

Application of a novel cationic starch in enhanced oil recovery and its adsorption properties

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Abstract—We report a preparation of water-soluble cationic starch and its application as an oil-displacing agent in chemical enhanced oil recovery. The singular sand-pack core-flood tests provide experimental evidence that the injection of the modified starch after the conventional water flooding can significantly enhance oil recovery and effectively reduce water-cut. To discuss the proposed oil-displacement mechanism of this cationic starch solution, its static and dynamic adsorption properties were also presented in this paper.

Key words: Cationic Starch, Enhanced Oil Displacement, Simulation Test, Adsorption Properties

INTRODUCTION

Cationic polymers are important functional materials that can be widely used as shale-control agent, demulsifier, blocking agent, and filtrate reducer for drilling fluid in the petrochemical industry [1-4]. Dimethylamine-epichlorohydrin condensates and homopolymers or copolymers of diallyldimethylammonium chloride are two major types of cationic polymers currently used in oilfields [5]. But three main issues-fewer varieties, process complexity and high cost-limit their wider application in the petrochemical industry. Thus, much research attention has been transferred to new fabrication technologies of cationic polymers by reactions between cationic etherifying agents and less expensive starch, cellulose, or polyacrylamide [6,7]. Polymerization of cationic monomers and chemical reactions of polymers are two popular ways to produce cationic polymers. The second method can be further divided into two different cationic modifications based on synthetic polymers (e.g., polyacrylamide) [8,9] and natural polymers (e.g. starch, cellulose, chitin, lignose), respectively. We once prepared a cationic polymer by reaction of 2,3-epoxypropyltrimethylammonium chloride and starch via a dry process and studied its application as a profile control agent in enhanced oil recovery (EOR) technique [7].

Herein, we report the preparation of water-soluble quaternary ammonium cationic starch through a solution method. The modified starch expresses better salt tolerance; it is significant for high-salinity reservoirs in EOR technique where the commonly used partially hydrolyzed polyacrylamide (HPAM) is unfit. The indoor simulation tests indicate that injecting this modified starch solution after conventional water flooding significantly enhance oil recovery and effectively reduce water-cut, which shows that this product could effectively play an oil displacement function. We also checked the adsorption capability of the water-soluble cationic starch on oil sand because the adsorption could change the surface wettability and elec-

trical property of the sand particles, which would then produce a positive influence on the effect of oil displacement [10,11].

EXPERIMENTAL SECTION

1. Materials

Water-soluble quaternary ammonium cationic starch was prepared by reaction of maize starch with 2-chloroethyltrimethyl ammonium chloride under mechanical stirring at 80 °C in the presence of catalyst NaOH. HPAM (3530S, SNF) was used as received without further purification. Both the modified starch solution and HPAM solution were prepared by using reservoir formation water (total salinity degree TSD=5,727 mg/L) as solvent. Model oil used in lab simulation was made from degassed oil of Gudao oilfield and engine oil; its viscosity at 70 °C was 72 mPa·s.

2. Physical Simulation Experiments

Quartz sands of six different mesh sizes, 30-40, 40-60, 60-80, 80-100, 100-150, and 200-300 mesh, obtained from Gudao oilfield were chosen to pack the sand-pack (Φ 25×200 mm) in the standard core flooding equipment. The porosity of the sand-packed model was measured by using the imbibition method. Then the model permeability was measured prior to simulation experiment by using reservoir formation water as the working medium, which could be calculated using Darcy's law:

$$K = \frac{\mu L Q}{\Delta P A} \quad (1)$$

where K is water permeability, μ is the viscosity of the fluid, L is the length of the sand-pack, Q is the flow rate of the fluid, ΔP is the differential pressure, and A is the cross sectional area of the sand-packed model.

Singular sand-pack core flooding tests were conducted to simulate the process of oil recovery in the reservoir. The sand pack was saturated with model oil. Formation water flooding was performed first and was not ended until the water-cut increased to 98%. It was followed by injection of 0.3-1.0 pore volume (abbr. PV) of the modi-

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fied starch solution. Finally, reservoir formation water was again flooded until there was no oil coming in the effluent. The changes of water-cut and oil recovery during the simulated experimental process were recorded.

3. Adsorption Test Procedure [12,13]

Static adsorption experiments were conducted by adding sand (100-150 mesh sizes) to the starch solution (liquid-solid ratio=50 mL/1 g) at constant temperature with shaking to evaluate the adsorption of the modified starch on oil sand. The amount of the starch in supernatant was determined by HP 8453 UV-Vis spectrophotometer based on the method reported by Qian [14]. At the end, the amount of modified starch retained by sand was then calculated as followed:

$$\Gamma = (\rho_0 - \rho) \cdot V / m \quad (2)$$

where Γ is the adsorbed amount (mg of modified starch/g of sand), ρ_0 and ρ are the initial concentration and equilibrium concentration of the starch solution, respectively, V is volume of the solution, and m is mass of oil sand. By comparison, static adsorption experiments of HPAM solution were performed as mentioned above.

Dynamic adsorption experiments were performed using a singular sand-pack core-flooding setup. First, the washed and dried oil sand was packed inside two sand-pack holders, respectively, and made their water permeabilities approximately equal. Next, pack 1 was saturated with the reservoir formation water and model oil successively and flooded by water to residual oil saturation. After that, 3 PV of 1,000 mg/L modified starch solution and 3 PV of reservoir formation water were injected through the pack 1 after another at a flow rate of 1 mL/min. The outlet concentration was recorded by the spectrophotometer. Finally, the dynamic adsorption amount was calculated as follows:

$$\Gamma_d = (\rho_1 V_1 - \rho_2 V_2) / m \quad (3)$$

where Γ_d is amount of dynamic adsorption, mg/g, ρ_1 and ρ_2 are the initial concentration of the modified starch solution and the outlet concentration of the starch, respectively, V_1 and V_2 are volumes of the injected cationic starch slug and the collected solution after successive water flooding, and m is mass of oil sand in sand pack. As a contrast experiment, 3 PV of HPAM solution and 3 PV of reservoir formation water were injected through Pack 2 one after another at the same flow rate. After checking the outlet polymer concentration by the spectrophotometer, we obtained the dynamic adsorption amount of HPAM based on formula 3.

4. Characterization

Viscosity measurements of modified starch and HPAM solutions were made by using a Brookfield DV-II+ viscometer. And their hydromechanics diameters were measured by a Malvern Zetasizer 3000 HS.

RESULTS AND DISCUSSION

1. Salt Tolerance of the Modified Starch

We used artificial mineralized water (TSD being from 1,000 to 20,000 mg/L) to prepare 2 wt% of cationic starch solutions and checked their viscosity changes. As shown in Fig. 1, the solution viscosity had no large decrease and showed a tendency toward stabilization when the salinity was above 3,000 mg/L. This indicates that

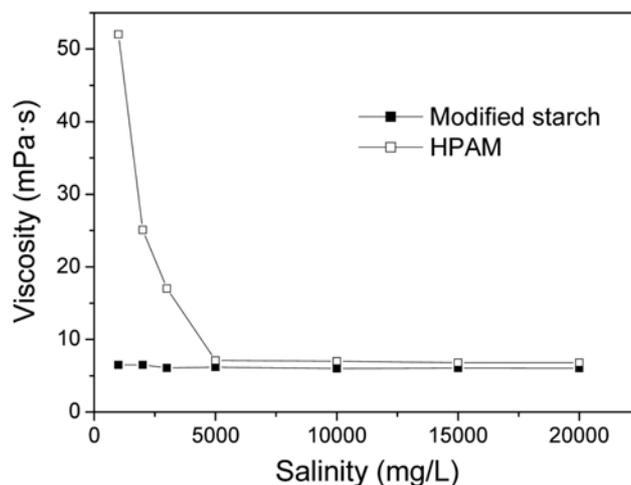


Fig. 1. Variation of viscosities of modified starch and HPAM solutions with salinity.

the effect of salinity on the viscosity of the starch solution is not obvious and this modified starch product expresses relatively strong salt tolerance. By comparison, we also prepared 1,500 mg/L of HPAM solutions by using the same mineralized water and recorded their viscosity changes. The viscosity of HPAM solution decreases quickly from 52 mPa·s to 7.1 mPa·s when the salinity increases from 1,000 mg/L to 5,000 mg/L (Fig. 1), which shows that HPAM solution has less salt-tolerance capacity. This insensitivity to salinity of the modified starch can also be analyzed from the variation of the hydromechanics diameters of the starch product and HPAM with salinity. With increasing of the salt content in HPAM solution, the hydromechanics diameter of the polymer molecules decreases from 610.4 nm to 223.8 nm (Fig. 2). It is because the increase of the amount of the strong electrolyte added weakens the repulsion between same charges on the molecular chain, which results in random coil of the molecular chain and decrease of the particle size. For the modified starch molecules, the hydromechanics diameter decreased obviously from 304 nm to 246.9 nm under the conditions of salinity raised from 0 to 5,000 mg/L, but after that, it changed slightly, even increasing solution salinity. So its viscosity loss is relatively less and its salinity tolerance is better than HPAM solution.

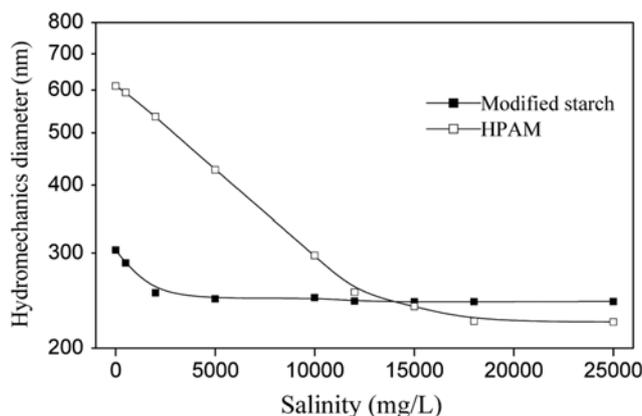


Fig. 2. Variation of hydromechanics diameters of modified starch and HPAM with salinity.

Table 1. Variation of oil recovery with concentration of injected starch solutions

Label	Permeability, μm^2	Cationic starch, %	Injected volume, PV	η_1 , %	η_2 , %	$\eta_2 - \eta_1$, %
1	1.46	1.0	0.43	50.6	68.6	18.0
2	1.44	0.5	0.45	53.7	64.0	10.3
3	1.40	0.3	0.44	54.7	63	8.3

η_1 : oil recovery after conventional water flooding, η_2 : the final oil recovery after injection of modified starch slug and successive water flooding

Table 2. Variation of oil recovery with injected volume of the starch solution

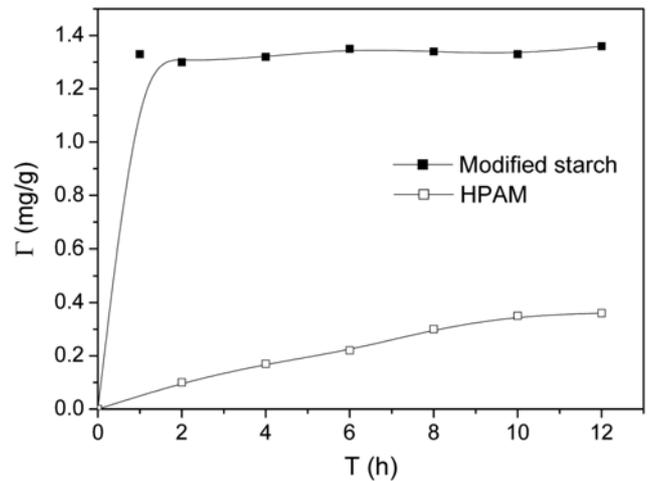
Label	Permeability, μm^2	Cationic starch, %	Injected volume, PV	η_1 , %	η_2 , %	$\eta_2 - \eta_1$, %
1	1.09	0.5	1.0	46.3	64	17.7
2	1.10	0.5	0.50	58.1	68.6	10.5
3	1.20	0.5	0.38	57.7	62.4	4.7

2. Physical Simulation Experiments

Standard singular sand-pack core-flood tests were performed to evaluate the oil displacement effect of the cationic starch from the following three aspects: concentration, injected volume of the modified starch solution, and residual oil saturation after conventional water flooding. If treated with nearly the same permeability of the sand packs and injected volume of the modified starch slugs, as shown in Table 1, the higher the solution concentration, the larger the enhanced oil recovery in courses of the cationic starch injection and successive water flooding. Taking account of the application cost, we chose 0.5 wt% of cationic starch solution to investigate effects of injected volume of the starch solution and residual oil saturation on the oil recovery. Table 2 indicates that, under the same concentration condition, the enhanced oil recovery after the conventional water flooding increased from 8.3% to 18.0% with increasing of the injected volume of the cationic product from 0.38 PV to 1.0 PV. It is believed that the improvement of intake volume enlarges adsorbed amount of the cationic starch in pore passage and interfacial action of the starch/model oil, which promotes oil displacement effect of the cationic starch system. Besides, the effect of the difference among residual oil saturations after conventional water flooding (namely, secondary recovery) on the cationic starch flooding is very obvious. When residual oil saturation decreased from 46.7% to 30.4%, the enhanced oil recovery in cationic starch and successive water flooding was reduced from 15.3% to 5.4% (Table 3). The above experimental results show that, with the increase of concentration and injected volume of the cationic starch, this product flooding

Table 3. Effect of residual oil saturation after conventional water flooding on oil recovery

Label	Permeability, μm^2	Cationic starch, %	Injected volume, PV	η_1 , %	η_2 , %	$\eta_2 - \eta_1$, %
1	1.13	0.5	0.50	53.3	68.6	15.3
2	1.07	0.5	0.50	58.1	68.6	10.5
3	1.17	0.5	0.50	69.6	75	5.4

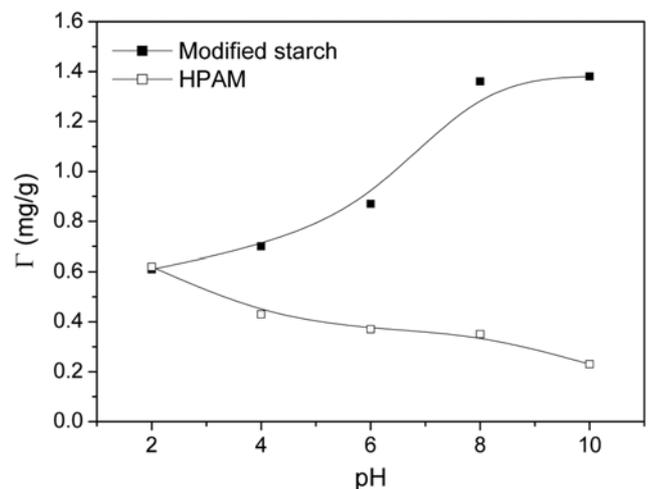
**Fig. 3. Static adsorbance of 200 mg/L of modified starch and HPAM solutions on oil sand at 298 K versus adsorption time.**

system after the secondary recovery obtains an ideal result in lab simulation experiments.

3. Adsorption Properties of the Cationic Starch on Oil Sand

The adsorption of polymer or surfactant on solid surface could change the surface properties, so we speculate that the adsorption of the modified starch on oil sand plays an active role in the enhanced oil recovery of this cationic starch flooding. Fig. 3 shows the static adsorption curves of cationic starch and HPAM solutions on oil sand at 298 K, respectively. It indicates that the adsorption rate of the starch solution is relatively fast and its adsorption equilibrium can be reached within 2 h under the action of electrostatic force. Saturated adsorption capacity is about 1.3 mg/g and remains mostly unchanged after that. For HPAM solution, it would take a longer time, about 10 h, to attain the adsorption equilibrium, and its adsorption capacity is about 0.35 mg/g, less than that of the modified starch solution.

The saturated adsorption capacity of the modified starch markedly rose with increase of pH value and it had a rapid increase when pH value was between 6-9 (Fig. 4), which was attributed to the charge

**Fig. 4. Static adsorbance of 200 mg/L of modified starch and HPAM solutions on oil sand at 298 K versus pH.**

characteristics of oil sand surface. There are two main types of charges on oil reservoir mineral: permanent charges and variable charges [15], while variable charges vary with the change of pH value. With the decrease of pH under acidic condition, the electropositivity of the variable charges gathers strength and the adsorption sites of the cationic starch on mineral gradually fall off, which results in the decrease of the adsorptive capacity. On the contrary, the increase of pH value under basic condition causes the increase of both variable negative charges and the absorption sites on mineral, so the adsorptive capacity of the cationic product improves. It can also be seen from Fig. 4 that the adsorption capacity of HPAM solution decreases with the increase of pH value, which is caused by the strengthened electrostatic repulsion between polymer molecules and oil sand surface. Fig. 5 shows two adsorption isotherms of the cationic starch solution at different reaction temperatures. The increase of temperature from 298 K to 343 K has no obvious influence on adsorptive capacity of the starch on oil sand. The equilibrium adsorption capacity of the cationic starch on oil-water interface is relatively lower and increases as the increase of pH value (Fig. 6), which is allied to the charge characteristics on crude oil interface. The characteristics are caused by protonation-deprotonation of organic molecules in crude oil. H^+ content is higher when pH value of the solution is lower under acidic condition. Meanwhile, protonation reaction is dominant on oil-water interface. The more H^+ results in the decrease

of amount of cationic starch adsorbed on the interface via electrostatic interaction. Under basic condition, improvement of pH value causes the increase of OH^- content, and the deprotonation reaction is dominant on oil-water interface, so the "solubility" of the starch can also increase.

Dynamic adsorbance of the modified starch is 0.23 mg/g, which is lower than its static adsorption capacity but higher than 0.11 mg/g of dynamic adsorption capacity of HPAM. One reason is due to incomplete adsorption of the product on sand surface. During injection of the modified starch slug and successive water flooding, the fluid tends to channel through high permeability zones or pore passages in sand pack holder rather than low porosity and low permeability zones. So the cationic product is not adsorbed on the whole sand surface, which partially decreases the adsorption capacity of the modified starch. Besides, the scouring action of the injected fluid is favorable to the desorption of adsorbed cationic starch, which also reduces its adsorption on solid surface.

The favorable static and dynamic adsorption properties provide a basic pre-condition for the wettability transition to hydrophilicity and improvement of sweep efficiency by decreasing the injected solution-adsorbed pore passage size. In the follow-up work, we will further study the oil displacement mechanisms of this water-soluble cationic starch as an oil displacement agent.

CONCLUSION

Simulation tests for enhanced oil recovery technology indicate that adding water-soluble cationic starch slug after conventional water flooding will improve the oil recovery efficiency markedly. By studying variations of its viscosity and hydromechanics diameter with solution salinity, we find that this cationic starch has better salt tolerance than often-used HPAM. For the enhanced oil recovery mechanism of this cationic solution, we investigated its adsorption characteristics on oil sand surface and oil-water interface in static adsorption tests. The results show that its adsorption rate is relatively fast and the adsorption capacity is pH-dependent. It was also found that the cationic starch possessed better dynamic adsorption capacity than HPAM.

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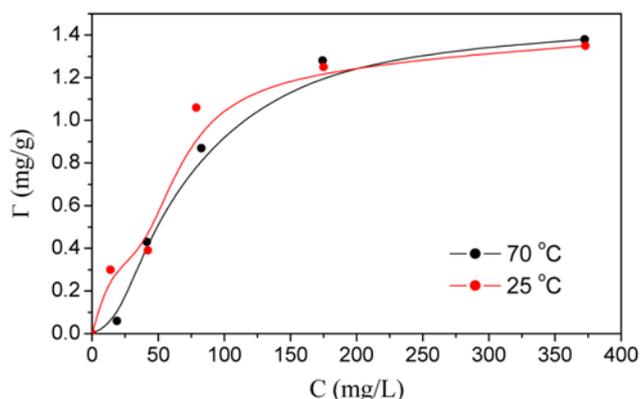


Fig. 5. Adsorption isotherms of the modified starch solution at 298 K and 343 K, respectively.

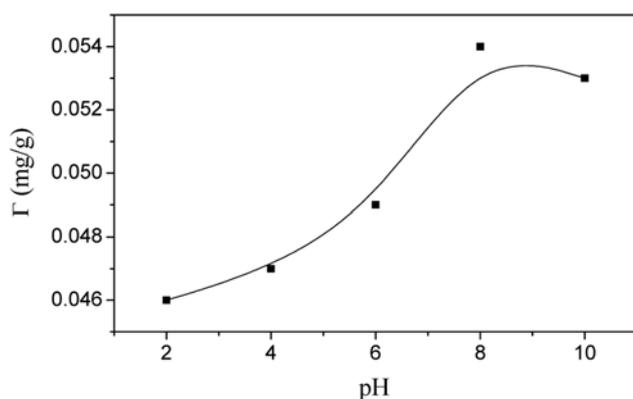


Fig. 6. Adsorbed amount of 400 mg/L modified starch solution on crude oil-water interface at 318 K.

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