Effect of Salinity of Concentration of Polymer Solution on Viscosity

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Abstract
Polymers are widely used in oil and gas industries such as in polymer flooding in Enhanced Oil Recovery (EOR). In field, polymer solution is made by mixing polymer powder with brine. However, polymers are very sensitive towards salinity of brine. High salinity can affect the viscosity of polymer solution.

The objectives of this research are to measure the rheological properties of Xanthan gum and HPAM solution as a function of shear rate, polymer concentration, salinity and to justify the relationship of the above variables which affecting the viscosity of polymers solutions. The methodology used in this research is experimental methods. Several experiments will be done to verify the effect of salinity, shear rate and polymer concentration on polymer solution viscosity. Polymer solutions will be prepared by using Xanthan gum and HPAM with different concentration ranging from 500 ppm until 2500 ppm. Each sample will be prepared by mixing with different salinity of brine (NaCl, CaCl2 and MgCl2). Viscosities of all these samples will be measured by using dial viscometer Fann 35A and digital LV Brookfield viscometer at 25°C (77°F). This project had been done conducted at Scomi GRTC, Shah Alam by using their chemicals, equipments and tools.

In conclusion, the finding of this project is Xanthan gum yield higher viscosities as a function of polymer concentration compared to HPAM solution. Still, both of polymers show increasing trending. Then, both polymers solution viscosity are affected by the salinity of brines and as well as type of salt (monovalent or divalent). Both of polymer solutions exhibit the non-Newtonian fluids, which are dependent on shear rate.

Introduction
Oil production has three different stages; primary (production by natural reservoir energy), secondary (production by supply of external energy into the reservoir by injecting fluids to increase reservoir pressure) and tertiary (enhanced oil recovery methods increase the mobility ratio of the oil in order to increase production). Over the lifetime of the oil field the pressure will fall, and at some point there will be insufficient underground pressure to lift the oil to the surface. In order to maintain the reservoir pressure, and sweep out oil in a more efficient way, water flooding as secondary oil production is a practical and effective way for many reservoir formations. A problem with water flooding is that in many cases, oil has higher viscosity than water, and this however may lead to an unstable displacement. Increasing the viscosity of injected water by adding a polymer will improve sweep during water flooding process. To solve the problem of unstable displacement during water flooding, polymer was suggested in the early 1960s. Polymer either biopolymers or synthetic polymers have several types of applications. Some of these applications are used in drilling or chemical flooding. In polymer flooding process, a water soluble polymer either biopolymer or synthetic is added to injected water. Water/oil mobility ratio is the only mechanism to describe why using polymer can make water flooding more efficient.

The specific objectives of this research project are to study the viscosity behavior of polymer solutions (Xanthan gum and HPAM) as a function of shear rate, polymer concentration, salinity including temperature and to justify the relationship of variables that affecting the viscosity behavior of polymer solutions. The scope of study for this research focus on type of polymer use which are HPAM and Xanthan gum polymers, concentration of polymer ranging from 500- 2500 ppm, salinity of brine ranging from 1- 10wt% and in the constant temperature 25°C.

The development and completion of this project is feasible judging from the objectives and scope of studies above. The overall period to complete the research is approximately 8 month. The project will focused more on the effect of salinity of brines and concentration of polymer. Based on the above statement, the research is feasible as the time allocated is sufficient for the student to do research in order to achieve the objectives.
Literature Review
The term rheology is defined as the study of the deformation and flow of different fluids in response to surface forces (stress). The mathematical relationship between stress and deformation rate (strain rate) is constitutive equation. The Newtonian relationship between stress and strain rate is the simplest example of a rheological constitutive equation as:

\[ F = \mu A \frac{dv}{dx} \]  
Equation 2.1

Where; \( F \) is force which applies on the surface of the fluid, \( A \) is the contact area between two adjacent layers in the fluids, \( \frac{dv}{dx} \) is the velocity gradient between the two layers, and \( \mu \) which is proportionality constant, is simply called fluid viscosity.

The fluid viscosity is simply defined as the fluid resistance to shear. Based on this simple definition it is possible to formulate fluid viscosity as:

\[ \sigma = \mu \gamma \]  
Equation 2.2

Which \( \sigma \) (Pa) is shear stress which implies on the fluid surface, \( \mu \) (Pa.s) is fluid viscosity and \( \gamma \) (s\(^{-1}\)) is shear rate. Generally as showed in equation 2.2, fluid may be classified as Newtonian or non-Newtonian fluids. The viscosity of Newtonian fluids, i.e. water, is constant and it is not a function of shear rate. Polymer solution generally classified as non-Newtonian fluids, i.e. the viscosity changes with shear rate and it is not constant. This change in the viscosity as a function of shear rate is different for different as shown in Figure 8 below.

In pseudo plastic fluids, known also as shear thinning, the viscosity decreases as shear rate increases, and vast majority of polymer solutions are shear thinning in their nature. Shear rate is not the only factor which can affect the viscosity of polymer solution, but there are several other parameters which may affect polymer viscosity behavior, i.e. molecular weight, polymer concentration, and the nature of polymer and solvent.

For all polymers, higher the polymer molecular weight and concentrations gives a solution with higher viscosity. This is because the polymer concentration changes the interactions among polymer molecules, and the molecular weight directly affects the chain size. While polymer with higher molecular weight gives a solution with higher viscosity, however they are easily shear degradable (mechanical degradation). For example, HPAM with high molecular weight is an effective viscosities polymer, but it is easily shear degradable.

To understand the effect of ions, monovalent and divalent, on the viscosity behavior of the polyelectrolyte solutions, the interaction of these ions with the charges on the polymer chain must be understood.

Molecules of polyelectrolyte in distilled water may be almost fully expanded due to the repulsion between the similar charged groups distributed along the polymer chain. In aqueous solvents because of positive mobile ions, the charges on the polymer chain are screened and degree of expansion decreases.

Salt ions can be divided into two categories which are monovalent ions and divalent ions. HPAM molecules are more sensitive to divalent ions. This is due to the strong binding between divalent ions and carboxyle group (COO\(^{-}\)). After a certain divalent ions concentration, HPAM will precipitate and this make HPAM unfavorable for EOR processes in high salinity/hardness condition. The negatively charged carboxyl or AMPS groups in high pH conditions induce extension of the molecules through electrostatic repulsion among the groups, thereby increasing viscosity; conversely, low pH conditions cause the molecules to become coiled, resulting in low viscosity.

Methodology
**Polymers used.** Hydrolyzed polyacrylamide (HPAM) as a synthetic polymer is readily water-soluble over a broad range of conditions. These polymers are unique in their strong hydrogen bonding, linearity, and very high molecular weight, approximately 14 million (provided by manufacturer). The polyacrylamide can be modified by changing some of the amide groups to carboxyl groups. This technique, known as hydrolysis, is accomplished by treating HPAM with a strong base. When only part of the amide groups are modified, the process is called partial hydrolysis, forming Partially Hydrolyzed Polyacrylamide (HPAM).

Xanthan gum is a biopolymers produced in pure future fermentation by the microorganism Xanthomonas Campestris. Three different monosaccharides making up the basic polymer structure are: mannose, glucose and glucuronic acid. Xanthan gum is the most commonly used polysaccharide in Enhanced Oil Recovery. The molecular weight of Xanthan is approximately around 2-4 million. The molecular structure of Xanthan gum gives a degree of rigidity to the plymer molecule which provides excellent resistance to mechanical breakage.

**Preparation of brines.** 1%, 3% and 9% Sodium Chloride (NaCl) Brines will be prepared. In addition, 1%, 3%, and 9% Calcium Chloride (CaCl\(_2\)) and Magnesium Chloride (MgCl\(_2\)) brines will be prepared for divalent salt. First, weight 50 grams of NaCl salt and dilute it with de-ionized water in beaker. Pour all the solution onti the 1L of volumetric flask; fill the rest until salt solution reached marked level. Label the volumetric flask with appropriate label and repeat these steps for CaCl\(_2\) and MgCl\(_2\) brines.
**Preparation of polymer solutions.** HPAM: One of the best mixing techniques used for polymer solution preparation is accomplished with a magnetically driven stirrer. The magnetic stirrer should be adjusted so that bottom of the solvent vortex is 30 to 50% of diameter of the beaker. To prevent the formation of “fish eyes”, the polymer must be added slowly and uniformly to the upper curve of the vortex. As soon as the entire polymer has been added, the stirrer is slowed to a low speed just to keep the solid particles from settling to the bottom of the beaker. The low speed mixing (60-80 rpm) is necessary to avoid mechanical degradation. After 2 to 3 hours the stirrer is turned off. The solutions are allowed to stand overnight and are stirrer about 20 minutes before use.

Xanthan gum: Dissolving Xanthan gum in a solution is a slow process which occurs in two stages. First, a gel is formed when the solvent molecules start to dissolve and to associate with the polymer chains. The second stage is strongly affected by the type of mixing. Xanthan gum solutions were prepared using a Silverson mixer which provided enough shear rates to thoroughly disperse the polymer particles and prevent gel formation. In this method the polymer particles were added slowly to the solvent and mixed for 5-10 minutes. Too high a shear rate resulted in mechanical degradation and too short a mixing time failed to break the gel.

**Measurement of viscosity.** The viscosities were measured on a Brookfield LV viscometer with a Ultra Low (U.L) light adaptor at 6 rpm (7.3 sec⁻¹). This low shear rate was chosen as most representatives of that encountered by mobility buffers in reservoirs under water flooding at typical rates. While it is acknowledged that this unit is not a precise, research-grade instrument, it is the most widely used viscometer for mobility control polymer solutions by both polymer suppliers and oil companies in the laboratory and field.

The viscosity of polymer solutions was measured as a function of shear rates using a rotational viscometer (Model Fann 35). The viscosity of the polymer solution was measured as a function of salinity at different shear rates (3, 6, 100, 200, 300, and 600 RPM). All the measurement are taken in room temperature (25°C).

**Result and Discussion**

**Effect of Polymer Concentration on Viscosity**

**Figure 11: Effect of polymer concentration on viscosity of polymer solutions**

Figure 11 shows the effect of polymer concentration on the viscosity of HPAM solutions. An increase in polymer concentration increases the solution viscosity. As the polymer concentration increases, the opportunity for molecular entanglement rises sharply, thereby increasing the viscosity. Conversely, at low polymer concentrations the tendency for entanglement is greatly decreased, reducing the viscosity.

It also illustrates the effect of polymer concentration on the viscosity of Xanthan gum solutions. It is obvious that an increase in polymer concentration increases the solution viscosity. This is clearly a mass effect resulting from more polymer molecules being dissolved in the solution.
Effect of salinity on viscosity of 2000 ppm of HPAM and Xanthan gum solutions

From Figure 12 and Figure 13, we can observe the influence of brine concentration on the polymer solutions (HPAM and Xanthan gum). The salinity of brine is expressed as a salt weight percent of total solution weight. As seen in Figure 13, that increasing brine concentration up to 6% tends to significantly increase Xanthan viscosity. In contrary, Figure 12 shows that the presence of brine in HPAM solutions is seen to reduce the viscosity to great extent. Hence, one may conclude that ion shielding by brine is associated with Xanthan solutions, while in the HPAM solution the shielding is disrupted. This is due to the salts that neutralize electrical charges along the polymer molecule. In this condition, the polymer chain coils into a tightly wound sphere, thereby exposing a minimum of surface to the solvent. This decreases the interactions between polymer particles and causes a decrease in viscosity. When HPAM polymer is dissolved in brine, repulsion between the carboxyl groups is reduced by an attraction between the brine cations and the anionic charge on the carboxyl group. This causes the molecule to be compressed from its enlarged state and results in a reduction of viscosity.

The effect of type of salt ions can be observed from Figure 12 and Figure 13. There are three types of brines which divided into two categories; monovalent ions, e.g. Na\(^+\) and divalent ions, e.g. Ca\(^{2+}\) and Mg\(^{2+}\). Both polymers are more sensitive to divalent ions compare to monovalent ions. It has been generally accepted this is due to the strong binding between divalent ions and carboxylate group (COO\(^-\)). In the presence of divalent ions HPAM and will precipitate and this make HPAM unfavorable for EOR process for high salinity condition.

Two contradicted trends are observed in the effect of divalent ions on viscosity of polymers on HPAM solution on Figure 12. The presence of Calcium ions greatly reduced the viscosity as the concentration of divalent ions increases. However, the presence of Magnesium ions still reduced the viscosity but its viscosity is stable when mixed with 6% or more salinity Magnesium Chloride brines. From Figure 13, the viscosity of Xanthan gum solution is not greatly affected but the trending line still showing the loss of viscosity as the salinity increases.
Effect of shear rate on viscosity

Figure 14 and Figure 15: Effect of Shear rate on viscosity of Xanthan gum solutions

Figure 14 shows shear viscosity versus shear rate for HPAM solutions at various polymer concentrations tested at 25 °C. As anticipated, HPAM solutions behave as non-Newtonian fluid at all ranges of polymer concentrations, where its viscosity changes with shear rate and it is not constant. It is also known as shear thinning, the viscosity decreases as shear rate increases, and Figure 15 shows the viscosity for Xanthan gum solutions in a function of shear rate (sec\(^{-1}\)) in order to investigate mechanical degradation. When the shearing effect on the two polymers is compared, the striking difference is that Xanthan gum appeared to be extremely shear stable because of the rigid rod structure, whereas HPAM was very sensitive to shear degradation because of the flexible coil molecules. The rate of polymer chain rupture in high shear flow depends on the molecular weight. Larger molecules offer more resistance to flow, consequently experienced larger shearing or elongational stresses. Average molecular weight for HPAM is 13 million and average molecular weight of Xanthan gum is around 2-4 million.

Conclusion
Viscosity data are presented for both HPAM and Xanthan gum polymers at 5 different concentrations in six salinities. The information can be interpolated to predict the viscosity behavior of any of these polymers at NaCl from 0 to 10% and at any shear rate from 5.109 to 1021.8 s\(^{-1}\). These data can facilitate the screening of polymer candidate for a particular chemical flood.

HPAM solution with de-ionized water yield more viscosity than Xanthan gum solution at the same concentration, 2000 ppm. However, in the presence of salt, viscosity of Xanthan gum solution increases with increasing salinity up until 6 wt% of NaCl brines. Excessive salt concentration which is more than 6% caused the viscosity reduction in Xanthan gum solution. For HPAM solution, presence of salt shows that the loss in viscosity as the salinity increases. The reduction in viscosity is adverse for cation salt such as Calcium Chloride and Magnesium Chloride brines. The effect of shear rate on polymer viscosity is studied and concludes that as the shear rate increases, the viscosity of polymer solution will be reduced. However, as the concentration of polymer increases, the loss of viscosity can be prevented during high shear rate.
Recommendations
I would like to suggest that this project is continued to study more polymers such as Guar gum, Carboxymethylcellulose (CMC), Hydroxyethylcellulose (HEC) and other associating polymers. Besides that, study should be focus on the effect of temperature on polymer solution viscosity. Another interesting factor for an investigation is the long term stability of the hydrogen ion (pH) concentration of polymer solution. Even though the molecular structure of Xanthan gum gives a degree of rigidity to the polymer molecule which provides excellent resistance to mechanical breakage, microbes are very effective in the destruction of the polymer molecule. Therefore, the effect of microbes on solution degradation should also be studied extensively.

References