodium hydroxide(NaOH), magnesium chloride ($MgCl_2$) and calcium chloride anhydrous ($CaCl_2$) were purchased from Tianjin Kermerl Chemical Research Institute. Partially hydrolyzed polyacrylamide (HPAM, hydrolysis degree =26%, M_w=2.5×10^7) was provided by DaQing Refining & Chemical Company.

FTIR spectrum of the copolymer was performed using a Nicolet FTIR 750 spectrometer. ^{1}H NMR spectrum of the copolymer was measured on a 400 MHz spectrometer with D_2O as the solvent. The rheological properties were studied by TA Rheostress Discovery DHR-2 rotational rheometer. The weight average molecular weight (M_w) of the copolymer was determined from the intrinsic viscosity [η] measurements by Ubbelohde viscometer [11].

2.2. Preparation of Zwitterionic Polyacrylamide

Series of zwitterionic polyacrylamide were prepared according to our previous work [11]. A certain mass of AM and anionic monomer were dissolved in deionized water at 10 ℃ under nitrogen atmosphere, and NaOH (10.0 wt%) aqueous solution was added into the above solution to adjust the pH value to 8.0. AIBA was added into the above system and the reaction mixture was stirred for 1 h

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at 25 ℃ under nitrogen atmosphere. Then a certain mass of cationic monomer aqueous solution, the aqueous solutions of APS and HMSNa were added into the reaction mixture and the mixture was stirred for 2 h at 10 ℃ under nitrogen atmosphere. The reaction mixture was heated to a certain temperature and reacted for 8 h. The mixture was cooled to room temperature and the solid formed through adding an amount of ethanol into the mixture. Then the crude solid was treated with a mixture of N,N-dimethylformamide and acetic acid (1:1 by volume) to remove the unmodified polyacrylamide. The zwitterionic polyacrylamide was dried at 60 ℃ for 10 h under vacuum conditions.

2.3. Measurement of Emulsification

The emulsification was investigated with bottle testing method at 60 ℃ for 240 min. The simulated emulsion was prepared by mixing the crude oil and the polymer solution (v_{water}:v_{oil}=4:1) in a homogenizer at a rotating speed of 10000 r/min for 10 min. The emulsification efficiency (DE) of polymers was calculated to evaluate the stability of simulated emulsions according to Eq.(1) .

$$DE=\frac{V_1}{V_0}\times 100\% \qquad (1)$$

where, V_1 is the volume of the separated water (mL), V_0 is the volume of the initial water (mL).

2.4. Core-Flooding Test

According to our previous work[11], the cores (4.5*4.5*30) were pretreated by 5% HCl solution and deionized water and dried under vacuum conditions. Then, simulated water (the mass ratio of NaCl, $CaCl_2$ and $MgCl_2$=60:4:3) was continuously injected the dried core (4.5*4.5*30) until a stable pressure was established to determine the permeability. The core was saturated by the simulated crude oil until no further water production, and was aged at 80 ℃ for 3 days. The simulate water was continuously injected until the water cut reached 98%. After water injection, the polymer solution was injected to displace simulated crude oil. The final oil recovery and the polymer recovery were calculated. The alkali-surfactant-polymer flooding test was similar as the polymer flooding test with alkali-surfactant-polymer solution as chemical oil displacement agent.

2.5. Molecular Dynamics Simulation

According to our previous work [12], molecular dynamics simulations of P(AM/AMBS/MAPTAC) at the oil/water interface were conducted using the Gromacs 2020 program and Gaussian 2016 **Error! Reference source not found.**, and undecane was simulated oil. The simulation box consisted a water film positioned between two oil layers and two P(AM/AMBS/MAPTAC) molecules were dispersed at the oil-water interface using Packmol **Error! Reference source not found.**. All systems were enclosed within a box of dimensions 10 nm × 10 nm × 14 nm. The simulation was conducted at a temperature of 60 ℃ and a pressure of 0.1 MPa. The simulated time period was 800 ps with a time step size of 2 fs.

3. Results and Discussion

3.1. Effect of Synthesis Conditions on the Property of Zwitterionic Polyacrylamide

3.1.1. Effect of Comonomers

When the molar concentration of *AM was* 0.3 mol/L, *the molar ratio of* AM and anionic monomer was 50:1, *the molar ratio of* AM and DMAEMA was 350:1, the concentration of AIBA was 0.03 wt%, the concentration of the second initiator was 0.03 wt%, the reaction temperature was 50 ℃, and the reaction time was 10 h. The effects of the type for anionic monomer (Figure 1) and the cationic monomer (Figure 2) on the M_w value of the synthesized copolymer and the apparent viscosity of the 2000 mg/L copolymer solution at 60 ℃ when the salinity (the mass ratio of NaCl, $CaCl_2$ and $MgCl_2$=60:4:3) was 5000 mg/L, and the results were listed in Table 1 and Table 2.

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Table 1. Effect of the type of anionic monomer on the properties of the copolymer.

Anionic monomer	$M_w \times 10^6$	Apparent viscosity(mPa·s)
AA	3.16	8.32
AMPS	9.99	19.10
AMBS	9.73	21.14

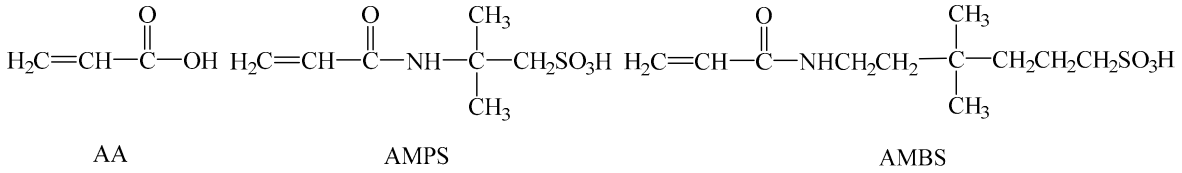

Figure 1. Chemical structure of anionic monomers.

As shown in Table 1, the M_w value and the apparent viscosity of the zwitterionic polyacrylamide with AA as anionic monomer were lower than those of other anionic monomers. This is because there are alkyl group and polar group in the molecules of AMPS and AMBS compared with AA. The steric hindrance effect of the alkyl group in the side chain decreases the repulsion between the monomers, which is conducive to copolymerization reaction to obtain the copolymer with high weight average molecular weight. In addition, the polar groups in the molecules inhibit the curling of polymer chains during the polymerization process. According to Table 1, the apparent viscosity of the solution for P(AM/AMBS/MAPTAC) with AMBS as anionic monomer was higher compared with AMPS. However, the M_w value P(AM/AMBS/MAPTAC) was lower than that of the synthesized copolymer with AMPS as anionic monomer. The higher apparent viscosity of P(AM/AMBS/MAPTAC) could be attributed to the enhanced intermolecular interactions caused by the specific polar groups and the long alkyl group in AMBS, which might promote the formation of a more entangled network structure in the solution, even with a lower molecular weight. These results indicate that the type of anionic comonomer significantly influences both the molecular weight and solution viscosity of the zwitterionic polyacrylamide , with AMBS showing potential advantages in improving viscosity despite its lower Mw compared to AMPS.

As shown in Table 2, the M_w values of the synthesized copolymer with positively charged compounds as anionic monomers were lower than those of the corresponding copolymers with uncharged compound as cationic monomers. This phenomenon can be attributed to the differences in the charge density and steric hindrance of the cationic monomers. DAC and MAPTAC with higher charge density tend to form stronger intermolecular electrostatic interactions, leading to the formation of more compact molecular aggregates during polymerization. These aggregates restrict the chain grow to form the copolymer with low M_w. In contrast, DMAEMA and DMAPMA have relatively lower charge density and larger steric hindrance from their side chains, which weakens the intermolecular association and forms the copolymer with high M_w. However, the variation of the apparent viscosity was opposite to the trend of the M_w values. The apparent viscosity is not only related to M_w but also strongly influenced by the intermolecular interactions. The strong association between the positively charged segments of DAC and MAPTAC copolymers leads to the formation of the entangled network structure in solution [15]. This network structure increases the resistance to flow, thereby significantly increasing the apparent viscosity. Even though the M_w of these copolymers is lower, the enhanced intermolecular association dominates the viscosity behavior, resulting in higher apparent viscosity compared to copolymers with DMAEMA and DMAPMA. MAPTAC was used as cationic monomer to synthesize the zwitterionic polyacrylamide (P(AM/AMBS/MAPTAC)) in this work.

Table 2. Effect of the type of cationic monomer on the properties of the copolymer.

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Cationic monomer	$M_w \times 10^6$	Apparent viscosity(mPa·s)
DMAEMA	9.73	21.14
DMAPMA	9.25	22.03
DAC	8.69	23.05
MAPTAC	9.15	23.96

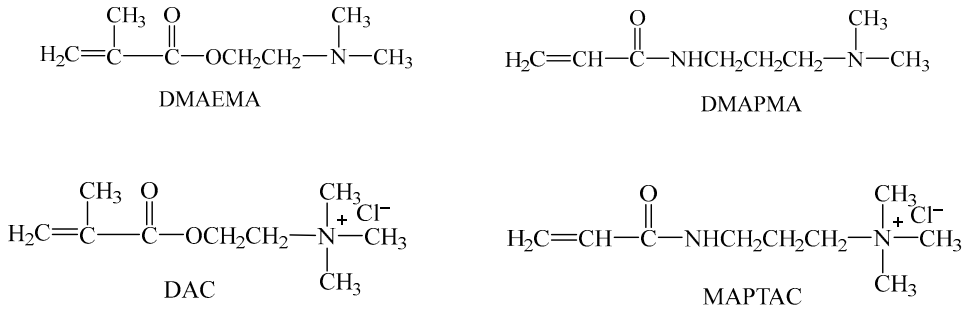
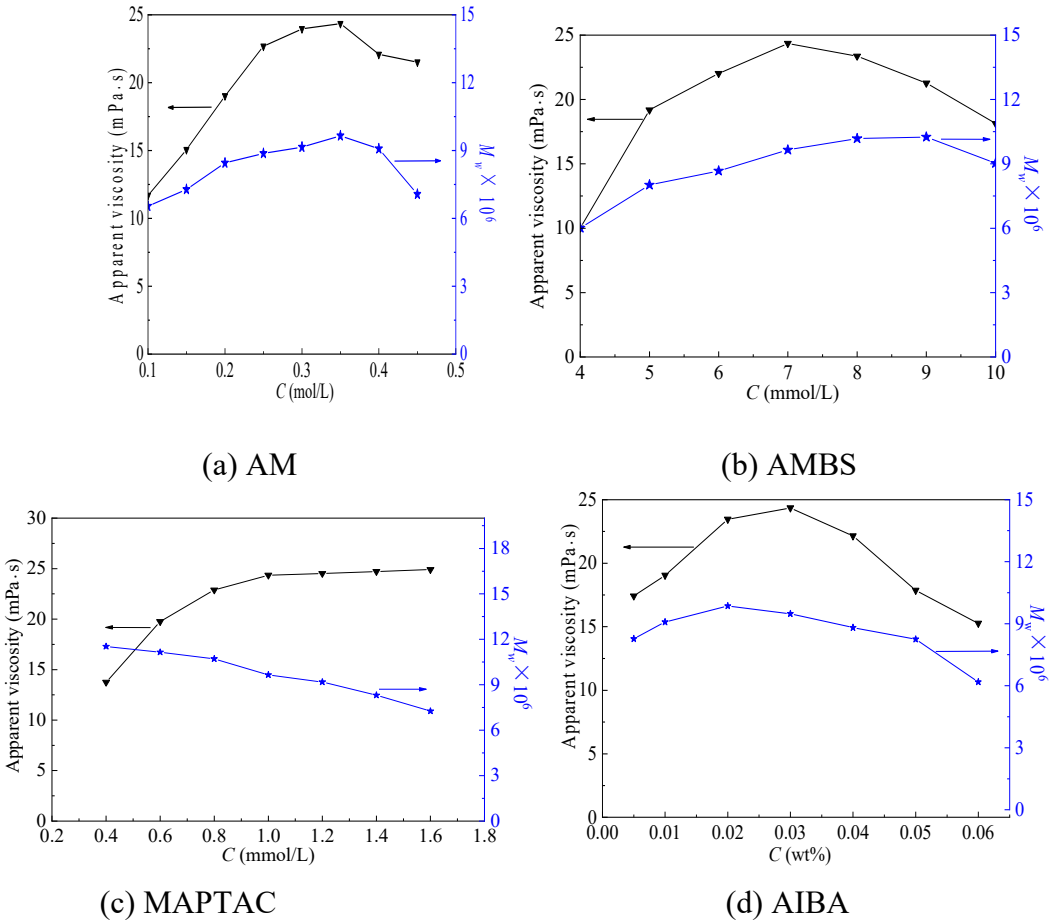


Figure 2. Chemical structure of cationic monomer.

3.1.2. Effect of Polymeric Parameters

Based on the above results of the copolymerized monomers, the effects of the polymeric parameters the M_w value of P(AM/AMBS/MAPTAC) and the apparent viscosity of the polymer solution of 2000 mg/L at 60 ℃ when the salinity (the mass ratio of NaCl, $CaCl_2$ and $MgCl_2$=60:4:3) was 5000 mg/L were investigated, and the results were shown in Figure 3.



(a) AM (b) AMBS

(c) MAPTAC (d) AIBA

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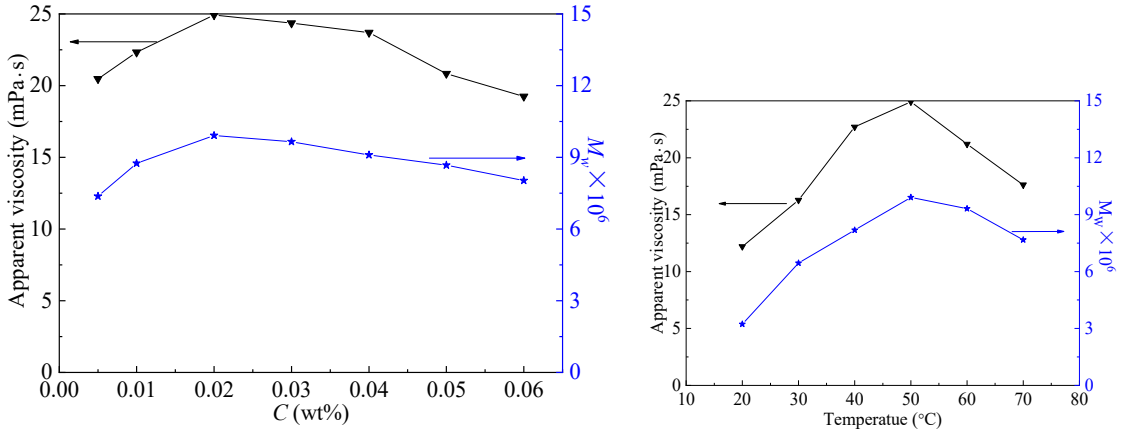

(e) Redox intiation system (f) Temperature

Figure 3. Effect of the copolymer conditions on the properties of P(AM/AMBS/MAPTAC).

The concentration of AM and AMPS play an important role in the synthesis of P(AM/AMBS/MAPTAC) and the M_w values and the apparent viscosity of P(AM/AMBS/MAPTAC) firstly increased and then decreased with the concentration of AM and AMPS (Figure 3 (a) and (b)). The M_w values and the apparent viscosity were up to the maximum when the concentration of AM and AMBS were 0.35 mol/L and 7 mmol/L, respectively. When the concentration of P(AM/AMBS/MAPTAC) was low, the higher of monomer in the polymeric system contributed to an increase of the polymeric activity with enhancing the monomer concentration, which was favorable to form the copolymer with high M_w. The greatest apparent viscosity of 23.96 mP·s (Figure 3 (a) and (b)) was obtained when the concentration of AM and AMBS were 0.35 mol/L and 7.0 mmol/L, respectively. With further increasing the monomers, the polymerization reaction was too fast to cause the increase of difficulty in heat dissipation, which enhanced the chain transfer rate to a decrease of the polymer molecular weight. Based on the effect of the concentration of AM and AMBS on the M_w values and the apparent viscosity of the synthesized copolymer, the optimum concentration of AM and the optimum concentration of AMBS were 0.35 mol/L and 7.0 mmol/L, respectively.

It was obvious that the M_w value of the synthesized copolymer decreased and the apparent viscosity of the solution increased with the concentration of MAPTAC, which was different with the effect of the concentration of AM and AMBS (Figure 3 (c)). This was because the neutralization between the cationic group in the MAPTAC molecule and the anionic group in the AMBS molecule for the weakly alkaline system may prevent the copolymerization rate, which led to decrease of the M_w value of the associated polymer. The neutralization had lower effect on the copolymerization rate at the low concentration of MAPTAC, and the effect increased with increasing the MAPTAC concentration. However, the apparent viscosity of the associated polymer solution firstly increases rapidly and then changes a little with an increase of the MAPTAC concentration. This is because the intramolecular association and intermolecular association interactions among the synthesized copolymers led to change of the microstructure of solution, such as viscosity, excess volume, heat of mixing [16]. Increasing of the MAPTAC concentration was conductive to the enhance of the association interactions, which led to an increase of the apparent viscosity of the solution of the associated polymer. Based on the effect of the MAPTAC concentration on the M_w values and the apparent viscosity of P(AM/AMBS/MAPTAC), the optimum concentration of MAPTAC was 1.0 mmol/L.

The effects of the initiator concentration in the two stages on the M_w values and the apparent viscosity of P(AM/AMBS/MAPTAC) were shown in Figure 3 (d) and (e). The M_w values and the apparent viscosity firstly increased and then decreased with an increase of the initiator concentration for the two stages. When the AIBN concentration in the first stage was 0.03 wt%, the M_w values and the apparent viscosity reached the maximum, and are 24.52 mP·s and 9.48×10^6, respectively.When the concentration of redox initiation system in the second stage was 0.02 wt%, the M_w values and the

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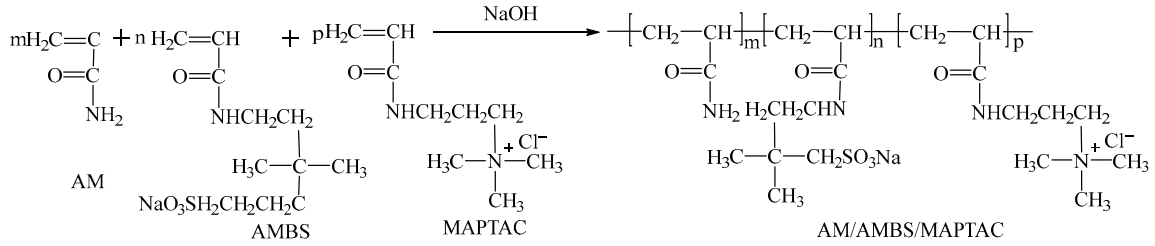
apparent viscosity were 24.92 mP·s and 9.91×10⁶, respectively. Based on the effect of the initiator concentration in the two stages on the M_w values and the apparent viscosity of P(AM/AMBS/MAPTAC), the optimum concentrations of AIBN and redox initiation system are 0.03 wt% and 0.02 wt%, respectively.

The M_w values and the apparent viscosity of P(AM/AMBS/MAPTAC) first increase and then decrease as the polymerization temperature increases (Figure 3 (f)). This is because the decomposition reaction of the initiator is inhibited at low temperature, producing a small amount of free radicals. The free radicals produced are sufficient to promote polymerization as the polymerization temperature increases. When the polymerization temperature is 50 ℃, the M_w values and the apparent viscosity reach the maximum. As the polymerization temperature further increases, a large number of free radicals are produced in a short time, resulting in chain termination and a reduction in the molecular weight. The optimum polymerization temperature is 50 ℃ in this work.

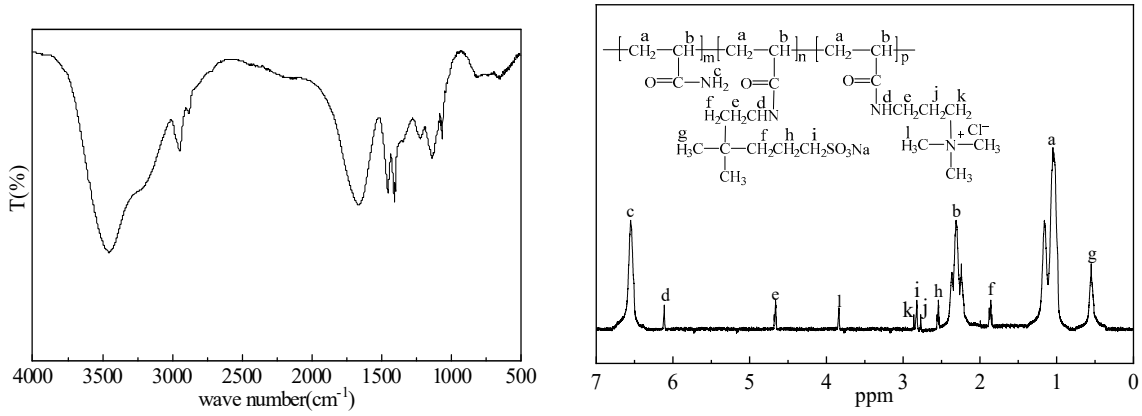
3.2. Characterization of P(AM/AMBS/MAPTAC)

P(AM/AMBS/MAPTAC) synthesized under the optimum polymerization conditions (Scheme 1) was characterized by FTIR and ^{1}H NMR, and the results are shown in Figure 4.



Scheme 1. Synthesis routes of zwitterionic polyacrylamide (P(AM/AMBS/MAPTAC)).

The N-H stretching vibration peak of the –CONH₂ and –CONH- groups in the repeating units was found at about 3500 cm^{-1} in the IR spectrum (Figure 4(a)). The C=O stretching vibration peak of the –CONH₂ and –CONH- groups peak appears at about 1640 cm^{-1}. Meanwhile, the peaks of -NH- bending vibration are observed at about 1400 cm^{-1} and 1220 cm^{-1}, respectively. The peaks at 1060 cm^{-1} and at 650 cm^{-1} are attributed to the S-O stretching vibration and the C-S stretching vibration, respectively. Meanwhile, the peak of the S=O asymmetric stretching vibration appears at about 1130 cm^{-1}. The peaks indicate that the monomers of AM, AMBS and MAPTAC are copolymerized successfully to obtain P(AM/AMBS/MAPTAC).



(a) IR (b) ^{1}H NMR

Figure 4. IR and ^{1}H NMR spectra of P(AM/AMBS/MAPTAC).

As shown in Figure 4(b), the protons (a) of -CH₂- of polymeric chain appeared at 0.91-1.37 ppm, and the protons (b) of -CH- of polymeric chain appeared at 2.13-2.59 ppm [17]. The chemical shift

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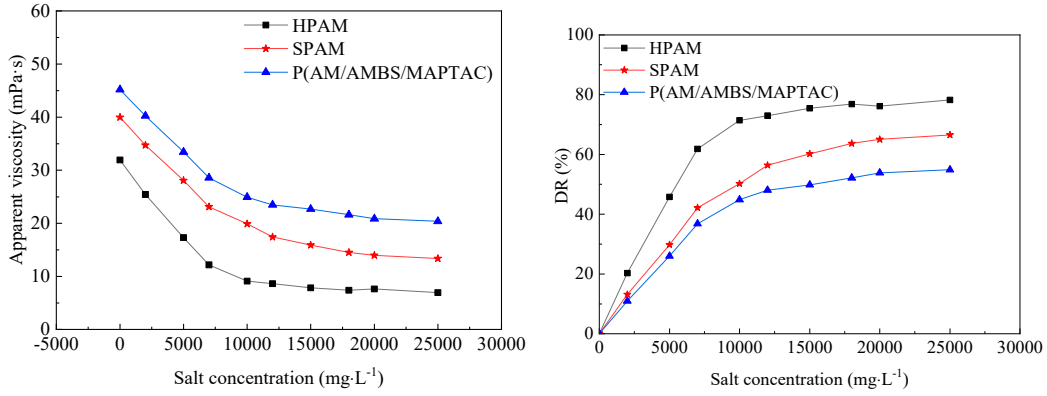
value at about 5.56 ppm were assigned to the protons (c) of –$CONH_2$ in the AM unit. The protons (d) of -CONH- of the AMBS and MAPTAC units appeared at about 6.12-6.15 ppm. The chemical shift values at 0.40-0.71 ppm were assigned to the protons (g) of -CH_3 in the AMBS units. The protons (i) of –CH_2- combined with -SO_3^{2-} in the unit AMBS appeared at about 2.83 ppm. The chemical shift values at about 2.77 ppm and 2.87 ppm were assigned to the –CH_2- protons of -CONH-C-CH_2-C-N- and -CONH-C-C-CH_2-N- in the unit MAPTAC, respectively. The chemical shift value at about 4.65 ppm was assigned to the protons of –CH_2- combined with -CONH- in the AMBS and MAPTAC units. The chemical shift value at about 3.84 ppm was assigned to the protons of -CH_3 in the MAPTAC units. Moreover, the integral area ratio of all the protons were agreed with the chemical structure, and they agreed well with the IR data to confirm the successful synthesis of P(AM/AMBS/MAPTAC).

3.3. Properties of P(AM/AMBS/MAPTAC) Solution

The salt tolerance values of the polymer solution (2000 mg/L) were studied at 60 ℃ and the shear rate of 150 s^{-1} when the mass ratio of NaCl, $CaCl_2$ and $MgCl_2$ was 60:4:3 (Figure 5) and the results showed that the apparent viscosity of three polymer solutions decreased with increasing of salinity. This was because the complexation between cation and polymer led to the shielding of the charges of the copolymer leading to the shrinkage of the copolymer backbone in the presence of salt [18]. The intrachain complexation in the polymer solution occurs at the low salinity, the intrachain and interchain complexations take place at the medium salinity, and the interchain complexation takes place at the high salinity [19], which leads to the decrease of the apparent viscosity of the copolymer solution.The apparent viscosity of the copolymer with sulfonic acid groups was higher than that of HPAM with carboxylic acid groups, and the apparent viscosity of the P(AM/AMBS/MAPTAC) solution with zwitterionic group was higher than that of SPAM (Figure 5(a)). Moreover, the P(AM/AMBS/MAPTAC) solution has good viscosity stability in the high salt system compared with HPAM and SPAM (Figure 5(b)). When the salinity was 10000 mg/L and the shear rate was 150 s^{-1}, the apparent viscosity and the viscosity reduction rates for the P(AM/AMBS/MAPTAC) solution were 24.92 mP·s and 44.86 %, respectively. Nevertheless, the apparent viscosity and the viscosity reduction rates for the HPAM solution were 9.12 mP·s and 71.43 %, respectively. This was because the complexation between carboxylic acid groups and metallic ions caused to a decrease of the solubility of HPAM, and the sulfonic acid groups have excellent salt-tolerance. The intermolecular hydrophobic associations of P(AM/AMBS/MAPTAC) with sulfonic acid group and quaternary amine group take place to inhibit the intrachain and interchain complexations, which increases the salt-tolerance [20] .



(a) apparent viscosity (b) viscosity reduction rate

Figure 5. Effects of salinity on the viscosity stability of the polymer solution .

The shear resistances of the polymer solutions (2000 mg/L) were studied at 60 ℃ when the salinity was 10000 mg/L (Figure 6), and the results showed that the apparent viscosity of all three polymer solutions decreases with increasing shear rate. This phenomenon was because the polymer chains form physical crosslink through mutual entanglement or van der Waals interactions and the crosslinks undergo continuous disintegration and reconstruction under molecular thermal motion

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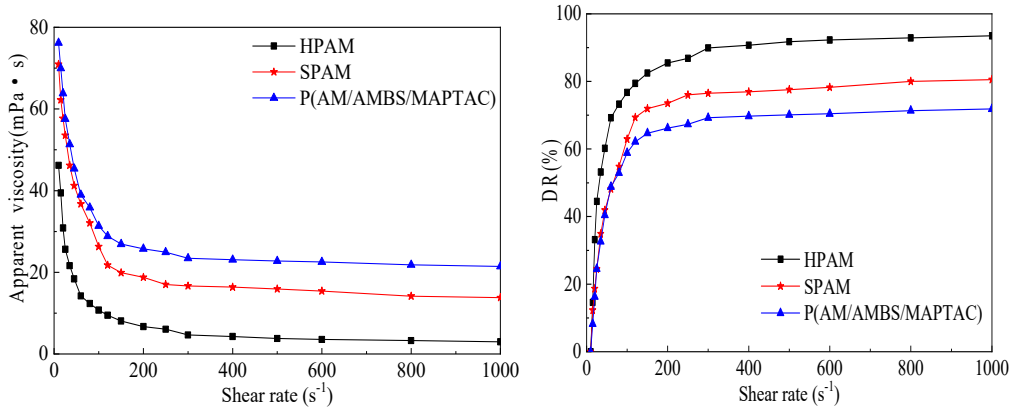
[21]. However, it is worth noting that the apparent viscosity of the three polymer solutions follows the trend P(AM/AMBS/MAPTAC) > SPAM > HPAM at the same shear rate (Figure 6(a)). The P(AM/AMBS/MAPTAC) solution has high apparent viscosity and good viscosity stability in the high shear rate compared with HPAM and SPAM (Figure 6). When the salinity was 10000 mg/L and the shear rate was 300 s^{-1}, the apparent viscosity and the viscosity reduction rates for the P(AM/AMBS/MAPTAC) solution were 23.45 mP·s and 69.23 %, respectively. Nevertheless, the apparent viscosity and the viscosity reduction rates for the HPAM solution were 4.66 mP·s and 89.91 %, respectively. This perhaps indicated that the zwitterionic group of P(AM/AMBS/MAPTAC) improved the shear resistance and the apparent visicosity of the polymer solution because the electrostatic interactions between the zwitterionic segments. The combined effects of zwitterionic electrostatic interactions and hydrophobic associations in P(AM/AMBS/MAPTAC) help maintain a higher level of entanglement, thus resulting in a slower decrease in apparent viscosity compared to the other two polymers. This superior shear resistance is crucial for polymer flooding applications, where the polymer solution is subjected to high shear forces during injection into reservoirs, ensuring that the solution retains sufficient viscosity to effectively displace oil.



(a) apparent viscosity (b) viscosity reduction rate

Figure 6. Effects of shear rate on the viscosity stability of the polymer solution.

3.4. Emulsification Performance of P(AM/AMBS/MAPTAC)

The emulsification performance of at various concentration was assessed at the salinity of 5000 mg/L and the temperature of 80 ℃ (Figure 7(a)). As was clearly showed in Figure 7(a), the emulsification performance of P(AM/AMBS/MAPTAC) was positively correlated to the polymer concentration and negatively correlated to the time. Increasing the polymer concentration was favorable for emulsifying of oil and the polymer solution, which was because the polymer molecules had two roles in the simulated emulsion. On the one hand, the polymer could adsorb at the oil-water interface to reduce the interfacial tension, thereby promoting the formation and stabilization of emulsion droplets. On the other hand, the polymer chains could form a three-dimensional network structure in the solution, which could prevent the aggregation and coalescence of emulsion droplets by increasing the viscosity of the continuous phase. When the polymer concentration was low, the number of polymer molecules at the interface was insufficient, and the network structure in the solution was not dense enough, so the emulsification effect was relatively poor. As the concentration increased, more polymer molecules participated in interface adsorption and network formation, leading to a significant improvement in emulsification performance. However, when the concentration exceeded a certain threshold, the improvement of emulsification performance tended to be stable, which might be due to the saturation of interface adsorption and the limited increase in solution viscosity caused by excessive polymer entanglement.

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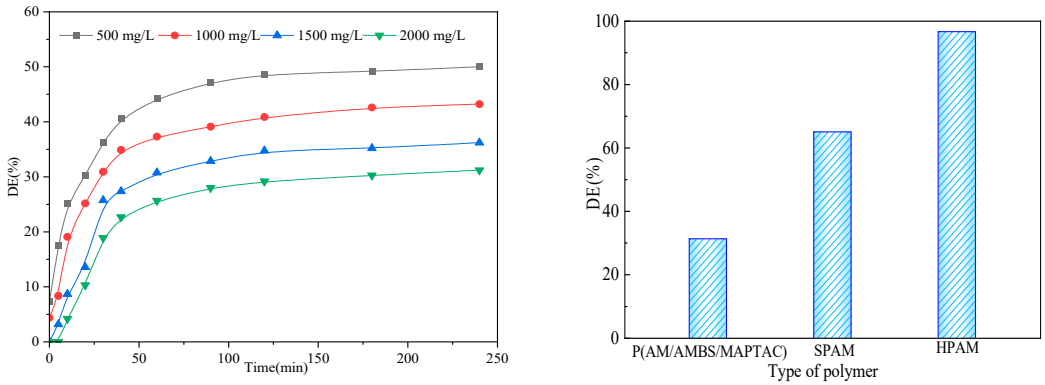
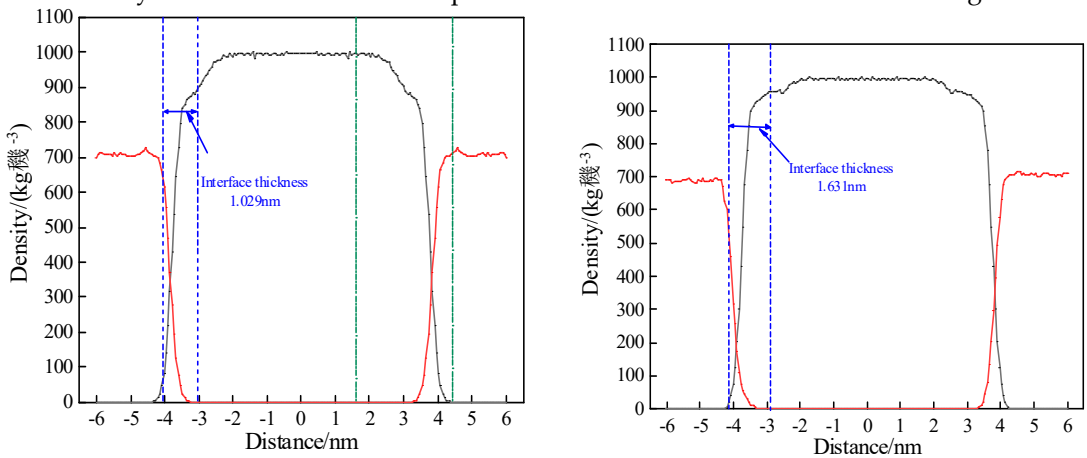


(a) Effect of concentration (b) Effect of the chemical structure

Figure 7. Emulsification properties of the polymer with different chemical structure.

In order to further understand the emulsification behavior of P(AM/AMBS/MAPTAC) with sulfonic acid and quaternary amine groups, the emulsification performance of HPAM and SPAM with the salinity of 5000 mg/L and the polymer concentration of 2000 mg/L was investigated at 60 ℃ for 4 h (Figure 7(b)). The simulated emulsion formed by P(AM/AMBS/MAPTAC) exhibited lower DE value than that of the simulated emulsions formed by HPAM and SPAM, indicating that the former has better emulsification stability. This phenomenon can be attributed to the synergistic effect of sulfonic acid and quaternary amine groups in P(AM/AMBS/MAPTAC). The sulfonic acid groups enhance the hydrophilicity of the polymer, while the quaternary amine groups improve the adsorption capacity at the oil-water interface, thereby reducing the interfacial tension more effectively. Additionally, the molecular weight and charge density of the polymer also play crucial roles. Higher molecular weight may lead to stronger steric hindrance, preventing the coalescence of emulsion droplets, while appropriate charge density can balance the electrostatic repulsion between droplets, further maintaining the stability of the emulsion system.

To investigate the effects of SPAM and P(AM/AMBS/MAPTAC) at the oil-water interface, molecular dynamics simulations were performed and the results were shown in Figure 8.



(a) Oil/water/TSPAM (b) Oil/water/ P(AM/AMBS/MAPTAC)

Figure 8. Z-direction density distribution of the oil/water/copolymer system.

The oil-water interface thickness for the SPAM system and the P(AM/AMBS/MAPTAC) system (Figure 8) was 1.029 nm and 1.631 nm, respectively. The increase in interface thickness indicated an improvement in the adsorption properties between oil and water. Compared with SPAM, P(AM/AMBS/MAPTAC) with its stronger lipophilicity and surface distribution at the oil-water interface, which led to an increase of the interface thickness to enhance the emulsification performance. P(AM/AMBS/MAPTAC) with amphiphilic structure was favorable for enhancing emulsification properties.

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3.5. Oil Displacement Performance of P(AM/AMBS/MAPTAC)

When the salinity of was 5000 mg/L and the temperature was 60 ℃, the effects of the concentration of P(AM/AMBS/MAPTAC) on the oil displacement efficiency for the polymer flooding system and alkali- surfactant-polymer flooding system are shown in Figure 9. The results of the oil displacement experiment indicated that P(AM/AMBS/MAPTAC) is favorable for enhanced oil recovery at 60 ℃ (Figure 8). For the polymer flooding, and the chemical oil recovery increases from 8.26 % to 16.95 % and the total oil recovery increases from 48.56 % to 57.48 % with increasing of the polymer concentration from 600 mg/L to 2000 mg/L (Figure 9(a)). For the alkali-surfactant-polymer flooding, the chemical oil recovery increases from 12.87 % to 18.54 % and the total oil recovery increases from 53.57 % to 58.36 % This phenomenon can be attributed to the fact that a higher polymer concentrations lead to an increase in the viscosity of the flooding system, which effectively improves the sweep efficiency by reducing the mobility ratio between the displacing fluid and the crude oil [5]. Additionally, the enhanced viscoelasticity of the polymer solution at higher concentrations helps to better plug the high-permeability zones, forcing the displacing fluid to flow into the low-permeability areas that were previously unswept, thereby increasing the overall oil recovery.

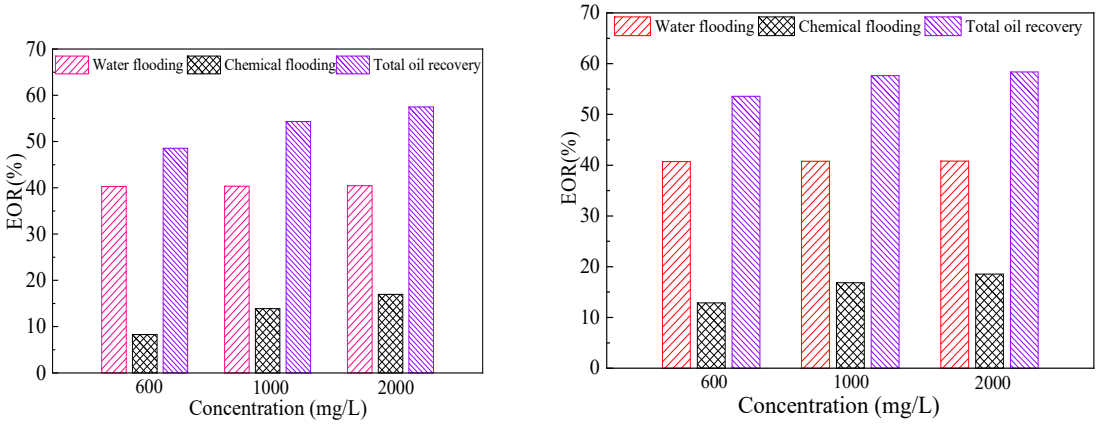

Figure 9. Effect of the concentration of P(AM/AMBS/MAPTAC) on the different flooding systems.

Compared with the polymer flooding (Figure 9(a)), the increase of the chemical oil recovery for alkali-surfactant-polymer flooding is relatively smaller (Figure 9(b)). This is because alkali-surfactant-polymer combines the macroscopic volumetric sweep efficiency improvement from the polymer due to reduction in water-oil mobility ratio with the ability of surfactants to enhance microscopic sweep efficiency [22]. This enhancement results from dramatic reduction of oil-water interfacial tension, which increases capillary number by orders of magnitude to the required range for efficient oil recovery. Alkali forms soaps by reacting with naturally occurring organic acid in the crude oil, which interacts synergistically with added surfactant to produce ultra-low interfacial tension [23]. The ultra-low interfacial tension is obtained by surfactant distribution between oil and water phase, and surfactant arrangement at interface of oil/water. This is controlled by pH value and ionic strength. The alkali injected with surfactant can reduce surfactant adsorption, play the role of ionic strength and lower interfacial tension. Addition of polymer increases the viscosity of its aqueous phase. The synergy of these three components, alkali-surfactant-polymer flooding is widely practiced in both pilot and field operations with the objective of achieving optimum chemistry at large injection volumes for minimum cost.

The effects of the chemical structure on the oil displacement efficiency for the polymer flooding system and alkali-surfactant-polymer flooding system are shown in Figure 10(a). Compared with HPAM and SPAM (Figure 10(b)), the polymer flooding and the alkali-surfactant-polymer flooding formed by P(AM/AMBS/MAPTAC) have high oil displacement efficiency. The enhanced oil recovery (EOR) is increased by 9.51 % and 10.57 % compared with HPAM ((Figure 10(a)). The good chemical oil recovery performance of P(AM/AMBS/MAPTAC) is probably attributed to two roles. On the one

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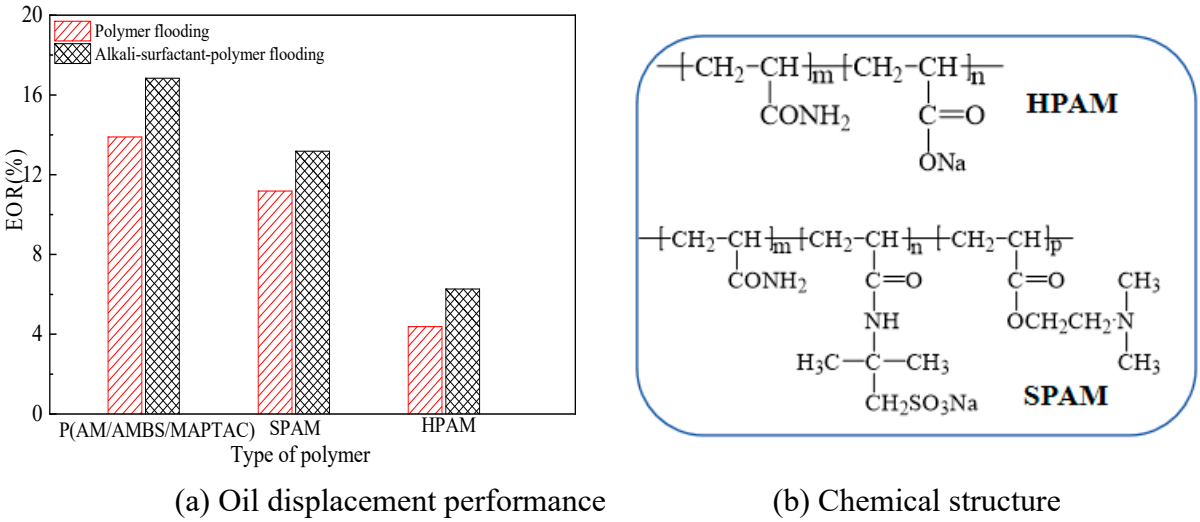
hand, the much higher viscosity of P(AM/AMBS/MAPTAC) at high temperature is responsible for the high chemical oil recovery. On the other hand, the ladder structure of P(AM/AMBS/MAPTAC) and the space steric hindrance from hydration can effectively improve the viscoelasticity of the polymer, which would increase the chemical oil recovery. Moreover, the emulsion formed by P(AM/AMBS/MAPTAC) with zwitterionic groups has higher stability than other emulsions, which is favourable for higher ultimate oil recovery.



(a) Oil displacement performance (b) Chemical structure

Figure 10. Effect of the chemical structure of polymer on the oil displacement efficiency.

4. Conclusion

The copolymer P(AM/AMBS/MAPTAC) with zwitterionic chemical structure was synthesized by segmentation initiation with AM, AMBS and MAPTAC as monomers. P(AM/AMBS/MAPTAC) with the sulfonic acid group and the quaternary amine group exhibits outstanding salt tolerance and shear resistance. Compared with HPAM and SPAM with higher M_w values, the P(AM/AMBS/MAPTAC) solution has higher apparent viscosity at the lower M_w value. Moreover, P(AM/AMBS/MAPTAC) exhibited higher emulsion stability and higher oil-water interface thickness than HPAM and SPAM because of the synergistic effect of sulfonic acid and quaternary amine groups in P(AM/AMBS/MAPTAC). The polymer flooding and the alkali-surfactant-polymer flooding formed by P(AM/AMBS/MAPTAC) had high chemical oil recovery and the oil displacement efficiency was higher than HPAM and SPAM in the polymer flooding and the alkali-surfactant-polymer flooding systems. As a result, this study holds significant guiding potential for the advancement of techniques aiming at enhancing oil recovery.

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