



Effect of a hydrophobically associating polymer on disproportionate permeability reduction to oil and water for sandstone reservoirs

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ABSTRACT

Because of the absence of amphiphilic, the disproportionate permeability reduction (DPR) performance of the traditional partially hydrolyzed polyacrylamide (PHPAM) or PHPAM-based gel in oil-wet sandstone reservoirs is barely satisfactory. Therefore, this study proposed a hydrophobically modified polyacrylamide (HMPAM) with amphiphilic in nature, and a series of experiments were performed on both water-wet and oil-wet sandstone core samples to investigate the DPR potential of it. According to the core flooding experiments, HMPAM flooding could reduce the water permeability of oil-wet cores by 93%, and only about 20% permeability reduction can be observed for the oil phase, showing the good DPR performance. In contrast, the traditional PHPAM had no obvious DPR effect on the oil-wet core. The big difference of DPR performance can be attributed to the gap between HMPAM and PHPAM in the adsorption capacity on sandstone surface. For oil-wet sandstones, the adsorption of HMPAM was 5.16 mg/g, while there was only 1.22 mg/g for PHPAM. The adsorption of HMPAM can narrow the pore throats and alter the wettability of the oil-wet rock surface, increasing the flow resistance of water, while hardly affecting the oil flow.

Keywords: Disproportionate permeability reduction; Hydrophobically modified polyacrylamide; Adsorption capacity; Wettability; Flow resistance

1. Introduction

Water flooding is an important technique for supplementing inherent energy to the formation, which resultantly reduces the decline in oil production during field exploitation [1–3]. However, high water-cut often occurs with long-term water injection due to various reasons such as reservoir heterogeneity, water-oil mobility ratio, and impractical developing measures [4,5]. Increased water production will not only put an extra load on fluid handling facilities, but also make pipelines more vulnerable to scaling and corrosion. Eventually, the oil well needs

to be shut down due to the uneconomical production of crude oil [6]. Tremendous research has been conducted on water-shutoff operation, and scientists mainly emphasize on the development and effective application of polymers and polymer gels [7,8]. Although significant research has been carried out in the synthesis of water-soluble polymers for enhanced oil recovery (EOR) operation, no prudent solution has been found to prevent oil permeability reduction in the formation [9–12]. The disproportionate permeability reduction (DPR) can be used to solely reduce the water permeability instead of influencing hydrocarbons' permeability, which shows a promising potential to

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control excess water production without compromising on oil production [13–25].

Partially hydrolyzed polyacrylamide (PHPAM) has wide applications in the water-shutoff treatment. It is commonly used by mixing with other additives (i.e., crosslinking agents) during the process of injection. The PHPAM can adsorb on the rock surface through the interaction of hydrogen bonds between polymer and rock surface [26,27]. And the stretching and entanglement of the PHPAM molecular chain can effectively decrease the cross-sectional area of the fluid-flow pathways, leading to a permeability reduction of the rock. Notably, PHPAM can provide water film in fluid-flow pathways, it can reduce the flow resistance of the oil phase. Therefore, the injected PHPAM can decrease the water permeability (K_{rw}) and have a minor effect on the oil permeability (K_{ro}). However, the high salt concentrations, high reservoir temperatures ($>70^{\circ}\text{C}$) and the applied shear rate may lead to degradation of traditional PHPAM, leading the poor DPR and EOR performances. Several studies demonstrated that the clay nanoparticles can be added into the polymer solutions to improve the thickening capability and enhance the thermal stability [28,29]. Besides, introducing ionic groups into water-soluble polymers is also an important method to improve their viscosity in formation water [26]. The cationic or anionic charges dissociates from branch chains of polyelectrolyte, which results in intramolecular repulsions, increasing the hydrodynamic radius of the polymer molecules and the solution viscosity [30]. It is worth mentioning that ionic polymers would not only increase the aqueous solution viscosity, but also easily adsorb on a rock surface [31]. Cationic water-soluble polymers will easily adsorb on negatively charged rock surfaces due to electrostatic attraction. Besides, on the basis of divalent crosslinking theory [32], polyanions can be linked with negatively charged rock surface through divalent cations crosslinking agents, such as calcium ions [33]. The increase of polymer retention in pore throats can further increase the flow resistance of water flow.

In addition to adding ionic groups to the water-soluble polymer, incorporating hydrophobic monomers into the polymer chains is an important way to further improve its tolerance of high temperature, high salt concentration and high shearing loads. The water-soluble polymer with a small number of hydrophobic groups ($<1\%$) distributed along the hydrophilic chains was called hydrophobically associating polymer. This type of polymer attracts much attention in terms of EOR operation [34]. Hydrophobically associating polymer can form a reversible three-dimensional network structure via the interactions between hydrophobic groups, leading to a high hydrodynamic volume and a good thickening behavior. More importantly, hydrophobically associating polymers have a good performance at harsh reservoir conditions (i.e., under the condition of high salt concentrations and high temperatures) [26]. Many hydrophobically associating polymers have been verified to display an increase in viscosity upon increasing the temperature. The increasing temperature will further decrease the solubility of hydrophobic groups and lower critical solution temperature (LCST) groups of the polymers. These less soluble components will self-aggregate

and thus form intermolecular associations, which leads to an increase in viscosity. For associative copolymers, it has also been observed that the addition of salts will lead to the increase of bulk viscosity [26]. The added salts can decrease the solubility of the hydrophobic groups and screen the electrostatic repulsion between molecular chains, which contribute to the intermolecular hydrophobic interactions and thus an enhancement of the solution viscosity [26].

Due to the good thickening behavior and the salt and temperature resistance, the hydrophobically associating polymers have been widely used as suspensions for drilling fluids and cement slurries. In addition, the use of hydrophobically associating polymers for EOR has ever been reported by many excellent articles. These studies focus on improving the polymer rheological properties at reservoir conditions and trying to design suitable molecular architectures to meet the EOR application requirements. However, few researchers have focused on the DPR mechanisms of hydrophobically associating polymers. The hydrophobic groups in hydrophobically associating polymers may adsorb on the oil-wet rock surfaces through hydrophobic association. This behavior may improve the polymer DPR performance in oil-wet reservoirs. As mentioned before, introducing ionic groups into polymer molecules can further increase the water flow resistance. In this current study, an ionic partially hydrophobically modified polyacrylamide (HMPAM) was synthesized to investigate the DPR mechanism in both water-wet and oil-wet sandstone reservoirs.

First, the HMPAM was synthesized via free radical polymerization. Then, the Fourier-transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) were employed to confirm its molecular structure and basic property of HMPAM. After that, the DPR performance of HMPAM was studied through core flooding experiments. Subsequently, the contact angle measurements were conducted to characterize the wettability alteration capacity of HMPAM. And a series of adsorption experiments were conducted to help to reveal the DPR mechanism of HMPAM. Experimental results showed that the proposed HMPAM may be a new candidate for the selective water-shutoff agent in EOR operation. The flowchart of work steps was shown in Fig. 1.

2. Experimental section

2.1. Materials

2.1.1. Chemicals

Acrylamide (AM), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), allyl chloride, N,N-dimethyldodecylamine (12DMA), ammonium persulfate, sodium bisulfite, and anhydrous alcohol were purchased from Aladdin Chemical Reagent Company. Calcium chloride anhydrous, magnesium chloride hexahydrate, sodium chloride, and sodium hydroxide were obtained from Sinopharm Chemical Reagent Company. Dimethyl silicone oil and hydrolyzed polyacrylamide (25% degree of hydrolysis) were acquired from Jiangsu Baomo Company. All chemicals were used without any further purification otherwise stated.

Brine water, which was used as a flooding fluid in the current experiments, was prepared by dissolving NaCl,

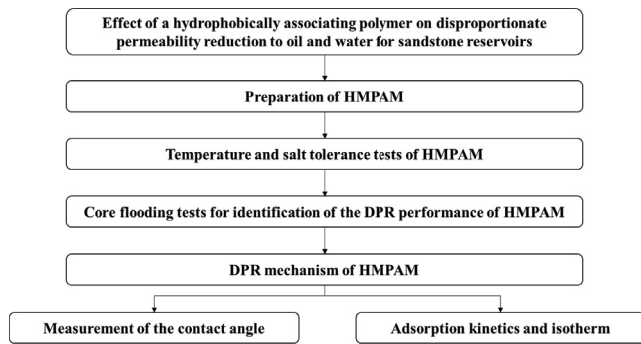
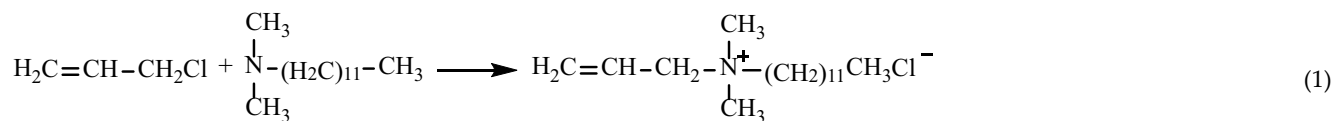


Fig. 1. Flowchart of work steps.

CaCl_2 and MgCl_2 in distilled water, and the weight proportions were 7, 0.6, and 0.2, respectively. The salt concentration of this brine water is 40,000 mg/L. The crude oil used in this study was obtained from Yanchang Oilfield. The density and dynamic viscosity of the crude oil were 0.773 g/cm³ and 8.21 mPa·s, respectively.

2.1.2. Rock samples

In this study, the quartz sandstones with the size of 40 mesh were obtained from Hai'an Company, China.



Subsequently, HMPAM was synthesized by AM, AMPS, and DDAAC through the free-radical polymerization in the aqueous solution, which attributed to the good water-solubility of the copolymer. Acrylamide (AM) and AMPS are the most used monomers for copolymerization due to their thermal stability, salt tolerance, and highly efficient polymerization effect [36,37]. DDAAC was used for providing hydrophobic and charged groups to the copolymer. The synthesis procedure is as follows: The monomers, including AM, AMPS, and DDAAC, with a weight concentration of 25% were dissolved in distilled water, respectively. And then, these solutions were mixed at the weight proportion ratio of 10:1:0.2. Meanwhile, the pH of this solution was adjusted to 10 by adding 5% sodium hydroxide solution.

All quartz sandstones were initially water-wet, but some of them were treated in dimethyl silicone oil for 48 h at 30°C to alter the wettability. These sandstones were used for the adsorption experiments. The artificial core samples used in the contact angle measurements and flooding experiments were obtained by the State Key Laboratory of Petroleum Resources and Prospecting at China University of Petroleum (Beijing), China. The characteristics of the core sample are presented in Table 1.

2.2. Preparation of HMPAM

Hydrophobically associating polymers generally possess a long carbon branch (i.e., 8–18 carbon atoms) distributed along the main backbone [35]. In this study, allyl chloride and 12DMA were chosen to synthesize dodecyl dimethyl allyl ammonium chloride (DDAAC) to obtain a long carbon chain. The synthesis procedure is as follows: The allyl chloride, 12DMA and anhydrous alcohol were dissolved in deionized water with the weight proportion ratio of 2:7.5:7.5. Then, this solution was poured into a high-pressure reactor and stirred by an electric mixer at a constant speed of 120 rpm under 50°C. After 48 h, the mixture was transferred to a flask to remove the anhydrous alcohol through vacuum distillation. Eq. (1) displays the quaternization reaction process of DDAAC.

After that, the solution was poured into a flask and stirred at 150 rpm in a water bath for 15 min at 55°C. The initiator solution containing 0.8% NaHSO_3 and 0.4% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was poured into the mixture. The stirring would stop when the viscosity dramatically increased. Finally, the synthesized polymer was purified with anhydrous alcohol and dried in an oven for 48 h at 65°C. This procedure was repeated three times. The FTIR (NEXUS 470 Fourier-transformation infrared spectrometer, Nicolet Instrument Technologies Inc., U.S.A.) was employed to determine the molecular structure of HMPAM. And the number-average molecular weight (M_n) and weight-average molecular weight (M_w) of HMPAM according to the 0.5% solutions were determined with GPC (GPC-20A, produced by Shimadzu Co.,

Table 1
Core sample characteristics

Core #	Constitutes	Length (cm)	Diameter (cm)	Permeability (μm^2)	Porosity (%)	Contact angle ($^\circ$)
1	Quartz and epoxy resin	6.0	2.45	800	22	42
2	Quartz and epoxy resin	6.0	2.45	800	22	42
3	Quartz, epoxy resin and dimethyl silicone oil	6.0	2.45	800	22	126
4	Quartz, epoxy resin and dimethyl silicone oil	6.0	2.45	800	22	126

sections were polished with unglazed porcelain. After measuring the initial contact angles of four cross-sections, core sections #1 and #3 were aged for 12 h in 5,000 mg/L HMPAM solution, and core sections #2 and #4 were aged for 12 h in 5,000 mg/L PHPAM solution. Afterwards, their contact angles were determined. It should be noted that the contact angles of water-wet cross-sections were determined based on crude sessile oil drop on the rock surface immersed in brine water with 40,000 mg/L salinity, whereas the contact angles of the oil-wet sections were measured with a sessile brine water drop on the rock surface immersed in oil.

The adsorption of polymers on rock surfaces has a crucial impact on the DPR effect of polymers as mentioned earlier. In order to verify whether HMPAM can yield a large amount and long-lasting adsorption, the interactions between HMPAM and sandstone were investigated. To give a fair evaluation, PHPAM was adopted as the comparison group. First, HMPAM solutions with different concentrations (i.e., 0.2% to 1.0%) were poured into flasks with 1.5 g quartz sandstones. These solutions were stirred with an electric stirrer at 250 r/min for 16 h in a water bath at 45°C to ensure the complete adsorption of polymers on the rock surface. Finally, after reaching the adsorption equilibrium, different polymer/sandstone dispersions were centrifuged and decanted to obtain polymer solution, and the concentrations were determined with a spectrophotometer ($\lambda = 546 \text{ nm}$). The equation used to calculate the amount of adsorbed polymer is as follows:

$$\Gamma = \frac{V(C_1 - C_2)}{G} \quad (6)$$

where Γ (mg/g) is the adsorption value (the mass of adsorbed polymers per unit mass of sandstone), V (L) is the volume of polymer solution, G (g) is the mass of sandstone, C_1 (mg/L) is the concentration of polymer solution before adsorption, and C_2 (mg/L) is the concentration of polymer solution after it reached adsorption equilibrium.

3. Results and discussion

3.1. Identification of molecular structure

Fig. 3 shows the typical absorption peaks of DDAAC and HMPAM in FTIR spectra. In the infrared (IR) spectrum of DDAAC, the adsorption peak at $3,409 \text{ cm}^{-1}$ corresponds to amide/ammonium radical. The peaks at $2,922$ and $2,852 \text{ cm}^{-1}$ are the absorption peaks of methyl and methylene, respectively. Besides, the peak at $1,616 \text{ cm}^{-1}$ represents the stretching vibrations of carbon-carbon double bonds. The long carbon chain generates a characteristic peak at 721 cm^{-1} . The IR spectra of HMPAM includes the characteristic absorption peaks of amide at $3,335$ and $1,650 \text{ cm}^{-1}$. It is noteworthy that sulfonates and long carbon chains are represented by peaks at $1,035$ and 690 cm^{-1} , respectively. Hence, this indicates that the synthesized HMPAM includes the absorption peaks of AMPS and DDAAC. Furthermore, C=C vibrations are barely visible in the IR spectrum of HMPAM. Thus, AM was involved in polymerization. These results demonstrate that the molecular structure of the synthesized HMPAM is consistent with the designed one. Therefore, it can be

concluded that HMPAM has been successfully synthesized. In the next step, the molecular weight of HMPAM was determined in a GPC test. The number-average molecular weight (M_n) was found to be 1.33×10^6 , and the weight-average molecular weight (M_w) was 2.79×10^6 .

3.2. Temperature and salt tolerances

According to Fig. 4, the viscosity of 0.5% HMPAM solution decreased with the increase of salt concentration. The added salt caused a shielding of the electrostatic interactions between polymer molecules, leading to the destructing of the polymer network and the loss of the solution viscosity [26,39]. Although the viscosity of HMPAM decreased with the increase of salinity, its viscosity was

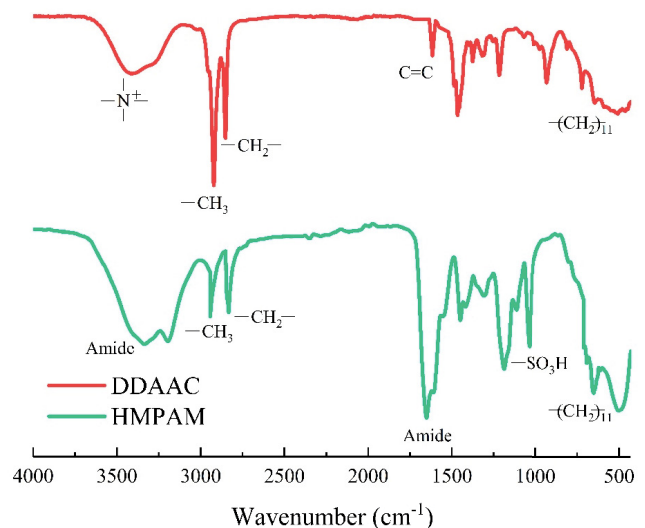


Fig. 3. Infrared spectra of DDAAC and HMPAM.

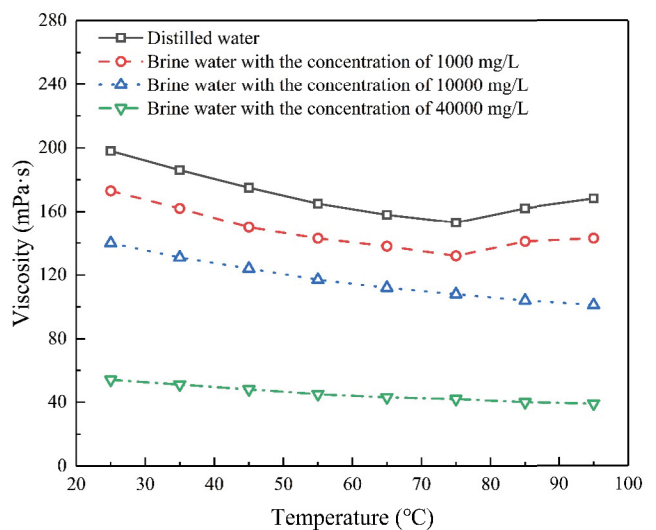


Fig. 4. Effect of salt and temperature on the viscosity of 0.5% HMPAM solution with the salt concentration of 0; 1,000 mg/L; 10,000 mg/L and 40,000 mg/L over the temperature range of 25°C–95°C.

higher than 100 mPa·s at the salinity of 10,000 mg/L. Besides, the HMPAM has a good performance on temperature tolerance. For distilled water and low salinity solution (i.e., brine water with the concentration of 1,000 mg/L), the viscosity of HMPAM solution decreased slightly with increasing temperature before 75°C, after which an increase of viscosity can be observed. This is because that the increase of temperature contributed to the decrease of the association strength of the hydrophobic groups, leading to the viscosity reduction [40,41]. However, when the temperature is higher than 75°C, the hydrophobic association changes from intramolecular association to intermolecular association due to the increase of the mobility of the polymer chains, resulting in a high hydrodynamic volume and thus a high viscosity [42]. Although this phenomenon cannot be observed under high salinity, HMPAM can maintain strong thermal stability. Overall, the synthesized HMPAM has good thermal stability and moderate brine compatibility, indicating a good potential for field applications.

3.3. Determination of DPR performance

In order to investigate whether the synthesized HMPAM can yield a good DPR performance, the selectivity

parameters (σ) were determined by means of core flooding experiments. The line graphs in Fig. 5 show the inlet pressure and permeability of four different core samples treated with HMPAM or PHPAM. In Fig. 5a (core #1), the initial water permeability (K_{w1}) was $556.581 \times 10^{-3} \mu\text{m}^2$ at 6 PVs. The permeability decreased after 0.25 PVs of HMPAM flooding and then was stabilized at $30.57 \times 10^{-3} \mu\text{m}^2$ (K_{w2}). After oil flooding, the permeability increased rapidly to $352.543 \times 10^{-3} \mu\text{m}^2$ (K_{o2}). The inlet pressure exhibited a completely different trend with permeability. It is worth mentioning that $(K_{w1} - K_{w2})/K_{w1}$ was 94.507% which exceeded $(K_{o1} - K_{o2})/K_{o1}$ by 71.411%. Results show that HMPAM effectively increased the flow resistance of water and have little impact on oil. Fig. 5c presents a similar trend to Fig. 5a, which indicates that HMPAM might exhibit a strong DPR effect in both water-wet and oil-wet core samples. As shown in Fig. 5b and d, after PHPAM flooding, it can be observed that the permeability changed little throughout the core flooding tests. According to Table 2, HMPAM yielded high selectivity parameters of 0.714 in core #1 and 0.734 in core #3. The corresponding selectivity parameters yielded by PHPAM in the other two cores were 0.575 and 0.310, respectively. Hence, the DPR performance of HMPAM is better than that of PHPAM, particularly in oil-wet core samples.

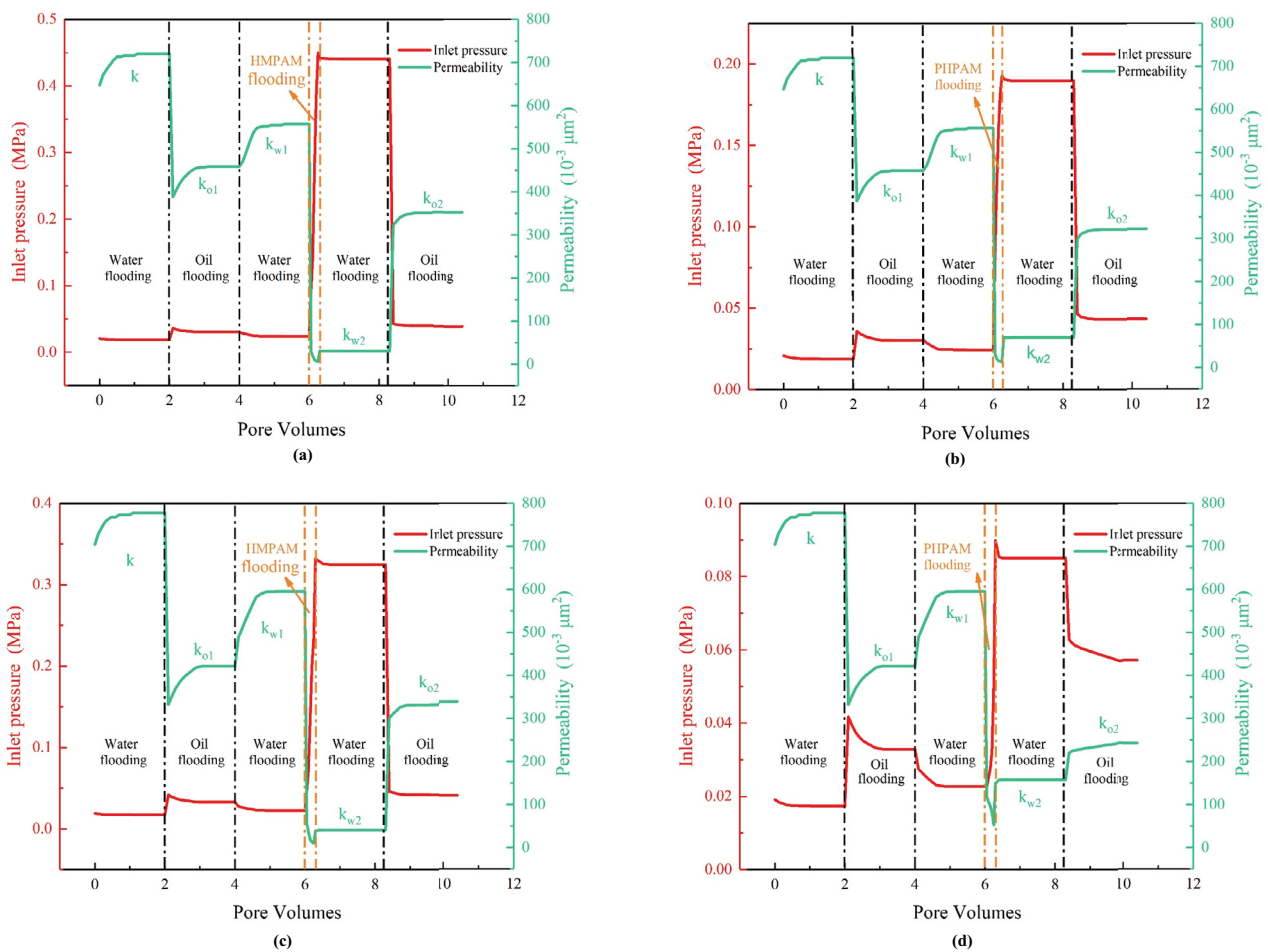


Fig. 5. Oil macro-displacement with (a) HMPAM and (b) PHPAM in water-wet core samples and (c) HMPAM and (d) PHPAM in oil-wet core samples.

3.4. Measurement of the contact angle

The wettability of a rock surface is one of the key factors which affects the oil-water relative permeability [43]. According to previous studies, the wettability alteration from oil-wet to water-wet can significantly improve the oil permeability and reduce the water permeability [44–47]. To investigate whether HMPAM can alter the wettability of the rock surface, the contact angles of cross-sections before and after polymer treatment were measured. As shown in Fig. 6, the contact angle of water-wet cross-sections (i.e., cores #1 and #2) slightly decreased after aging with HMPAM and PHPAM. HMPAM and PHPAM were easily adsorbed on the rock surface through hydrogen bonds. The non-adsorbed part of the molecular chains always exhibits stronger hydrophilicity than the rock surface, which leads to a more water-wet rock surface. As for oil-wet core samples, after the HMPAM treatment, the contact angle of the cross-section of core #3 decreased from 127.3° to 34.5°, indicating the occurrence of the wettability alteration. While, after aging with the PHPAM, the contact angle of the cross-section of core #4 hardly changed. The hydrophobic groups on the

branch chains of HMPAM molecules were easily adsorbed on the oil-wet rock surface, and the non-adsorbed parts (i.e., hydrophilic backbones) extended outward, altering the wettability of the rock surface. In contrast, PHPAM has no hydrophobic groups, so it cannot alter the wettability of the oil-wet rock surface. Therefore, the HMPAM performs better DPR behavior in oil-wet reservoirs than PHPAM can be attributed to its' capacity of wettability alteration.

3.5. Adsorption kinetics and isotherm

The polymer retention in pore throats can significantly increase the flow resistance of water, while hardly affecting oil flow. In other words, the adsorption of polymers on rock surfaces plays an important role in DPR performance. The adsorption kinetics and isotherm of HMPAM were determined by adsorption experiments. As shown in Fig. 7, the adsorption amounts of HMPAM and PHPAM on water-wet and oil-wet sandstone increased in the first 16 h. After 4 h, approximately 1 mg HMPAM adsorbed on 1 g water-wet and oil-wet sandstone, respectively. While only 0.5 mg PHPAM was adsorbed in this period. After 16 h, the adsorption

Table 2
Results of core flow tests with HMPAM and PHPAM

Core #	K_{w1} ($10^{-3} \mu\text{m}^2$)	K_{w2} ($10^{-3} \mu\text{m}^2$)	K_{o1} ($10^{-3} \mu\text{m}^2$)	K_{o2} ($10^{-3} \mu\text{m}^2$)	$(K_{w1} - K_{w2})/K_{w1}$ (%)	$(K_{o1} - K_{o2})/K_{o1}$ (%)	F_{rw}	F_{ro}	σ
1	556.581	30.57	458.422	352.543	94.507	23.096	18.207	1.300	0.714
2	556.581	71.003	458.422	322.126	87.243	29.731	7.839	1.423	0.575
3	595.542	41.497	422.293	339.234	93.032	19.668	14.352	1.245	0.734
4	595.542	158.441	422.293	243.443	73.395	42.352	3.759	1.735	0.310

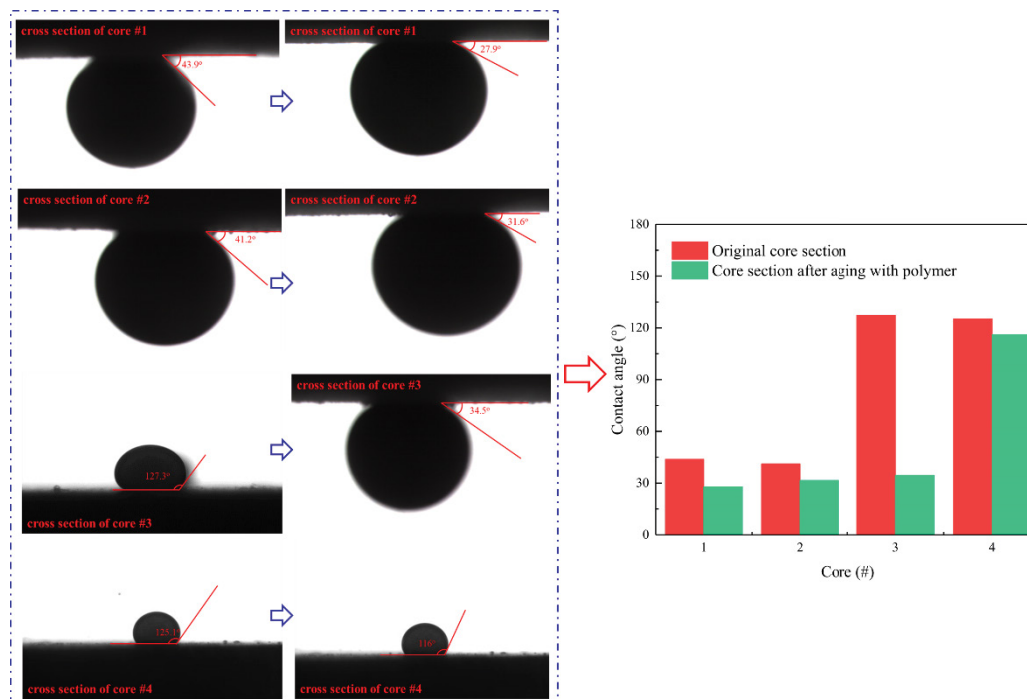


Fig. 6. Contact angles of cross-sections of cores #1 to #4 before and after aging with HMPAM (core #1 and #3) or PHPAM (core #2 and #4).

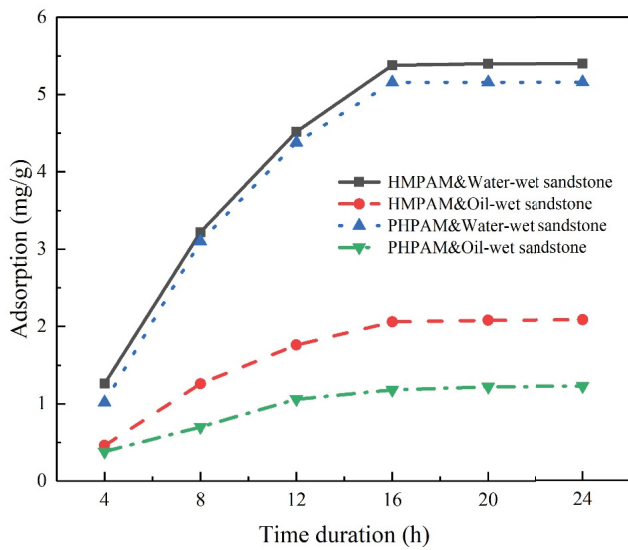


Fig. 7. Adsorption kinetics of HMPAM and PHPAM on sandstone surface.

amount of HMPAM was 5.4 mg per 1 g water-wet sandstone, and the adsorption amount of PHPAM was 2.08 mg/g. A more significant difference can be observed in the adsorption experiments of oil-wet sandstones, the adsorption of HMPAM was 5.16 mg/g, while there was only 1.22 mg/g for PHPAM. It indicated that the adsorption capacity of PHPAM on sandstone surfaces is much lower than that of the HMPAM, particular for oil-wet sandstone. This is mainly because the interactions between HMPAM and sandstones are significantly different from the interactions yielded by PHPAM and sandstones. The adsorption of HMPAM on the sandstone is mainly attributed to the intermolecular hydrophobic association interactions yielded by the hydrophobic groups of HMPAM and the long-chain alkanes in oil film on the oil-wet rock surface, and the electrostatic interactions between ammonium radicals of HMPAM and negatively charged inorganic matter on the sandstone [34,48,49]. However, PHPAM can only yield weak hydrogen bonding interactions with sandstone [50,51]. The monolayer adsorption was limited by the surface area, which would finally reach saturation. To determine the equilibrium concentration of HMPAM, the adsorption isotherm was plotted based on experimental results. According to Fig. 8, the adsorption amount of HMPAM on water-wet and oil-wet sandstones increased sharply with the HMPAM concentration increasing before 5,000 mg/L, after which it remained nearly constant. According to this adsorption isotherm, the HMPAM concentration should be 5,000 mg/L in DPR applications.

On the basis of the above experimental results, we can summarize the DPR mechanism of HMPAM as follows. The rock surface of oil reservoirs is always negatively charged and oil-wet due to the adsorption of crude oil. After HMPAM injection, the positively charged ammonium radical groups on its molecular chain link with the negative charges of the rock surface through electrostatic forces, which promotes the adsorption of HMPAM on the rock surface. In addition, the hydrophobic groups on the branch chains of HMPAM molecules can associate with long-chain alkanes

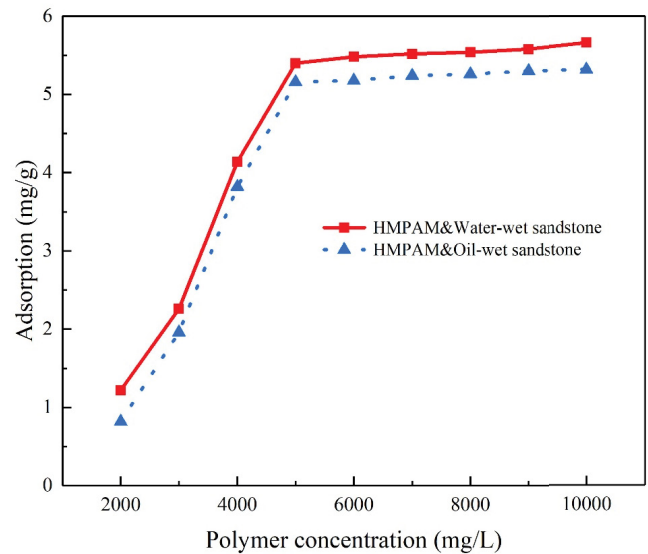


Fig. 8. Adsorption isotherm of HMPAM on oil-wet sandstone surface.

in oil film through hydrophobic association forces, further promoting the adsorption of HMPAM on the rock surfaces. After retention of HMPAM on the pore throats, the hydrophilic backbones extended outwards that resulting in the wettability alteration of rock surfaces. It increased the flow resistance of water but have little effect on the oil flow. Therefore, it can be inferred that HMPAM leads to a low water permeability with little effect on oil permeability, which results in a good DPR performance in oil reservoirs.

4. Summary and conclusions

In this study, a modified polymer with a unique ionic hydrophobic part was prepared via free-radical polymerization which has the potential to be applied in DPR experiments. The adsorption experiments and contact angle measurements help to reveal the DPR mechanism of HMPAM. The main results are as follows: The oil-water selectivity parameters yielded by HMPAM in water-wet and oil-wet cores were 0.714 and 0.734, respectively, which was significantly higher than traditional water-soluble polymer. According to a series of analysis experiments, 0.5% HMPAM can yield 5.40 mg/g adsorption on the water-wet sandstone and 5.14 mg/g on the oil-wet sandstone. These adsorptions narrowed the pore throats and altered the wettability of the oil-wet rock surface, increasing the flow resistance of water, while hardly affecting the oil flow.

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