RHEOLOGICAL INVESTIGATIONS OF PARTIALLY HYDROLYZED POLYACRYLAMIDE – HEXAMINE – HYDROQUINONE GELS

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ABSTRACT

The rheological behaviour of polymer gel is the fundamental parameter for its application in the profile modification job in the oilfields. It is prepared by the combination of polymer, cross-linker and saline water. The reaction between polymer and cross-linker results in the formation of a 3-dimensional polymer gel network at reservoir conditions which forms a barrier to water flow in the reservoir. To ascertain the flow of the gel solution through the tubing to the petroleum formation before the formation of stiff gel, the study of rheological behaviour is essential. In this study, partially hydrolyzed poly acrylamide has been cross-linked with hexamine and hydroquinone cross linkers to form gel. The experimental investigation furnishes that the polymer solutions have good flow ability before the stiff gel formation which shows its potential for adequate pumping time before reaching the formation and better placement of polymer gel in the petroleum reservoir during profile modification jobs.

KEYWORDS: Rheology, Polymer Gel, Temperature, Viscosity, Profile Modification

INTRODUCTION

The crosslinked polymer gel systems are most commonly used for permeability modification in petroleum reservoir formations. In this technique, polymer gel system is injected into the high permeability zone, watered-out zones to block or plug-off that portion of the reservoir. This result in diversion of water subsequently injected into the oil rich zones, improving sweep efficiency of the water and increased oil recovery.[1][2]

In the crosslinked polymer gel systems, several organic and inorganic crosslinkers are used in the high molecular weight water soluble polymer solution to produce a three dimensional structure of gel. The polymer crosslinker solution is pumped into high permeability fractures or fracture networks in the reservoir through injection wells, where it produces the polymer gel network at reservoir temperature and diverts injected water or gas to unswept zones and improves the distribution of injected fluids into a heterogeneous reservoir. Depending on the polymer and crosslinkers composition, these gels are thermally stable, and the gel times are controllable over a wide temperature range.[3][4]

For pumping the polymer gel solutions through the tubing into the formation the study of the rheological behavior is essential for certain duration depending upon the depth of the well to ascertain flow ability of gel solution before the formation of stiff or rigid gel.[5][6]. The time for the stiff or rigid gel formation can be controlled from minutes to week by varying the formulation parameters.[7][8]. The temperature, polymer concentration, crosslinker concentration, pH and salinity are the important parameters which affect on the rheological behavior of the polymer gel system.[9][11]. Hence, the rheological behavior of partially hydrolyzed polyacrylamide (PHPA)-hexamine-hydroquinone gel solutions under different conditions were thoroughly studied for better placement of this gel in the petroleum reservoir during profile modification jobs.
EXPERIMENTAL WORK

Materials

The materials used for this work are partially hydrolyzed polyacrylamide, hexamine, hydroquinone, sodium chloride, hydrochloric acid and sodium hydroxide. Partially hydrolyzed polyacrylamide, in the form of white crystalline powder (procured from Oil and Natural Gas Corporation Limited, Mumbai, India) was used as the water soluble polymer for carrying out the experimental work. The organic cross-linkers hexamine was obtained in solid form from renowned manufacturer (hexamine: Otto Kemi Mumbai, India. Hydroquinone is procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. Sodium chloride is used to maintain the salinity of polymer gelant, purchased from Nice Chemical Pvt. Ltd. Cochin, India. Hydrochloric acid and sodium hydroxide are used for the adjustment of pH. (Hydrochloric acid: Central Drug house Ltd. New Delhi, India and sodium hydroxide: S. D. Fine-Chem Ltd. Mumbai, India).

Equipment

All rheological measurements were performed in a stress controlled Physica Rheolab MC1 (Figure 1). It is a rotational rheometer based on the Searle principle. It features a DC motor drive and optical encoder which provides excellent speed regulation, dynamic range and transient response. These features provide superior performance in comparison with rheometers using gear driven (indirect) or stepper motor drives. It enables precise measurements of fluid viscosity over the widest range of conditions available today. This machine is not equipped with a high pressure cell and measurement at high temperature is not allowed. Hence, gel had to be cured in hot air oven. The cured samples were transferred to the rheometer and tests were conducted at 30°C.

Figure 1: PhysicaRheometer MC1

Experimental Procedure

Initially stock solution of partially hydrolyzed polyacrylamide in brine solution (1.0 wt. %) was prepared and kept for aging at ambient temperature for 24 hrs. Further fresh solution of PHPA-HMTA-Hydroquinone gel was prepared in brine ahead of mixing the polymer and crosslinkers to form gelant. The appropriate solution of partially hydrolyzed polyacrylamide, hexamine-hydroquinone and brine were thoroughly mixed at room temperature by magnetic stirrer. The pH of the gelant solution was measured by Century CP-901 digital pH meter. The pH of the gelant was maintained using 1N sodium hydroxide
and 1N hydrochloric acid. Finally, the solution was transferred into small glass bottles and kept at the desired temperature in the hot air oven. At regular intervals of time rheological behavior at different shear rates was measured using rhometer.

RESULTS AND DISCUSSIONS

Ageing Effect on the Rheological Behavior of PHPA-HMTA-Hydroquinone Gel Solution

The gel point is defined as the time needed to reach the inflection point on the viscosity vs. time curve (Figure 2). This method has been widely used by several authors \(^\text{[12]}\). Before the gel formation, the viscosity of the gelling solution is relatively low; therefore, it can be measured accurately. After the gel formation, it will be hard to get an accurate viscosity value. The strength of the cross-linking polymer solution is hard to measure and also hard to define, when the gel has reached a certain high strength \(^\text{[13]}\).

![Figure 2: Effect of Time on Evolution of Rheological Behavior of PHPA-HMTA-Hydroquinone Gel Solution at 100°C and pH 8.5 (PHPA 1.0 wt %, HMTA 0.4 wt % and Hydroquinone 0.4 wt %)](image)

Before gel formation, the viscosity of the gelling solution is relatively low; therefore it can be measured easily and accurately but after gel formation it is hard to obtain accurate readings \(^\text{[12]}\). Thus, the mechanical strength of cross-linked partially hydrolyzed polyacrylamide gel increases with the increase in temperature. The elastic modulus increased gradually upon the addition of the cross-linkers until it reached a constant level indicating that the gel formation reaction is over. When the measurements were taken it was observed in each case that initially the reading remains constant for some time known as
the induction time and then it starts increasing indicating the onset of gelation. Addition of cross-linker to the solution increased until it reached a maximum where increasing the cross-linker concentration results in syneresis. Higher concentrations of cross-linker prevented gel formation. Therefore, there are concentration limits that crosslinker should not exceed in order for the gel to form and this is known as critical crosslinker concentration. Initially the viscosity was found to decrease due to temperature as is known for any solution which in this case may be due to the breaking up of the molecular chains as a result of cross-linking reaction. As the time progresses polymer undergoes hydrolysis and the gelant starts thickening which results in an increase in viscosity. Also it was observed that the values of gelant viscosity increases with temperature at constant shear rate, which reflects that the viscosity of crosslinked polymer gel solution increase with temperature with the passage of time. This increased viscosity leads to gel formation which in turn behaves as flow diverting agent or blocking agent for controlling excessive water production in the oil fields.

![Figure 3: Effect of Temperature on Evolution of Rheological Behaviour of PHPA-HMTA-Hydroquinone Gel Solution at pH 8.5 (PHPA 1.0 wt%, HMTA 0.4 wt% and Hydroquinone 0.4 wt %)](image)

**Effect of Polymer Concentration on the Rheological Behavior of PHPA-HMTA- Hydroquinone Gel Solution**

Due to cross-linking a lattice like structure is formed which consists of two domains: dilute domain (free draining space) and dense domain (non-draining space). The dense domains are centered on the cross-linked regions where the polymers are bound together and extend outward by the entanglement of the free polymer onto the cross-linked regions. They are much less permeable than the dilute domains. 

![Figure 4: Effect of Polymer Concentration on Evolution of Rheological Behaviour of PHPA-HMTA-Hydroquinone Gel Solution at Ph 8.5 and 100°C (HMTA 0.4 wt% and Hydroquinone 0.4 wt %)](image)
Even at the lowest polymer concentration, all the cross-linker reacts with polymer to form gel hence an increase in polymer concentration will mainly increase the number of free polymer coils which increases the viscosity of the gelant (Koohi et al., 2010). In order to check the effect of polymer concentration, five solutions were prepared in brine of 1.0 wt% salinity with PHPA concentrations of 0.8, 0.9, 1.0, 1.1 and 1.2 wt% with the same concentration of HMTA (0.4 wt.%) hydroquinone (0.3 wt.%). Figure 4 depicts the change in viscosity with increase in polymer concentration. The gels at higher concentration were very stiff in nature and formed in lesser time interval. This analysis was done with the help of bottle testing after certain time intervals.

**Effect of Crosslinkers Concentration on the Rheological Behavior of PHPA-HMTA- Hydroquinone Gel Solution**

A comparative study of the variation of apparent viscosity of different polymer gelants having the same concentration of both the cross-linkers with a constant polymer concentration of 1.0wt % at room temperature is shown in the flow curve of Figure 5. The graph showed that the value of viscosity increases with an increase in concentration of the cross-linkers at constant polymer concentration.

![Figure 5: Effect of Crosslinkers Concentration on Evolution of Rheological Behaviour of PHPA-HMTA-Hydroquinone Gel Solution at Ph 8.5, Time Intervals 5 hrs and 100 °C (PHPA 1.0 wt.%)](image)

The constant concentration of PHPA 1.0 wt% to study the variation in gel strength at room temperature. Thus, greater concentration of the cross-linker results in the increase of gel strength of the polymer gel. Figure 5 depicts the increasing trend of viscosity with an increase in concentration of HMTA and hydroquinone during gelation. As shown in Figure 5 the readings were taken at a shear rate of 124, 628 and 1200 sec⁻¹ after 5 hrs of gelation at a temperature of 100°C. This shows that the mechanical strength of the gel formed increases with an increase in concentration of cross-linkers.

The lower the cross-linkers concentration, the worse the degrees of cross-linking. The solubility of the polymer gel increases with low cross-linking density; therefore the degree of water swelling of the gel gets reduced. Hence the gels of weak strength are formed. The shear stress increases with an increase in concentration of cross-linkers since greater cross-linking takes place on the polymer chain.

**Effect of Salinity on the Rheological Behavior of PHPA-HMTA- Hydroquinone Gel Solution**

Gelants were prepared in brines containing various salts concentrations. In this study, NaCl was used to examine the effect of sodium ions on the gelation time of this system. It was observed that at a given shear rate, the apparent viscosity
diminished as NaCl concentration increased. Different samples were prepared with a constant polymer content, PHPA 1.0 wt.%, HMTA 0.4 wt.% and hydroquinone 0.3 wt.% in brine of salinity varying from 1.0 wt.% to 4.0 wt.%. Then, the viscosity of these solutions was measured at 30°C at different shear rates as shown in Figure 6. The excess monovalent cations present in gel system screen the negative charges on the polymer molecule structure so that the positive cross-linker ions could not easily access the negative sites to react with them thus the cross-linking density decreases with reduction in elastic modulus of the gel (Cai and Huang, 2001). The elasticity of the gelants decreased with increase in salinity.

**Figure 6: Effect of Salinity on Evolution of Rheological Behaviour of PHPA-HMTA-Hydroquinone Gel Solution at pH 8.5, Time Intervals 5 hrs and 100 °C (PHPA 1.0 wt.%, HMTA 0.4 wt.% and Hydroquinone 0.4 wt.%)**

**Effect of pH on the Rheological Behavior of PHPA-HMTA-Hydroquinone Gel Solution**

Different polymer gel systems have different range of pH over which they can maintain their stability. The pH range over which the experiments were carried out was from 7.0 to 9.5. Figure 7 shows the pH ranges between 7.0 to 9.5 have no significant effect on the gelation time. From the experiments carried out in the laboratory it was found that HMTA/hydroquinone cross-linked partially hydrolyzed polyacrylamide is stable up to pH 9.5. Above pH 9.5 proper gelation did not take place and syneresis also occurred due to excess crosslinking. The results indicate that a suitable solution pH range for partially hydrolyzed polyacrylamide, hexamine and hydroquinone cross linking is between 7.0 to 9.5

**Figure 7: Effect of pH on Rheological Behaviour of PHPA-HMTA-Hydroquinone Gel Solution at 8.5 pH, Time Intervals 5 hrs and 100 °C (PHPA 1.0 wt %, HMTA 0.4 wt % and Hydroquinone 0.4 wt %)**
CONCLUSIONS

The following conclusions may be drawn from present study:

- The viscosity of partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel solution increases with increase in ageing time, temperature, polymer concentration and crosslinker concentration.

- The partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel solution shows the negligible effect on pH and salinity.

- The partially hydrolyzed polyacrylamide-hexamine-hydroquinone gel solution behaves like a non-Newtonian shear thinning fluid.

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