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Retention Behaviors of Hydrophobically Associating Polyacrylamide Prepared via Inverse Microemulsion Polymerization Through Porous Media

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The retention behavior of hydrophobically associative polyacrylamide (HAPAM) with homogeneous composition in porous media was investigated. The results showed that HAPAM could exhibit different retention behavior, compared to PAM due to the existence of hydrophobic association group in HAPAM molecular frame. The critical association concentration could also be reflected by the curves between HAPAM concentration and retention amount. The retention amount of HAPAM was higher than that of polyacrylamide (PAM) and was smaller than the absorption amount of HAPAM. The retention mechanism was mainly controlled by adsorption mechanism.

Keywords: Hydrophobically associating polyacrylamide, retention behavior, adsorption, porous media, polymer flooding

1 Introduction

Polymer retention is the phenomenon whereby polymer molecules become trapped in the pores of porous media during injection. In general, mechanisms identified are adsorption of the polymer on the porous media surface, mechanical entrapment of the polymer molecules, and hydrodynamic retention (1). Retention of polymer in oil reservoir is an important parameter for polymer flooding simulation. It is also important to take into account the retention effects when conducting injections. The retention of polymer molecules in porous media can cause an additional resistance to flow and a decrease in polymer concentration, both of which can be detrimental to injections that are aimed to maintain a mobile polymer front (2, 3). Along with reduced viscosity, retention of the polymer molecules causes a delay

in the arrival of the polymer front because of a decrease in polymer concentration (4).

Over the past decades, hydrophobically associating polyacrylamide (HAPAM) derived by incorporating a relatively small amount (generally less than 2 mol%) of hydrophobic groups onto a polyacrylamide backbone have stimulated increasing attention due to their noticeable ability in controlling the viscosity at various shear rates. Owing to its excellent viscosity building capacity, HAPAM has resulted in a wide application in oilfield exploitations, including drilling, polymer flooding, chemical flooding and profile modification, etc. (5–9). The characterization of properties in solution of these polymers has been the subject of several recent studies (7–9), but still very little is known regarding their behavior of retention in porous media (10, 11). It's a pity that there is no report about retention behavior of HAPAM with homogeneous composition. Though retention mechanism of partially hydrolyzed polyacrylamide (HPAM) and PAM in porous media could be known to some extent (1–4), there could be huge difference retention behavior between HAPAM and PAM due to the existence of hydrophobic associative group on HAPAM backbone. Since the existence of hydrophobic microdomain formed by hydrophobic associative group may influence the retention behavior of HAPAM during injection, an understanding of HAPAM retention mechanisms involved is necessary.

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Because the polymer flooding simulation, engineering project and dynamic forecast will depend on the retention behavior of HAPAM through porous media, it's important to obtain the retention property of HAPAM. The objective of this work is to investigate the retention behavior of HAPAM during injection in porous media based on simulating oil reservoir. For comparison, the behaviors of neutral polyacrylamide (PAM) without associating group are also studied.

2 Experimental

2.1 Materials

HAPAM and PAM were prepared as described (12). Natural sand (99% pure SiO_2) was pretreated to eliminate organic impurities that might interfere with retention measurement. The sand was treated with 1M HCl to remove initially present carbonates, and rinsed with distilled water until the rinsing water reached pH 7. Water (resistivity $> 18\text{M}\Omega\text{cm}^{-1}$) prepared by distillation for three times. Other reagents were all of analytical grade.

2.2 Determination Method

Polymer injections were run in the following procedure. The clean core was saturated with NaCl solution and the steady-state pressure distribution was measured at constant injection rate. Then, polymer solution was injected into the core at the same rate till the 1.0 normalized concentration. The polymer slug was followed by several pore volumes of the same NaCl solution. Flow was interrupted at each change of fluid while the pump and pipeline were flushed. Injection of NaCl solution continued until polymer was not detectable in the effluent. The same polymer solution was injected again till the 1.0 normalized concentration. All effluent was collected in test tubes using the fraction collector. The effluents containing polymer were analyzed to determine polymer concentration with bleach method. Then, the relationship curves between polymer normalized concentration and injected volume could be obtained (Fig. 1).

$$\text{IPV} = 1 - \text{PV}_1 \quad (1)$$

$$\text{RPV} = \text{PV}_2 - \text{PV}_1 \quad (2)$$

$$Q_r = \frac{\text{RPV} \times V_p \times C_0}{W_s} \quad (3)$$

Where Q_r , IPV, RPV, V_p , C_0 , and W_s are dynamic retention amount, inaccessible pore volume of polymer solution, retention pore volume of polymer solution, pore volume, polymer initial concentration and sand weight, respectively. The Cr is the concentration ratio of polymer initial concentration to polymer effluent concentration.

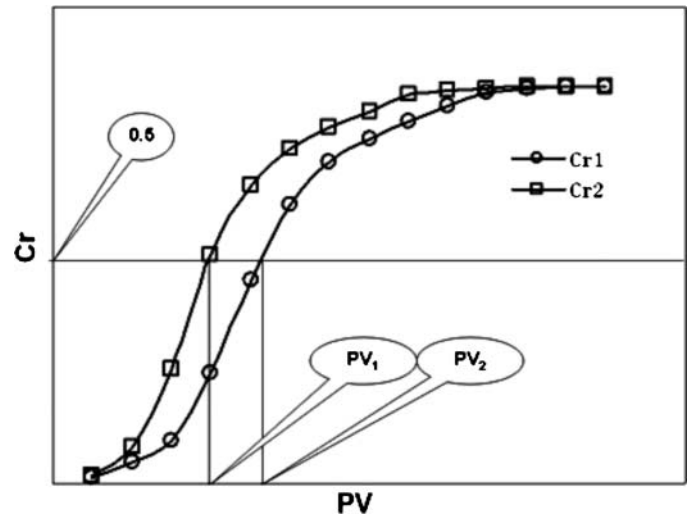


Fig. 1. Schematic illustration of determination of polymer retention.

3 Results and Discussion

3.1 Effect of Temperature on Polymer Retention

In Figure 2, the polymer concentration was 1500 mg/L, 8000 and 30000 indicated that the concentration of NaCl was 8000 mg/L and 30000 mg/L, respectively. The experimental temperature varied from 30 to 70°C. The flux of polymer solution was 20 mL/h. As shown in Figure 2, the retention of PAM decreased with increasing temperature from 30 to 50°C and the retention almost kept constant from 50 to 65°C. The retention of HAPAM exhibited small reduction from 30 to 40°C, drastic reduction from

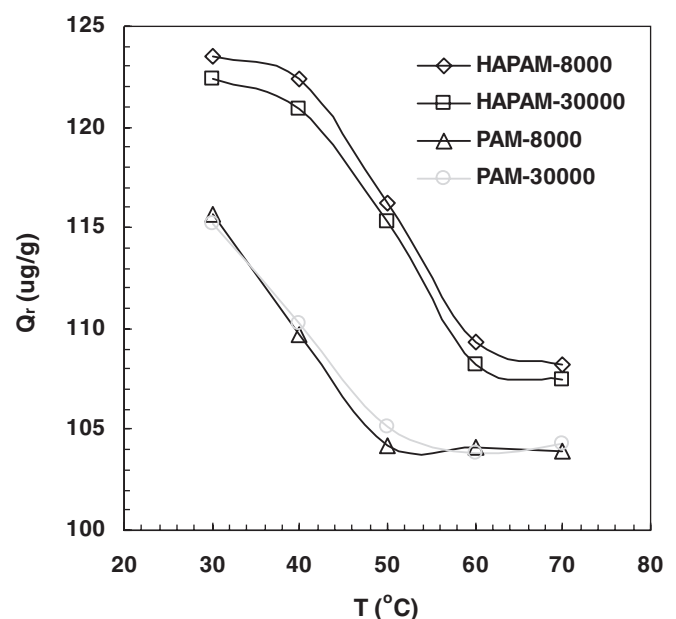


Fig. 2. Influence of temperature on polymer retention.

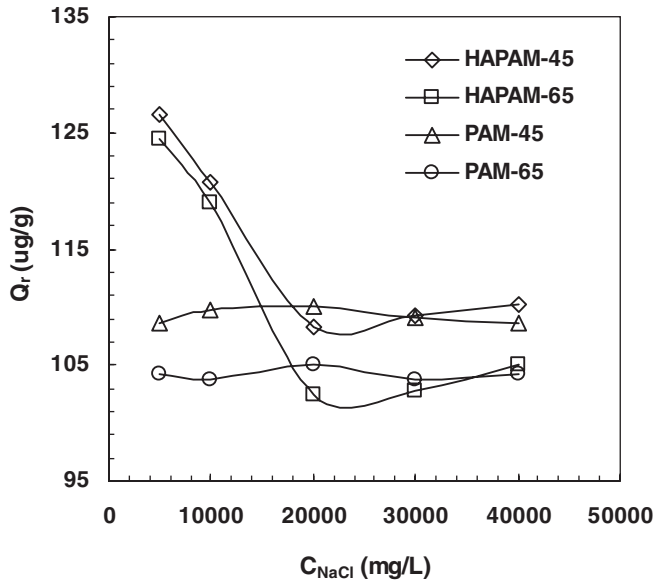


Fig. 3. Influence of salinity on polymer retention.

40 to 60°C with the increase of temperature. The retention of HAPAM almost showed independence on temperature change. In general, the adsorption on porous media was preferential when retention occurred (4, 13). The adsorption of PAM on sand surface exhibited great reduction from 30 to 50°C with the increasing temperature, resulting in the decrease of retention in porous media. Because the adsorption of PAM on sand surface kept relatively constant from 50 to 70°C, the inter-entanglement between flowing polymer molecules and adsorbed polymer molecules was almost independent of temperature change (13). Due to the strong inter-molecular association, partly conquering the influence of temperature change at low temperature, the adsorption of HAPAM kept constant, leading to the relatively constant retention in porous media. The temperature played an important role in destroying the hydrophobic association microdomain induced by HAPAM molecules at the range of 40 to 60°C, the retention of HAPAM showed drastic decrease. From 60 to 70°C, the hydrophobic association interaction become very weak due to the break of temperature, so, the retention of HAPAM was highly similar with PAM. From 30 to 60°, the retention of HAPAM was higher than that of PAM. It could contribute to the inter-molecular hydrophobic association interaction.

3.2 Effect of Salinity on Polymer Retention

In Figure 3, the polymer concentration was 1500 mg/L, 45 and 65 indicated that the experimental temperature was 45 and 65°C, respectively. The temperature was designed according to Daqing Oilfield and Shengli Oilfield major reservoir temperature. The concentration of NaCl varied from 5000 to 45000 mg/L. The flux of polymer so-

lution was 20 mL/h. As indicated in Figure 3, the retention of HAPAM decreased with an increase of NaCl when $C_{NaCl} < 20000$ mg/L. It seemed to be lower than that of PAM. Then, the retention of HAPAM showed weak dependence on NaCl. It seemed to faintly increase with increasing temperature. For PAM, it's another way around. NaCl gave little impact on retention of PAM in porous media. The retention curves almost kept horizontal. It's well known that the major retention mechanism was ascribed to polymer adsorption on porous media. The factor to influence polymer adsorption will still change the polymer retention. For another, the hydrodynamic size of polymer molecule will decrease due to salinity, resulting in the reduction of polymer retention induced by mechanical entrapment. The adsorption rule of PAM was similar to that of retention, indicating that the adsorption mechanism plays primary role in retention (1). Because the concentration of HAPAM was higher than its critical association concentration, higher salinity (higher than critical NaCl concentration) could strengthen the molecular interaction between adsorbed HAPAM molecules and flowing HAPAM molecules, leading to the weak increase in HAPAM retention with increasing temperature. PAM was a neutral polymer, the adsorption depends on the formation of a hydrogen bond and change of polymer conformation and the Na^+ had no obvious influence on these interactions, so, the retention seemed to be independent from salinity.

3.3 Effect of Injection Rate on Polymer Retention

In Figure 4, the polymer concentration was 1500 mg/L. 45-8 and 65-30 indicated that the experimental temperature

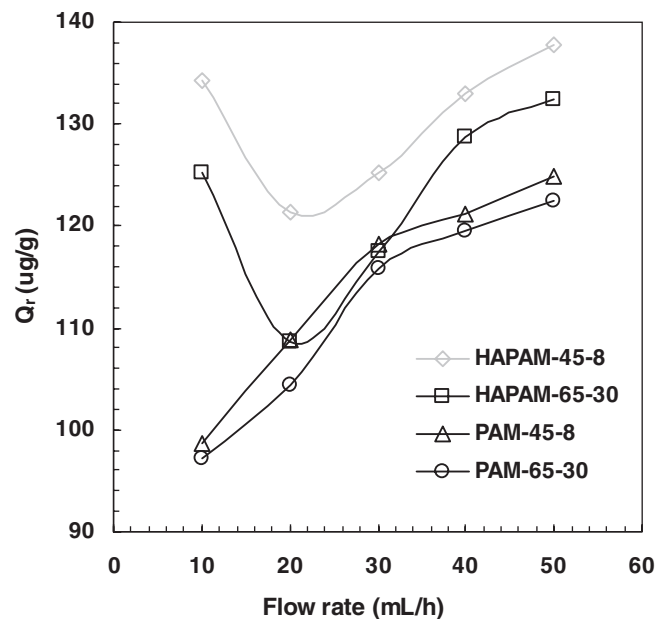


Fig. 4. Influence of flux on polymer retention.

used. As shown in Figure 4, retention of HAPAM dramatically decreased with the increasing flow rate from 10 to 20 mL/h; it's another way around while flow rate varied from 20 to 50 mL/h. For PAM, the retention of polymer in porous media kept increasing with the increase of flow rate at the range of 10~50 mL/h. Only at the high flow rate, the increase tendency of retention decreased weakly. It's well known that PAM molecules size become larger, resulted from hydrodynamic effect, with increasing flow rate, which make the retention increase due to loss of ability to through narrow pore sand crevices (14, 15). For HAPAM, the shear rate will increase with increasing flow rate, which could destroy HAPAM molecular association interaction, namely shear thinning. And then, the HAPAM molecules coil size correspondingly decrease. On the contrary, hydrodynamic interaction could increase the HAPAM molecules coil size. At the range of 10~20 mL/h, shear thinning plays a major role in change of HAPAM molecule coil size, indicated that the retention of HAPAM decrease with increasing flow rate. During 20~50 mL/h, the effect of shear thinning was smaller than hydrodynamic interaction, showing the contrary results.

3.4 Effect of Polymer Concentration on Polymer Retention

45-8 and 65-30 indicated the experimental temperature and the concentration of NaCl used. The flux of polymer solution was 20 ml/h. As shown in Figure 5, the retention of HAPAM in porous media increased with increasing polymer concentration. It's obvious that there was a turning point when the polymer concentration was about 1000 mg/L. The retention increase tendency became more drastic while the HAPAM concentration was higher than 1000 mg/L. It means that there could be a critical association concentration (CAC) when the HAPAM was flooded through porous media. When the HAPAM concentration was higher than CAC, the HAPAM molecular association interaction was strengthened resulted in increase of hydrophobic microdomain formed by adsorbed HAPAM molecules and flowing HAPAM molecules. The adsorption amount of HAPAM will increase, which could make the retention of HAPAM increase in porous media. PAM could not exhibit CAC when flooded porous media, so, it could not show turning point.

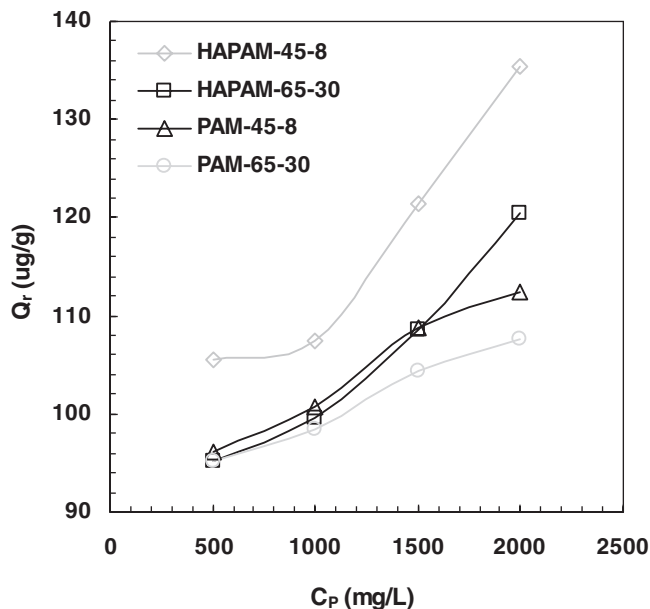


Fig. 5. Influence of polymer concentration.

3.5 Comparison Between Polymer Retention and Adsorption

As indicated in Figure 6, the nominal concentration was 1 when the injected volume was 3.5PV, namely saturation retention. It will reduce easily polymer loss resulted from polymer retention. Table 1 showed that the sand-packs physical parameter were all similar. All of them belonged to high filtered porous media, which could grant reproducibility of core-flow experiment.

Table 1 indicated that the dynamic retention and static adsorption of HAPAM was higher than that of PAM correspondingly. The static adsorption amount of HAPAM and PAM was higher than dynamic retention of HAPAM and PAM correspondingly. One could understand this like that: there were some sand-packs inaccessible pore volume, crevices and narrow pores and "compactness face," which could reduce the contactable surface of polymer adsorption. The adsorption of polymer will correspondingly decrease. Besides, the fluids wash could also weaken the polymer interaction. On the contrary, the static adsorption was determined in incompact sand grain and the solid/liquid ratio was very small. As a result, the dynamic retention of

Table 1. The result of polymer retention and adsorption

Sample	Experiment condition	m_s (g)	PV (mL)	ϕ (%)	K (μm^2)	Q_r ($\mu\text{g/g}$)	Q_a ($\mu\text{g/g}$)
HAPAM	45°C, 8000mg/L NaCl	39.01	8.94	27.41	1.23	121.4	12108
	65°C, 30000 mg/L NaCl	40.00	8.52	26.11	1.08	108.6	11100
PAM	45°C, 8000 mg/L NaCl	40.10	8.55	26.23	1.10	108.8	3518
	65°C, 30000 mg/L NaCl	40.21	8.74	26.80	1.16	104.4	2987

Note: The polymer injected concentration is 1500 mg/L. Q_a represents the static adsorption amount.

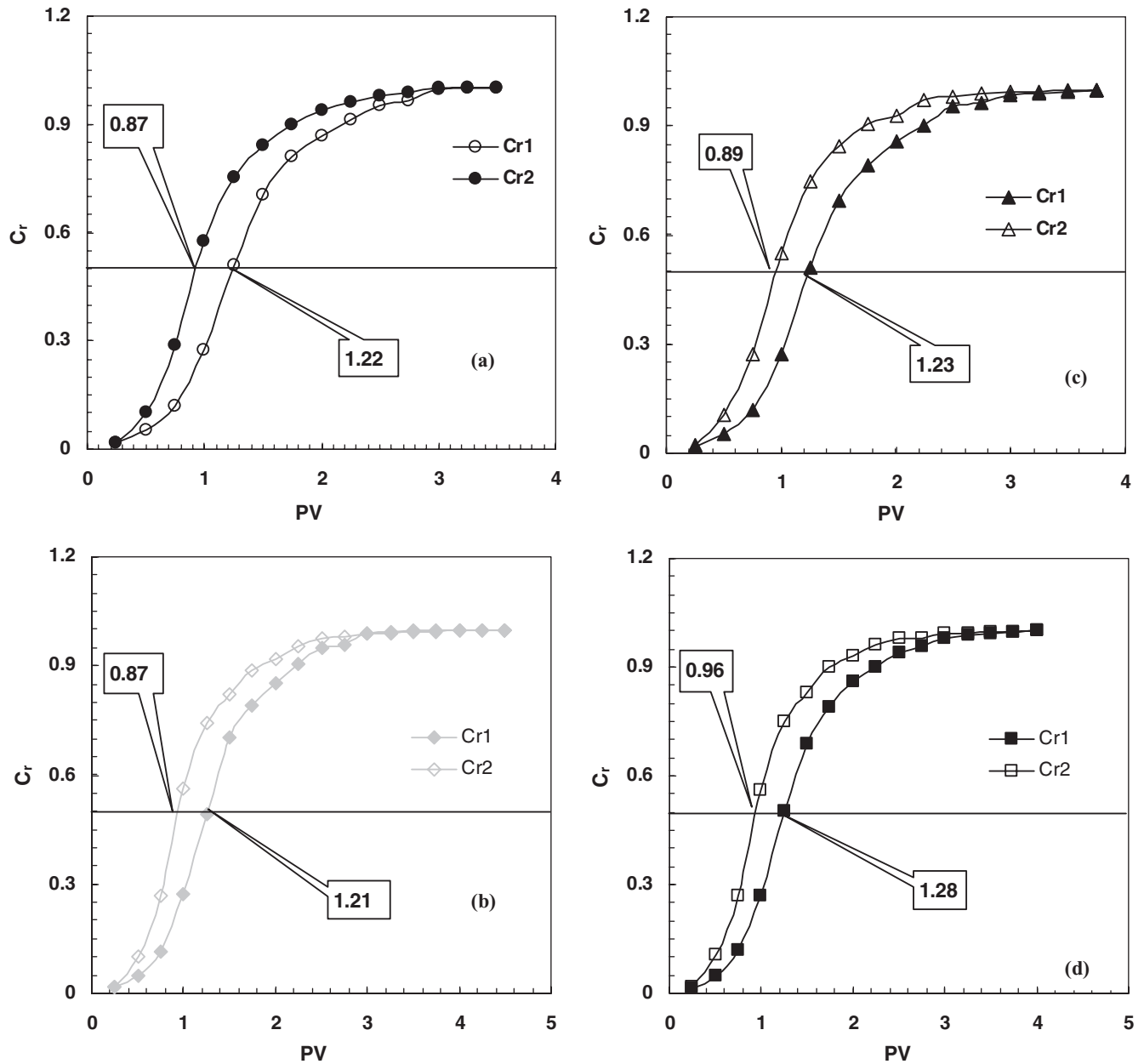


Fig. 6. The relationship between injected polymer volume and polymer concentration of spillage: (a) HAPAM, $T = 45^{\circ}\text{C}$, $C_{\text{NaCl}} = 8000 \text{ mg/L}$; (b) HAPAM, $T = 65^{\circ}\text{C}$, $C_{\text{NaCl}} = 30000 \text{ mg/L}$; (c) PAM, $T = 45^{\circ}\text{C}$, $C_{\text{NaCl}} = 8000 \text{ mg/L}$; (d) PAM, $T = 65^{\circ}\text{C}$, $C_{\text{NaCl}} = 30000 \text{ mg/L}$.

polymer in porous media was lower than the adsorption of polymer (16, 17).

It is well known that the inaccessible pore volume could increase with the increasing polymer molecular weight. In this paper, the molecular weight of HAPAM and PAM was similar. However, the inaccessible pore volume of HAPAM is bigger than that of PAM. When the PAM molecules flow through the strait pore throat, the polymer molecular weight could decrease due to the high rate shear. So, it can

enter into the smaller pore. For HAPAM, it could enter into porous media by breaking the “dynamic physical cross-linking” and then re-associate with each other. As a result, the HAPAM coil size was bigger than that of PAM, resulted in the above results.

Though there was huge deviation by using polymer static adsorption to reflect field polymer flooding, it is still used to choose suitable polymer for polymer flooding due to convenience.

4 Conclusions

Retention property of HAPAM with composition homogeneity in porous media was investigated. HAPAM could exhibit different retention behavior compared to PAM. It is the hydrophobic association interaction that made the adsorption behavior of HAPAM differ from PAM. At the range of determined temperature, retention behavior of HAPAM was obviously different from that of PAM due to the existence of hydrophobic association interaction group in HAPAM molecular frame. The retention of PAM was almost independent of salinity, but for HAPAM, the adsorption first decreased and then increased with the increasing salinity. The process was similar with the adsorption process, indicated the retention was mainly controlled by adsorption mechanism. HAPAM retention in porous media first decreased and then increased with the increasing flux of polymer solution. However, PAM kept constantly increase. There was an obvious turning point on the curves between HAPAM concentration and retention, indicating that there was still critical association concentration. The dynamic retention and static adsorption of PAM was smaller than that of HAPAM correspondingly. The static adsorption amount of HAPAM and PAM was higher than dynamic retention of HAPAM and PAM correspondingly.

Further research about HAPAM to enhance oil recovery will appear in our future papers.

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