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Solution Association Characterization of Hydrophobically Associating Polyacrylamide Obtained from Produced Fluids

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The hydrophobically associating polyacrylamide (HAPAM) obtained from produced fluids with compositional homogeneity was systematically investigated by zero-shear viscosity, fluorescence, sand-pipes experiment and adsorption behavior. The results showed that HAPAM obtained from produced solution through porous media has been possession in hydrophobic association character. The critical association concentration (CAC) determined by viscosity method, fluorescence spectroscopy method and micro-pore method have no obvious change compared with the original polymer. The hydrophobic associative capability of HAPAM obtained from produced fluids was smaller than that of original HAPAM. Compared to original PAM and PAM obtained from produced fluids, HAPAM obtained from produced fluids still exhibits promising applied potential. It reveals the possibility that HAPAM obtained from produced could be re-used for enhance oil recovery.

Keywords: Hydrophobically associating polyacrylamide produced fluids, re-injection solution association, character adsorption property

1 Introduction

In 1964, Pye and Sandi Ford found that the mobility of water/brine used in water flooding could be reduce efficiently by adding small amount of a water-soluble polymer (1,2). Since then, numerous laboratory studies and field tests about polymer flooding have been carried out. Naturally, partially hydrolyzed polyacrylamide (HPAM) becomes the effective candidate. It's a pity that HPAM are salt sensitive and can be mechanically degradation. In order to conquer the shortage of HPAM, a new kind of water-soluble polymer, called hydrophobically associating polyacrylamide (HAPAM), was introduced in oilfield exploitation process. HAPAM derived by incorporating a relatively small amount of hydrophobic groups onto a polyacrylamide backbone are especially attractive due to their noticeable ability in controlling the viscosity at various shear rates (3,4). Owing to its excellent viscosity building capacity, this kind of polymers has received a wide application in oilfield exploitations (5–9).

Polymer flooding processes have been increasingly applied in the oil fields due to their high ultimate oil recovery. For conquer a hot potato, there are two methods which could be put in practice. One major technical challenge is how to reduce the amount and the cost of chemical used so that polymer flooding can become cost-effective as well (10). Another is the disposal of polymer flooding produced fluid which have residual polymer and could polluted environment. In general, the produced fluids were chemically oxidized by adding oxides (11,12), resulting in the waste of resource and increasing cost of polymer flooding, or re-injection of polymer was the another useful method which could reduce the capital cost. Therefore, successful characterization and reuse of these produced chemicals can substantially reduce the capital cost and the environmental impact, especially for HAPAM.

For HAPAM obtained from produced fluids, the special hydrophobic interaction is firstly considered. Therefore, one of our major tasks is to investigate whether the hydrophobic association interaction property of HAPAM obtained from produced fluids in aqueous solution could take place. Further, if this phenomenon exists, could the critical association concentration (CAC) of HAPAM

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undergo noticeable changes? This work will provide the technical support for polymer flooding. Up to now, to the best of our knowledge, there is no related research about successful characterization and reuse of these produced fluids contained HAPAM.

2 Experimental

2.1 Materials

HAPAM and PAM were prepared as described (13). Natural sand (99% pure SiO_2) was pretreated to eliminate organic impurities. 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 $> 18M\Omega cm^{-1}$) prepared by distillation for three times. Other reagents were all of analytical grade.

2.2 Preparation of HAPAM and PAM Obtained from Produced Fluids

Coreflow experiment is a classical method to simulate polymer-flooding through oil reservoirs (Fig. 1). By this method, the HAPAM and PAM obtained from produced fluids could be formed. The stock solution of HAPAM and PAM were prepared. The standard solutions were prepared daily by serial dilution of stock solution prior to use. A certain amount of quartzose sand was filled in the sand pipes. One of middle container was filled with water, while the other was filled with either HAPAM or PAM solution. In the first step, the permeability of sand pipes was measured when the water was allowed to flood though sand pipes. Secondly, the polymer solution was allowed to flood though sand pipes with constant polymer flux (20 ml/h). The produced fluids were collected and then were poured into an excess of the mixture of ethanol and acetone, and the precipitated polymers were separated and washed several times. They were filtered and dried under vacuum at 60°C. Herein, to make a difference between original polymer and polymer obtained from produced fluids, the original HAPAM and PAM was still called HAPAM and PAM;
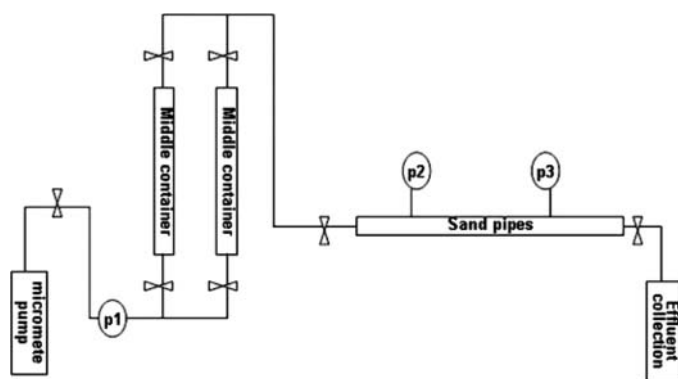
the HAPAM and PAM obtained from produced fluids was called HAPAM-pf and PAM-pf.

2.3 Characterization of Hydrophobe Content

The sample was prepared according to oxygen flask combustion (15). The measurement method and condition were referred to literature (16).

A Dionex model DX-500 IC (Sunnyvale, CA) equipped with a GP40 gradient pump, a Dionex Ionpac AS16 analytical column (4 × 250 mm), an Ionpac AG16 guard column (4 × 50 mm), a Dionex ED40 conductivity detector and a Dionex ASRS-ULTRA (4 mm) suppressor were used for the analysis of anions. Injections of 150 μl of sample were performed.

2.4 Rheology

Stock polymer solutions were prepared by dissolving appropriate amounts of polymer with distilled water. Gentle magnetic agitation was applied after 1 day of prehydration. The final solutions of desired concentration were obtained by diluting the stock solutions with distilled water. Before measurements, polymer solutions were left without agitation for at least 1 day to reach equilibrium. The viscosity was measured at 25 ± 0.1°C using Physical MCR301 (Anton Paar).

2.5 Fluorescence Spectrometry

Fluorescence spectra were recorded on an LS50B luminescence spectrometer (Perkin–Elmer). The desired polymer solutions were prepared by dissolution of dry polymer sample in pyrene-saturated distilled water. All measurements were performed at 25 ± 0.1°C. Emission spectra were obtained with an excitation wavelength 335 nm. The ratio I_1/I_3 of the intensities of the first and the third vibronic peaks for the emission spectrum provides an estimate of relative hydrophobicity of the local environment.

2.6 Sand-Pack Flow Experiment

The sand-pack flow experiment was performed under the same conditions like rheology and fluorescence experiment. The detail can be seen in the literature (17).

2.7 Adsorption Measurements

Polymer adsorption on sand surface was measured by the depletion method (18): suspensions containing varying weight per cents of the solid were prepared in a given solvent and equilibrated for 24 h at 25°C. A polymer solution containing the same electrolyte was then added to the mineral suspension weighed to the required solid/liquid weight ratio. The polymer/mineral suspension was then gently agitated for 24 h at 40°C before the suspensions were centrifuged to allow solid and solution separation. The adsorbed amount was then calculated according to

Fig. 1. A typical schematic presentation of coreflow setup.

Table 1. Hydrophobe content of polymer

Sample	Hydrophobe content (%)
HAPAM	97.13
HAPAM-pf	95.89
PAM	0
PAM-pf	0

the difference between the initial polymer concentration and the concentration measured in the supernatant after contact with the mineral. For determining the concentration of the polymer used in this work, the method described by Allison (19) was found quite suitable.

3 Results and Discussion

3.1 Rheology of HAPAM-pf

Based on its high sensitivity, selectivity, the ion-exchange chromatography is suitable for trace analysis at the level of μg/l, therefore, it is suitable for quantitative analysis of bromide in HAPAM. For accuracy, parallel experiments were performed. The result is the average value of each team experiments. Table 1 presented the hydrophobe content of four kinds of polymer. The hydrophobe content of HAPAM and HAPAM-pf is 97.13% and 95.89%, respectively. There is a little loss of hydrophobe after through porous media. It could be the hydrolyzation of ester group in hydrophobic group. Besides, there is still no hydrophobe group detected with PAM and PAM-pf, indicating that the determined results were relatively accurate.

3.2 Rheology of HAPAM-pf

In order to characterize hydrophobically associative water-soluble polymer, the critical association concentration (CAC) was advanced. Feng thought that there was an obvious difference for CAC due to the difference of measurement method (20). As a result, the CAC obtained by viscosity method was named critical association concentration of viscosity method (CAC_V).

As shown in Figure 2, the CAC_V of HAPAM and HAPAM-pf is no obvious difference, which seem to be 4500 mg/L. For PAM-pf, it has no sudden turning point on the viscosity-concentration relationship curves. It also means that HPAM-pf could exhibit hydrophobically associative interaction after through the porous media. Besides, more information could be gotten from Figure 2. It's obvious that the polymer's viscosity decreased correspondingly due to the polymer chain broken. For PAM-pf, the viscosity was about half of the PAM. The viscosity of HAPAM-pf was 30% of HAPAM-pf. It shows that HAPAM could flow though the porous media by breaking the association structure and molecular chain, but PAM may though the porous media only by polymer molecular chain broken. Because of absence of accuracy for viscosity method, the difference
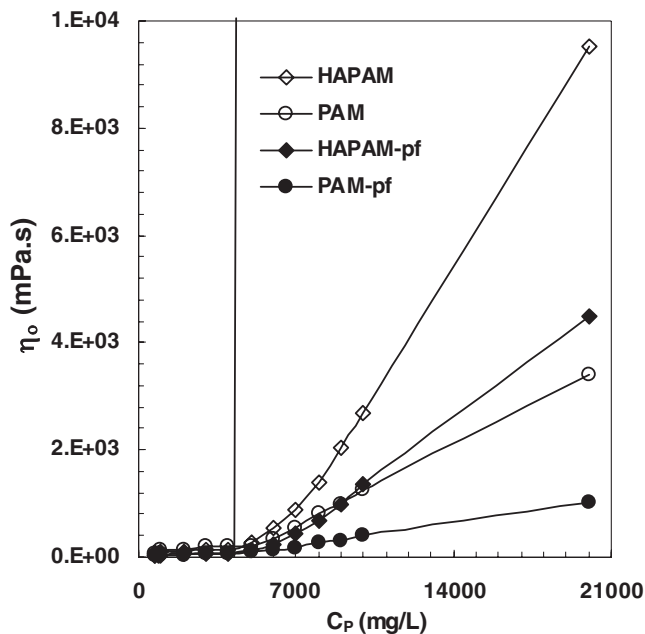

Fig. 2. Zero-shear viscosities as a function of polymer concentration.

of CACV between HAPAM and HAPAM-pf can't be calculated to an inch.

3.3 Polymer Molecules Aggregation Behavior

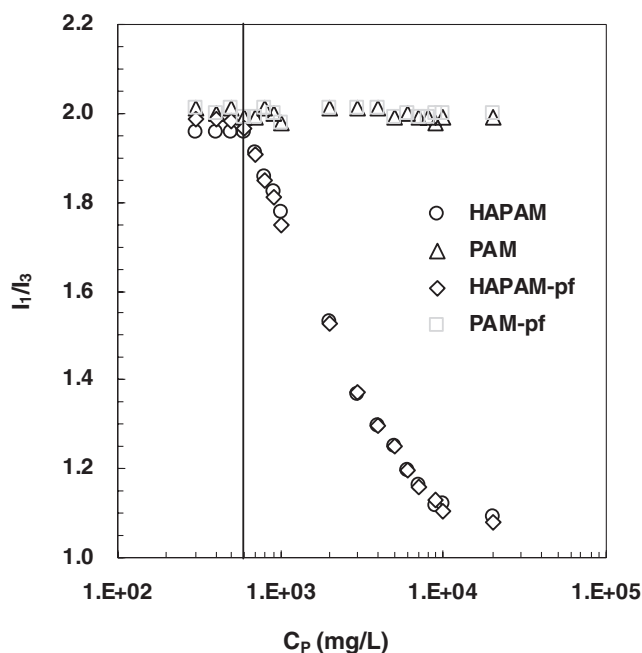Figure 3 presented the relationship between polymer concentration and viscosity. The formation of hydrophobic

Fig. 3. Intensity ratio of I_1/I_3 plotted against polymer concentration for HAPAM and PAM.

microdomain in aqueous media could be detected by florescence spectrometry with using the pyrene molecule probe. The pyrene molecules could penetrate into these micordomains, resulting in the drop of I_1/I_3 value from 2 to appr.1.1–1.2. The hydrophobic association character of HAPAM has been proved in the literature (20). Though the macro-hydrophobic association character of HAPAM-pf has been conformed (Figure 2), the micro- hydrophobic association character could not be sure. As shown in Figure 3, the florescence curves of PAM and PAM-pf appear to be overlapped, the same as the curves of HAPAM and HAPAM-pf. It indicated that the hydrophobic microdomain still has existed after the HAPAM flood through porous media. The transitory net-structure could be broken automatically when the polymer molecules flood through the capillary. However, there is no evidence which can indicate the PAM molecules chain are broken after being flooded through the capillary in Figure 3. But Figure 3 showed that the transitory net-structure of HAPAM can rebuild in stock solution.

3.4 Effect of Polymer Concentration on Resistance Factor

Figure 4 presented a resistance factor (RF) against polymer concentration with a stable flooding rate (0.02 cm/s). The experimental temperature is 45°C. It's well known that the critical association concentration could be determined by a micro-pore method (20). Based on this method, the CAC can be defined as critical association concentration of micro-pore method (CAC_M). As shown in Figure 4, RF increases drastically with the increase of HAPAM and HAPAM-pf concentration, indicating that there is a drastic increase for relative viscosity of HAPAM and HAPAM-df, especially for higher polymer concentration. That's mean
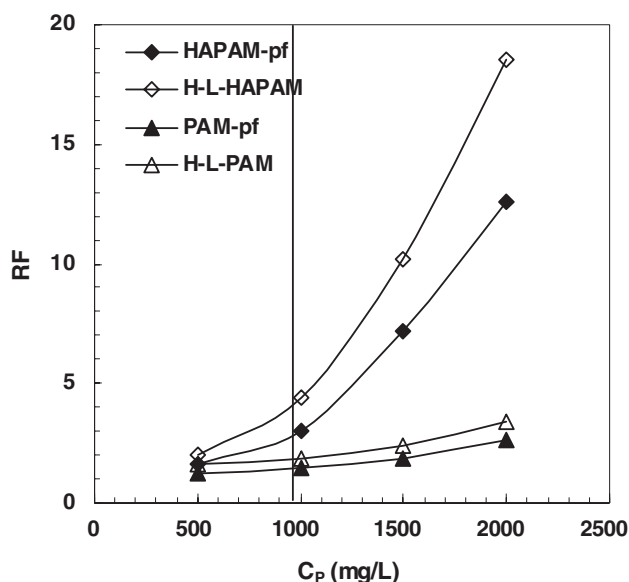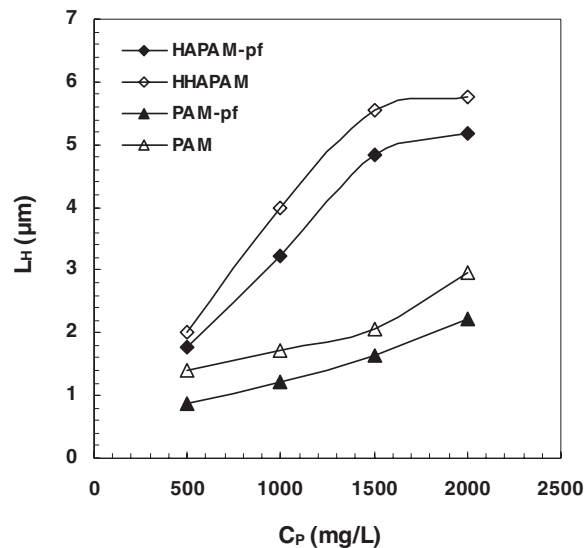

Fig. 4. Influence of Polymer Concentration on RF.

Fig. 5. Effect of polymer concentration on effective hydrodynamic thickness (L_H).

that the CAC_M of HAPAM-pf is near to 1000 mg/l. It's true that the RF of HAPAM-pf is obviously smaller than that of HAPAM. This could be partly broken for HAPAM molecules chain after through porous media. Figure 4 also presented that the RF of PAM-pf is still smaller than that of PAM. By calculation, the relative decrease coefficient indicated that HAPAM is more obvious than PAM. It means that molecule chain fracture will give a strong impact on a HAPAM net-structure. It's lucky that the RF of HAPAM-pf is still out and higher than that of PAM-df.

3.5 Effect of Polymer Concentration on Effective Hydrodynamic Thickness

Figure 5 presented effective hydrodynamic thickness (L_H) against polymer concentration with stable shear rate $(200s^{-1})$. The nominal shear rate is varied from the higher value to a lower value. The experimental temperature is 45°C. In general, L_H represented the effective hydrodynamic thickness on a solid surface when the polymer solution floods through porous media (21); it can be figuratively said as the polymer dynamic absorption thickness. As a result, the thicker the L_H is, the stronger the molecules interaction. As indicated in Figure 5, L_H of HAPAM-pf and PAM-pf were correspondingly lower than that of the original polymer which showed that the polymer molecules interaction is weakened due to the polymer molecules chain fracture. After calculation, it is found that the relative decrease coefficient of HAPAM is smaller than that of PAM, indicating that PAM molecules chain fracture is more serious than HAPAM and HAPAM molecules which can get through capillary with abreaking association net-structure. Fuerthermore, L_H of HAPAM-pf is obviously larger than
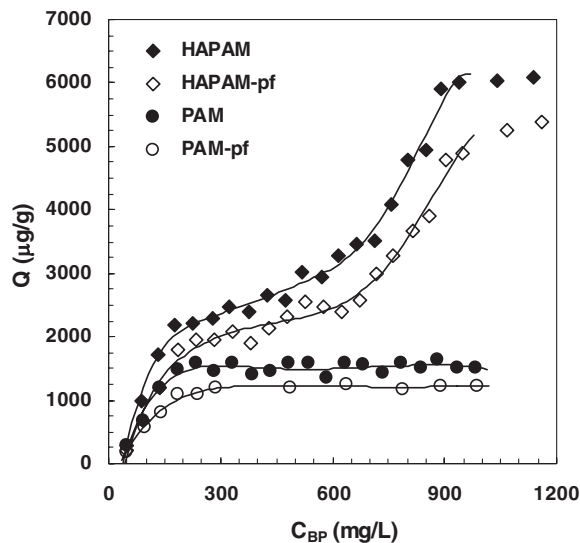
Fig. 6. Adsorption isotherms of polymer.

Fig. 7. Influence of the temperature.

that of PAM and PAM-pf, which can show the possibility of HAPAM-pf re-injection for enhanced oil recovery.

3.6 Adsorption Behavior

In Figure 6, the adsorption behavior of HAPAM and PAM on silica was measured at pH 7, 45°C and in 8000 mg/l NaCl with fixed ratio of solid to liquid (0.01). It's well known that polymer adsorption on a negatively charged surface is governed by the competition between attractive forces (i.e., Van der Waals interactions, entropic contribution or specific interactions) and electrostatic forces that can be either repulsive or attractive (18). These factors could influence the adsorption amount of polymer on solid surface. Another important factor is the molecules length of polymer. As shown in Figure 6, the adsorption isotherms of PAM and PAM-pf were a classical type of isotherm, i.e., first an increase in the adsorbed amount with polymer concentration and then a pseudo-plateau for polymer concentrations above 300 mg/l corresponding to the saturation of the surface by the PAM chains. For HAPAM and HAPAM-pf, there were no obvious plateau region but the adsorbed amount increases continuously with the polymer concentration in the solution. For careful comparison, one could found that the adsorption decrease coefficient of HAPAM is obviously larger than that of PAM with the increasing polymer concentration. Herein, one can imagine that what's important the HAPAM molecules size for increasing hydrophobic association capability of HAPAM. It's confirmed that the adsorption amount of HAPAM is higher than that of PAM due to the presence of many hydrophobic associative points. The HAPAM molecules chain fracture could be consider as the hydrophobic associative points decreased (18). Therefore, the relative adsorption amount
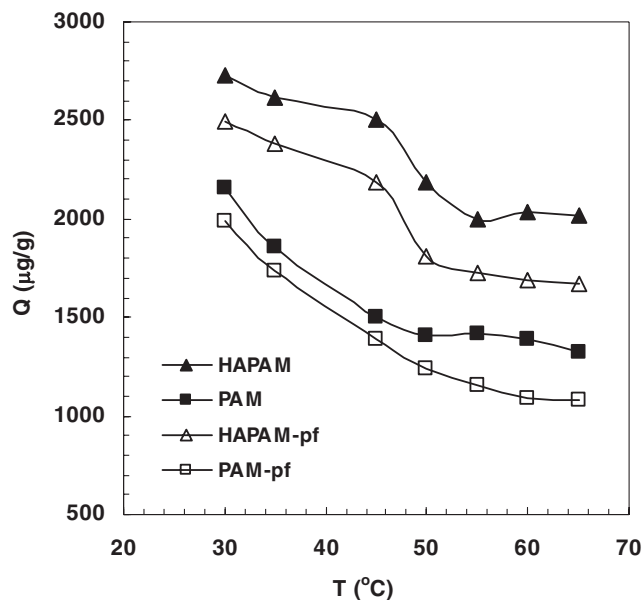
decrease coefficient of HAPAM is more serious than that of PAM.

3.7 Effect of Temperature on Polymer Adsorption Behavior

In Figure 7, the concentrations of NaCl were 8000mg/l. The adsorption temperature varied from 30 to 65°C. The solid/liquid ratio was 0.01. The polymer concentration was 400mg/l. As indicated in Figure 7, the adsorption behaviors of HAPAM and HAPAM-pf in NaCl aqueous solution seem to be similar with increasing temperature from 30 to 65°C. The same as PAM and PAM-pf. There is an obvious difference for relative adsorption decrease coefficient, especially at higher temperature. This behavior could be understood like that the capability to resist temperature interaction deceases dramatically with the loss of some "hydrophobic associative points". However, HAPAM-pf still exhibit strong property of hydrophobic association, because the adsorption amount of HAPAM-pf is still obviously higher than that of PAM and PAM-pf.

4 Conclusions

Solution association characterization of HAPAM obtained from produced fluids was investigated systematically. The hydrophobe content of HAPAM-pf was somehow lower than that of HAPAM due to the hydrolyzation of ester group in hydrophobic group. The critical association concentration of HAPAM-pf was measured by three methods: viscosity method, micro-pore method and fluorescence method. The results showed that there is no obvious difference for critical association concentration determined between HAPAM and HAPAM-pf. HAPAM-pf can also

exhibit hydrophobic association property. Besides, the relative decrease coefficient of zero-viscosity, resistance factor, effective hydrodynamic thickness and adsorption for HAPAM is higher than for PAM, indicating that HAPAM molecules size will have strong impact on net-structure. However, the resistance factor and effective hydrodynamic thickness of HAPAM-pf were obviously higher than that of PAM and PAM-pf, which means that there is the possibility of re-utilization for enhance oil recovery.

Further research about HAPAM for enhance oil recovery will appear in our future paper.

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