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# Solution and Adsorption Properties of Hydrophobically Associating Polyacrylamide Prepared in Inverse Microemulsion Polymerization

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The hydrophobically associative polyacrylamide (HAPAM) with homogeneous composition was prepared in inverse microemulsion polymerization. The homogeneity was proved by polymerization kinetic. The critical association concentration (CAC) was measured by three methods: viscosity method, fluorescence method and micro-pore method. The results showed that the HAPAM still could exhibit hydrophobic association interaction in porous media under flowing condition. HAPAM could present adsorption of multi-layer due to the hydrophobic association interaction. It's the hydrophobic association interaction that made the adsorption behavior differ from neutral PAM.

**Keywords:** Hydrophobically associating, polyacrylamide solution, property adsorption, property inverse, microemulsion polymerization

## 1 Introduction

Over the past decades, hydrophobically associating water-soluble polymers have stimulated increasing attention due to their noticeable ability in controlling the viscosity at various shear rates. Among these polymers, hydrophobically associating polyacrylamide (HAPAM) derived by incorporating a relatively small amount (generally less than 2 mol %) of hydrophobic groups onto a polyacrylamide backbone are especially attractive (1–4). Owing to its excellent viscosity building capacity, this type of polymers has resulted in a wide application in oilfield exploitations, including drilling, polymer-flooding, chemical flooding and profile modification, etc. (5–13).

Nowadays, there are many methods to prepare HAPAM, such as micelle polymerization and inverse microemulsion polymerization (14–18). The characterization of properties in solution of these polymers has been the subject of several recent studies (10–13), but still very little is known regarding their behavior at a solid/liquid interface (19–21). As a polymer-flooding agent, it's important to know the

adsorption behavior of HAPAM at a solid/liquid interface, because the polymer-flooding simulation, engineering project and dynamic forecast will depend on the adsorption behavior of HAPAM. Though the adsorption behavior of polymer-flooding agents, such as polyacrylamide and Xanthan Gum, at oil reservoir, have been known, HAPAM could be differ from the traditional polymer-flooding agent due to the association group in polymer backbone. The objective of this work is to investigate the hydrophobic association interaction in oil reservoir and the adsorption behavior of HAPAM at mineral surfaces. After a description of the viscous properties in solution, the adsorption behavior of the polymers is considered. The influence of NaCl concentration and temperature has been studied on the adsorption properties. 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 (17, 18). Natural sand (99% pure SiO<sub>2</sub>) was pretreated to eliminate organic impurities that might interfere with adsorption 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

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> 18 M $\Omega$ cm<sup>-1</sup>) prepared by distillation for three times. Other reagents were all of analytical grade.

## 2.2 Rheology

Concentrated stock polymer solutions were prepared by dissolving appropriate amounts of polymer with distilled water in a 500 mL flask. Gentle magnetic agitation was applied after 1 day of prehydration. The final solutions of desired concentration were made up in 50 ml conical flasks by diluting the stock solutions with distilled water and mixing in a thermostatic water bath shaker (25°C) for about 12 h. 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).

## 2.3 Fluorescence Spectrometry

Steady fluorescence spectra were recorded on an LS50B luminescence spectrometer (Perkin–Elmer). A series of solutions were prepared by dissolution of dry polymer sample in pyrene-saturated distilled water. All measurements were performed at room temperature. Emission spectra were obtained with an excitation wavelength 335 nm and a slit width of 2 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.

## 2.4 Sand-Pack Flow Experiment

The sand-pack flow experiment was performed under the same condition like rheology and fluorescence experiment. The detail could be seen in the literature (22).

## 2.5 Adsorption Measurements

Polymer adsorption on sand surface was measured by the depletion method: suspensions containing varying weight per cents of the solid were prepared in a given solvent and equilibrated for 24 h at 25°C. 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 determined from 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 (23) was found quite suitable.

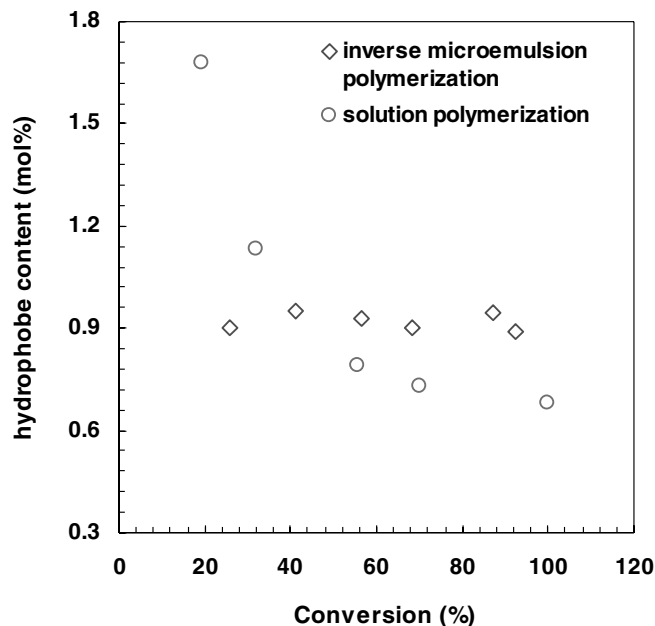


Fig. 1. Drift of the hydrophobic monomer during the polymerization.

## 3 Results and Discussion

### 3.1 Composition Homogeneity of HAPAM

The conversion of monomers is determined as described in the literature (17). As noted in Figure 1, the hydrophobe content of HAPAM prepared inverse microemulsion polymerization did not vary with the conversion of monomers. For solution polymerization, it was another way around. It shows that polymerization in inverse microemulsion leads to sample more homogeneous in composition than those prepared in solution polymerization. The HAPAM used in the following discussion is prepared in inverse microemulsion.

### 3.2 Solution Behavior

As shown in Figure 2, the viscosities of polymers increase linearly with the increasing polymers' concentration from 0 to 5,000 mg/l. Above 5000 mg/l, viscosity of HAPAM increases dramatically with the HAPAM concentration variance. For PAM, the viscosity was obviously lower than HAPAM due to the absence of hydrophobic group on polymer backbone. Herein, the viscosity break-point corresponding to HAPAM concentration is called critical association concentration of the viscosity method ( $CAC_V$ ).

The aggregation of HAPAM can be studied on the molecular level using fluorescence spectroscopy with pyrene as a probe due to its sensitivity to the polarity of microenvironment. The formation of hydrophobic microdomain in aqueous media and the penetration of pyrene molecules into these domains lead to the drop of  $I_1/I_3$  value from

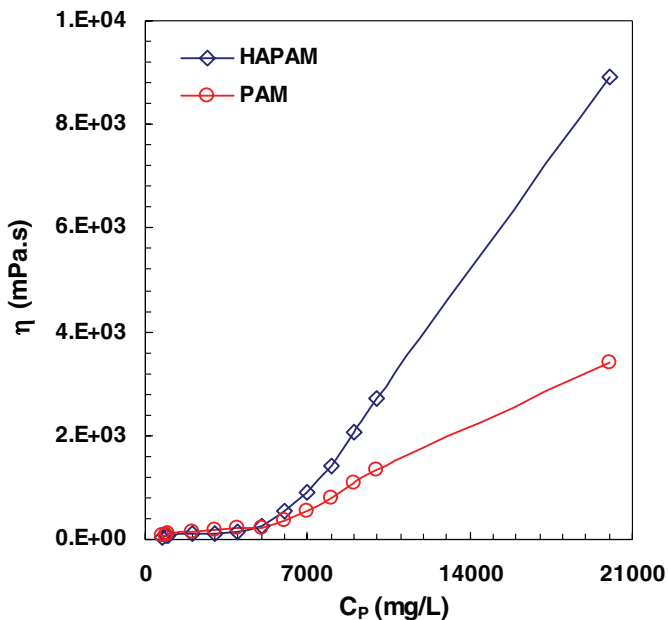


Fig. 2. Zero-shear viscosity plotted as a function of polymer concentration.

2 to appr.1.1–1.2. In general, the critical association concentration (CAC) is determined as an inflexion point of the curve  $I_1/I_3$  as a function of concentration. Herein, the CAC is called critical association concentration of fluorescence method ( $CAC_F$ ). As indicated in Figure 3, only HAPAM has  $CAC_F$ . There is an obvious inflexion point for HAPAM when the HAPAM concentration is about 600 mg/l.

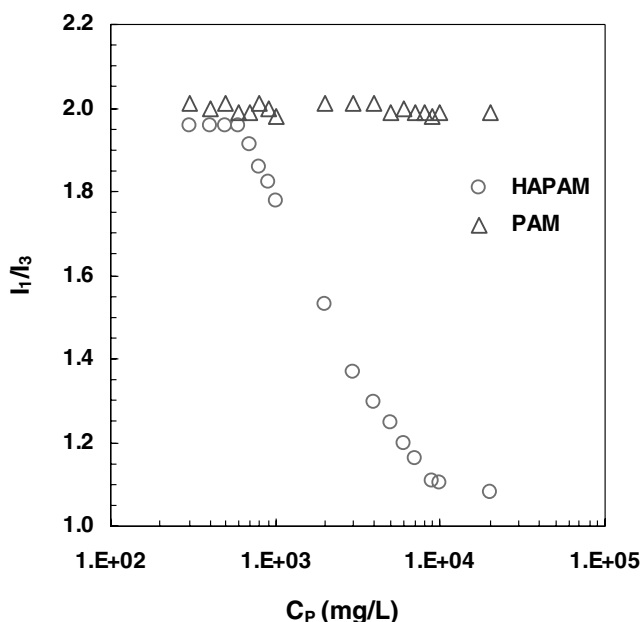


Fig. 3. Intensity ratio of  $I_1/I_3$  plotted against polymer concentration for HAPAM and PAM.

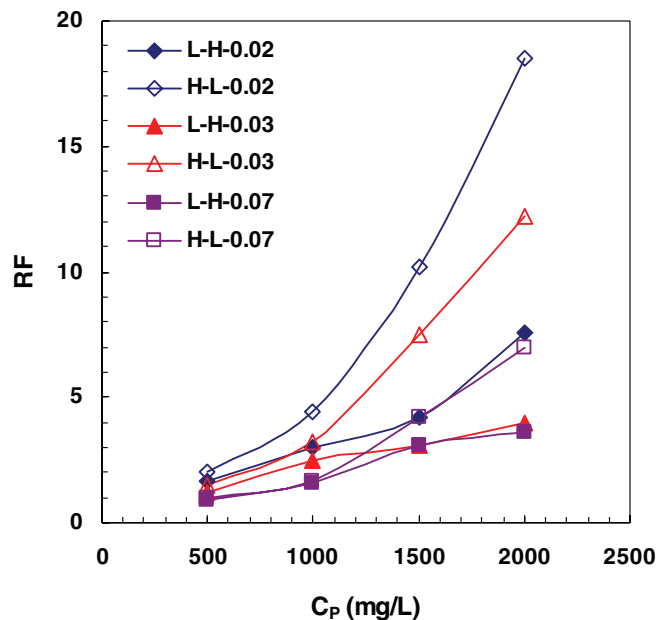


Fig. 4. Influence of HAPAM concentration on RF.

However, for PAM, there is no inflexion point when the PAM concentration varies from 300 to 2000 mg/l.

Figures 4 and 5 present the resistance factor (RF) against polymer concentration under three kinds of shear rate. L-H indicates that the nominal shear rate is varied from the lower (L) value to higher (H) value; H-L indicates that the nominal shear rate is varied from the higher (H) value to lower (L) value. As shown in Figure 4, the resistance factor increases drastically with the increase of HAPAM

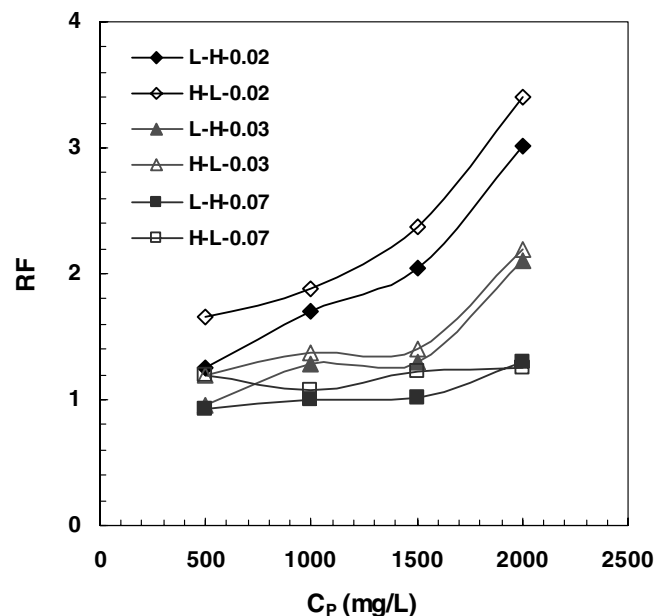


Fig. 5. Influence of PAM concentration on RF.

concentration, indicating that there is a strong increase for relative viscosity of HAPAM, especially for a lower nominal shear rate. Apart from this, it could be observed that the hysteresis phenomena became increasingly serious when the concentration of HAPAM solution increased. For example, at a lower concentration of 500 mg/l,  $\Delta RF$  was no more than 1; but at a concentration of 2000 mg/l,  $\Delta RF$  could reach far beyond 10. In sharp contrast, this would not happen for PAM solutions. Instead, the hysteresis phenomena became more and more subtle. The great difference between the behaviors of HAPAM and PAM solutions could be explained as follows: The association between the hydrophobic side chains of HAPAM could be regulated by the shearing force, that is to say, when the frontal velocity of HAPAM solutions changed from higher values to lower values, the network structures of HAPAM could well be recovered. Thus, HAPAM could exhibit the unique fluidic properties as compared with PAM. Herein, the inflexion of RF for HAPAM corresponding to HAPAM concentration is a defined critical association concentration of micro-pore method ( $CAC_M$ ). As for HAPAM, the  $CMC_M$  is about 900 mg/l.

It is true that the CAC determined by fluorescence spectroscopy is smaller than that determined by a micro-pore method and viscosity method. This can be easily understood: when the polymer concentration is too low, the intermolecular chains aggregation is too weak to drastically increase the viscosity of HAPAM, resulting in the increase of CAC determined by a viscosity method. It also showed that HAPAM could still exhibit a property of strong hydrophobic association in an oil reservoir and the  $CAC_M$  was close to  $CAC_F$ .

### 3.3 Adsorption Behavior

In general, 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. The adsorption of PAM on natural sand was supposed to occur via hydrogen bonds between the polymer and silanol groups of the mineral surface. Figure 6 presented the adsorption behavior of HAPAM and PAM on silica at pH 7, 45°C and in 8000 mg/l NaCl for a different ratio of solid to liquid. It's obvious that the adsorbed amount decreases with a Solid/Liquid ratio due to an aggregation of mineral particles induced by the adsorption of the high molecular weight polymer. This dramatically decreased the surface accessible to the polymer for further adsorption. The adsorption amount should be calculated using an adsorbed amount extrapolated at zero Solid/Liquid ratio. It corresponded to the adsorption maximum when no flocculation of the mineral particle by polymer bridging has taken place. Because of the lack of precision of the extrapolated values at zero Solid/Liquid ratio, one could measure an Solid/Liquid ratio of 0.01 to

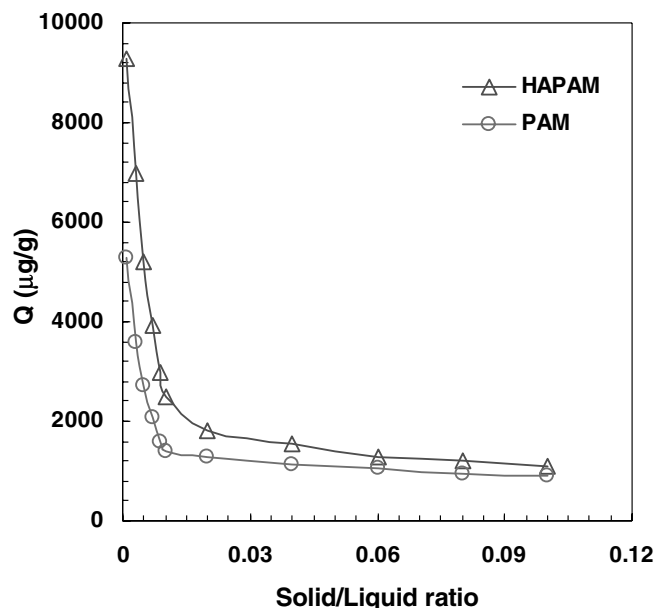


Fig. 6. Influence of the solid/liquid ratio.

plot the isotherm. Because the variation of the adsorbed amount with the polymer concentration follows the same trend (Figure 6) as the extrapolated values at this very low ratio, corresponding to a volume fraction of  $3.7 \times 10^{-3}$ , for comparison, the adsorption isotherm has been determined under the same conditions as those for PAM.

Figure 7, 45 indicated that the adsorption temperature was 45°C and the concentration of NaCl was 8000 mg/l; 65 indicated that the adsorption temperature was 65°C and the concentration of NaCl was 30000 mg/l. As shown in

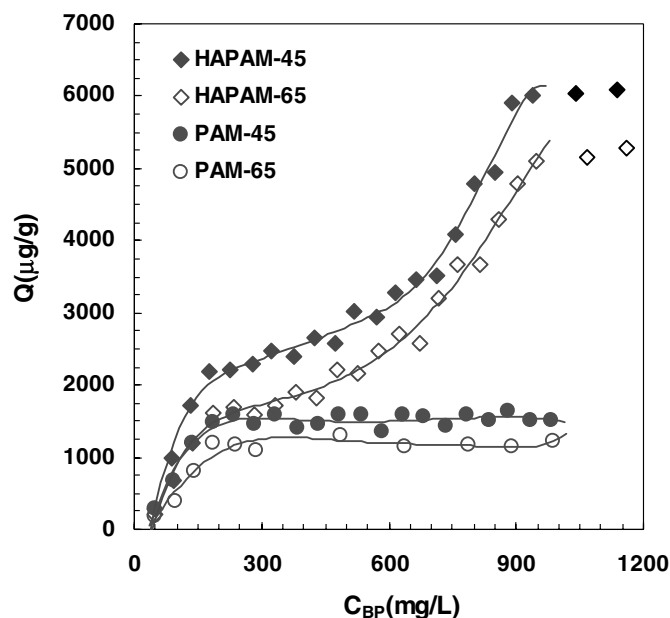


Fig. 7. Adsorption isotherms of HAPAM and PAM.

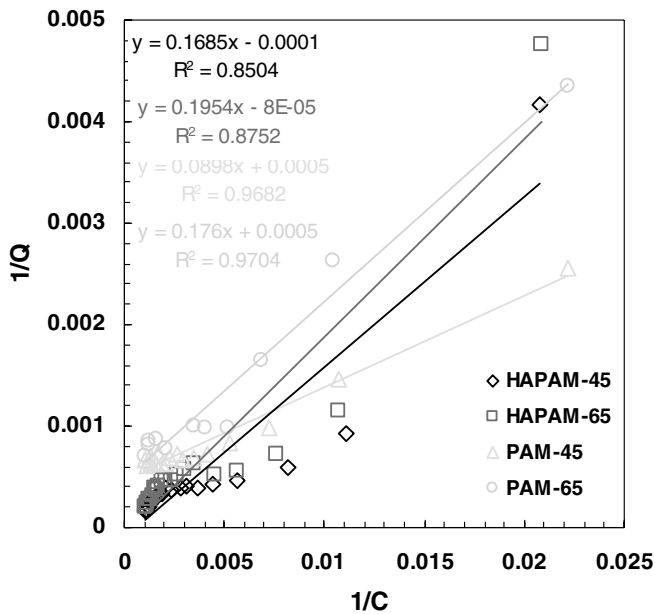


Fig. 8. Langmuir fitting for HAPAM and PAM.

Figure 7, the adsorption isotherms of PAM were a classical type of isotherm, i.e., first an increase in the adsorbed amount with polymer concentration and then a pseudo-plateau for PAM concentrations above 300 mg/l corresponding to the saturation of the surface by the PAM chains. For HAPAM, there were no plateau regions, but the adsorbed amount increases continuously with the concentration of HAPAM in the solution.

To further understand the HAPAM adsorption behavior, a Langmuir model and Freundlich model were used to fit the experiment results (Figures 8 and 9).

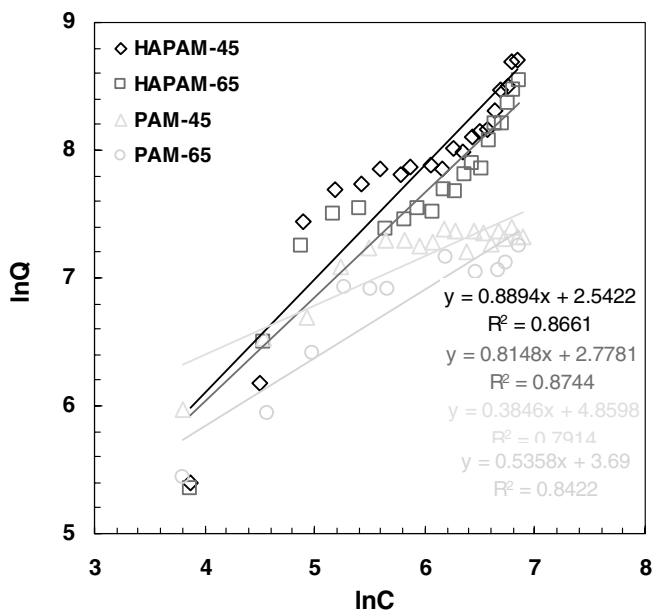


Fig. 9. Freundlich fitting for HAPAM and PAM.

Langmuir model:

$$\frac{C}{Q} = \frac{1}{bQ_m} + \frac{1}{Q_m}C \tag{1}$$

Freundlich model:

$$\frac{Q}{Q_m} = kC^{1/n} \text{ or } \ln Q = \frac{1}{n} \ln C + \ln k Q_m \tag{2}$$

Here, C, Q, and  $Q_m$  are the same as previously described, and b, n, as well as k, are constant under specific conditions. It is well known that the Langmuir isotherm, an ideal model, performs a dynamic adsorption process with the reciprocation between adsorbed and unadsorbed polymer molecules and no interaction between these adsorbed molecules. Freundlich isotherm can validate in many adsorption processes, though empirical in origin, allowing one or more interactions between adsorbed molecules or adsorbed molecules and sand surface being involved in the dynamic process. As shown in Figure 8, the correlation of the curve from Langmuir isotherm fitting for PAM was obviously better than for HAPAM. In contrast, in Figure 9, the correlation of the curve from Freundlich isotherm fitting for HAPAM was superior to PAM. This indicates that the process of HAPAM adsorption on a sand surface was more complicated than PAM, a more or less interaction being involved in the dynamic process. Clearly, if there is no interaction among HAPAM molecules, the adsorption isotherm for HAPAM and PAM should be similar.

A schematic of the conformation of the polymer chains adsorbed at a solid/liquid interface that is envisaged is presented in Figure 10 (19). For PAM, the adsorbed layer was composed of trains, loops and tails. The pseudo-plateau of the isotherm indicates saturation of the surface by the PAM. For HAPAM, adsorption of multiple layers of HAPAM chains occurs with an increase of the HAPAM concentration. The adsorbed layer was composed of chains which had segments in contact with the surface and some chains which, at a given time or in a “frozen” state, were not directly in contact with the surface but were linked through hydrophobic interactions to other chains that were adsorbed on the surface. Similar results were reported by Tanaka and Pefferkorn (24, 25). They thought that the associative polymer adsorbed on a solid/liquid interface could also have trains, loops and tails, which have many associative points and these associative points could have interaction with the unadsorbed HAPAM molecules by hydrophobic association interaction. Compared with PAM, larger adsorbed amounts were observed for HAPAM as well as isotherms characterized by an adsorbed amount that increases rapidly up to a plateau region, followed by another increase.

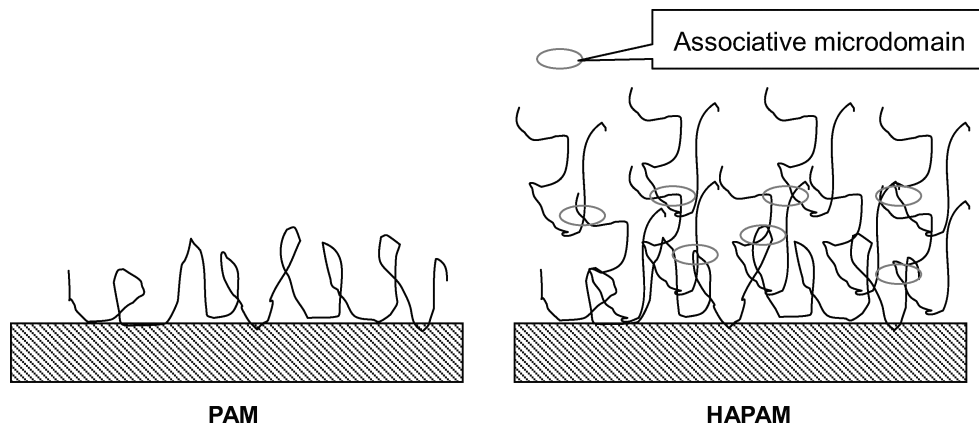


Fig. 10. Schematic of the conformation of adsorbed layers formed by HAPAM or PAM at a solid/liquid interface.

3.4 Effect of Temperature on Polymer Adsorption Behavior

In Figure 11, the concentrations of NaCl were 8000 mg/l and 30000 mg/l, respectively. The adsorption temperature varied from 30 to 65°C. The solid/liquid ratio was 0.01. The polymer concentration was 400 mg/l. As shown in Figure 11, the adsorption of PAM in NaCl aqueous solution decreased dramatically with increasing the temperature from 30 to 50°C and the adsorption kept almost constant from 50 to 65°C. Because the adsorption of neutral polymers results mainly from direct hydrogen bond interactions between polymers and sand, it's easily conceivable that the adsorption decreased when the hydrogen bonds started to break. For HAPAM, the adsorption decreased lentamente with the increase of temperature from 30 to 45°C; the adsorption decreased drastically from 45 to 55°C and then remained nearly constant at a temperature between 55

and 65°C. This could be interpreted as: during the lower temperature, the hydrophobic association interaction could be strengthened with the increase of temperature resulting in the increase of the adsorption; on the other hand, the hydrogen bonds could be broken with an increased temperature leading to the decrease of the adsorption. However, the hydrogen bonds play a major role in adsorption of HAPAM on a sand surface, the decrease of adsorption of HAPAM was no more obvious than PAM from 30 to 45°C. From 45 to 55°C, the hydrophobic association interaction become very weak and the hydrogen bonds have been seriously broken, resulting in the drastic decrease of adsorption of HAPAM. This also showed that HAPAM could not exhibit a strong property of hydrophobic association.

3.5 Effect of Salinity on Polymer Adsorption Behavior

In Figure 12, the adsorption temperatures were 45°C and 65°C, the solid/liquid ratio was 0.01, the polymer concentration was 400 mg/l. As indicated in Figure 12, the adsorption of HAPAM decreased with the increasing NaCl concentration while  $C_{NaCl} < 20$  g/l; the adsorption of HAPAM seemed to increase weakly, while  $C_{NaCl} > 20$  g/l. For PAM, it's another way around. The adsorption of PAM remained nearly constant from 0 to 40 g/l. Because 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, the adsorption seemed to be independent from salinity. However,  $Na^+$  in solution could change the association interaction. When the concentration of  $Na^+$  was less than the critical NaCl concentration,  $Na^+$  could weaken the hydrophobic association interaction, resulting in the decrease of the adsorption; When the concentration of  $Na^+$  was higher than the critical NaCl concentration,  $Na^+$  could strengthen the hydrophobic association interaction, leading to the increase of the adsorption. It's true that the increase of adsorption was inconspicuous.

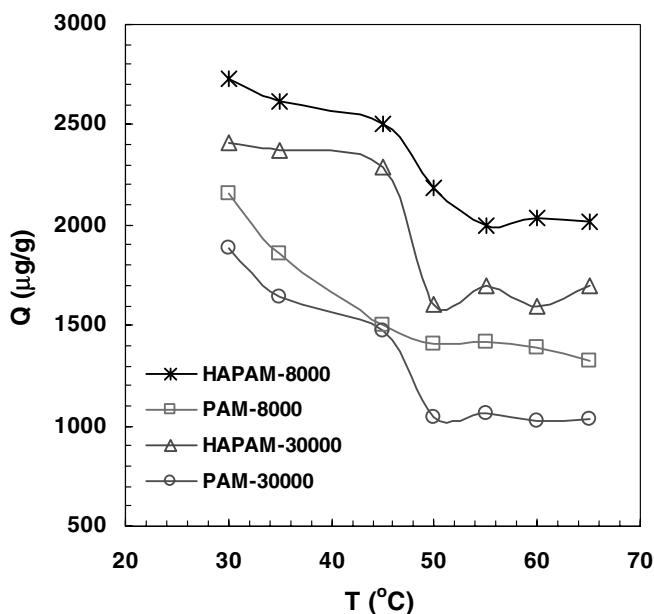


Fig. 11. Influence of the temperature.

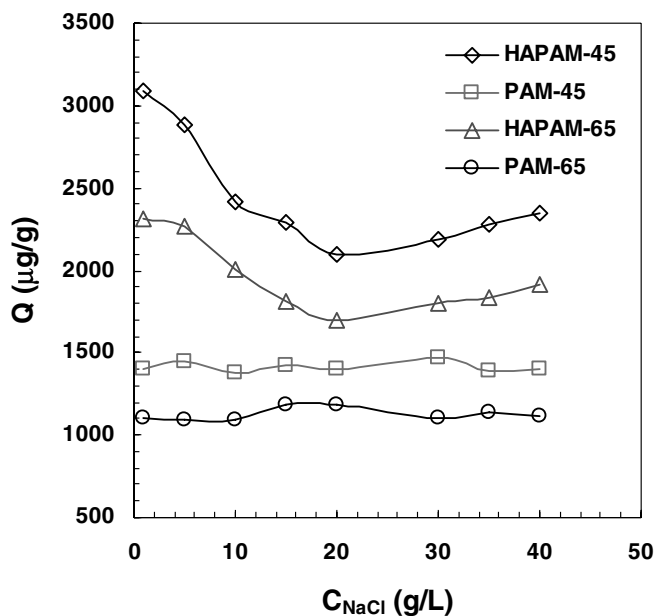


Fig. 12. Influence of the Salinity.

#### 4 Conclusions

Solution property of HAPAM with composition homogeneity was investigated. The critical association concentration was measured by three methods: viscosity method, micro-pore method and the fluorescence method. The critical association concentration determined by a different method followed this relationship:  $CAC_F < CAC_M < CAC_V$ . The  $CAC_M$  was much closer to  $CAC_F$ . It also proved that there was still hydrophobic association interaction of HAPAM in the oil reservoir with flowing conditions. HAPAM could exhibit multi-layer adsorption behavior, but a classical Langmuir adsorption behavior for PAM. Freundlich model fitting showed that HAPAM should be a multi-layer adsorption due to the special interaction (hydrophobic association interaction). It is the hydrophobic association interaction that made the adsorption behavior of HAPAM differ from HAPAM. At a lower temperature, the adsorption decreased lentamente with the increase of temperature. It's another way around for PAM. The adsorption of PAM was almost independent from salinity, but for HAPAM, the adsorption first decreased and then increased with the increasing salinity.

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

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