Rheological behavior of terpolymer (PAM-ATBS-NVP) in polymer flooding for enhanced oil recovery: impact of concentration, salinity and nanoparticles

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ABSTRACT

The application of polymer flooding for enhanced oil recovery has resulted in the retrieval of an additional 10%–20% from the original oil in place (OOIP). The main objective of this study was to investigate the rheological behavior of terpolymer (PAM-ATBS-NVP) in polymer flooding for enhanced oil recovery. The effect of concentration, temperature, salinity/hardness, and nanoparticle type/concentration was assessed under different reservoir conditions. The results showed that, as the shear rate increased, the viscosity of the polymer decreased which reflected shear thinning behavior and when the polymer concentration increased, the viscosity of the polymer increased. The polymer also provided good thermal stability. Despite this terpolymer being designed to tolerate harsh condition of temperature and salinity/hardness, the viscosity of the polymer decreased with higher salinity/hardness. Using three types of nanoparticles (NPs), the viscosity of the polymer did not change for two NPs which were alumina NP and titanium NP while the viscosity of the silica NP-polymer mixture decreased with respect to the silica NP concentration. This difference in the behavior between NPs was due to the adsorption of the polymer molecules to the silica NP surface.

Keywords: Enhanced oil recovery; Terpolymer; Rheological behavior; PAM-ATBS-NVP; Nanoparticles

1. Introduction

Enhanced oil recovery (EOR) technology has received heightened attention due to increasing global energy demands. Only about 20%–40% of the oil can be recovered using current technology with 60%–80% remaining in the reservoir. On the other hand, the application of an enhanced oil recovery (EOR) process provides an opportunity to extract an additional 20%–30% oil from the reservoir. The potential is considerable because a 1% increase in oil production would correspond to the equivalent of 2 y of current world consumption [1].

Polymer injection in enhanced oil recovery (EOR) involves adding powdered or emulsified polymers to the injection water, making the water more viscous and decreasing mobility. In addition, some polymers may adhere to the reservoir rock and decrease the permeability of the water phase, resulting in a decrease in the mobility ratio [1] (Muskat [2]; Stiles [3]; Aronofsky and Ramey [4]; Dyes et al. [5]). Two of the synthetic water-soluble polymers that have most frequently been used for chemical EOR techniques are PAM (polyacrylamide) and hydrolyzed polyacrylamide (HPAM) [6]. They were the first choices for

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application due to their low cost, insensitivity, and stability [7]. By creating a terpolymer based on PAM, ATBS, and NVP with varying percentages, researchers were able to develop the application envelope because of their thermal and chemical stabilities [8] (Vermolen et al. [9]; Alfazazi et al. [10]; Gaillard et al. [11]). On the other hand, the concept of combining nanotechnology with different EOR methods has already been reported and the results indicated that a whole new range of techniques can be developed using the advantages of nanoparticles [12,13]. The use of this kind of combination in EOR has increased the performance of oil wells after water flooding with the recovery factor improving and decreasing residual oil saturation [13].

The injection of polyacrylamides can cause environmental problems. The polymers appear degraded in the produced water after injection, that means after their passages into the reservoir. The natural degradation of polyacrylamides results in fractions of toxic acrylamide that can put at risk the local ecosystem and human health. It also poses the problem of an increase of in the difficulty of the separation of water-oil mixtures or suspensions. Researchers around the world have studied these problems. They have concluded that biodegradation using microorganisms was the only solution and they were even able to work on mechanisms to make this biodegradation as a new source of nitrogen and carbon. [1,14,15]. Furthermore, since rheological properties are mainly related to viscosity and elasticity, the rheological behavior of polymers has received much attention, considering the application of these polymers in industry, especially in enhanced oil recovery operations. The performance of polymer solutions varies such as viscosity loss due to shear rates. Polymer type, concentration, temperature, and salinity that exist in reservoirs are also factors that can affect performance [16].

The main objective of this study was to investigate the rheological behavior of terpolymer (PAM-ATBS-NVP) in polymer flooding for enhanced oil recovery. The effect of concentration, temperature, salinity/hardness, and nanoparticle type/concentration was assessed under different reservoir conditions.

2. Material and methods

2.1. Raw material

A terpolymer was available from Hoechst as a viscosifier of water-based fluids, having a medium to high salinity, having a molecular weight of at least 5×10^6 g/mol and able to form a stable crosslinked gel without first subjecting. This polymer was derived from 40% by weight of ATBS, 30% of acrylamide, and 30% of NVP. It was a white powder of molecular weight between 7 and 9 million daltons, its character was anionic and its activity 80%. The water used in the experiments was ultrapure.

Three available commercials nanoparticles (NPs) namely, alumina NP (Al_2O_3), nanosilica (SiO_2), and titanium oxide NPs (TiO_2) were purchased from Biochem Chemopharma (France). Sodium chloride (NaCl), and calcium chloride ($CaCl_2$) were obtained from PanReac (Chicago, US) to make the brine solutions. All the NPs and the polymer were used as received without further modification and purification.

2.2. Preparation of solutions

For the preparation of the polymeric solutions, the API-RP-63 recommended practices were taken as a basis: Initially, a stock solution was prepared by mixing a targeted quantity of polymer dry powder with an ultrapure water using the overhead stirrer to a 5,000 ppm solution [17]. Once the stock solution was ready, the dilutions were prepared. It should be noted that the diluted solutions were made just before putting them on the rheometer.

For the concentration and temperature tests, well-defined quantities of the stock solution were mixed with ultrapure water with different concentrations from 500 to 2,500 ppm. To simulate reservoir salinity and study the effect of mono- and divalent ions on the polymer solution rheology, two different synthetic brine were prepared in ultrapure water, first synthetic brine which was composed of 100% NaCl in a range from 1,000 to 150,000 ppm, while the second synthetic brine and for the hardness tests was made up of 50,000 ppm of NaCl and $CaCl_2$ was in the range of 0–5,000 ppm. Otherwise for the nanoparticle tests, different amounts of the 3 types were powdered in a diluted solution of 2,000 ppm each. Once the solution was ready, it was transferred to the rheometer for rheological measurement and tracing of the viscosity curves.

2.3. Rheological measurement

A Malvern Kinexus Ultra⁺ Rheometer (France) was employed that provided viscosity measurement and temperature control for increasing shear rates and had the space program that drove the instrument and allowed measurement and analysis.

The type of cassette, used was cylinder because it could hold a cup containing liquid or pasty samples. The geometry utilized was the Cup and Bob. This geometry would ensure an accurate measurement.

To obtain the flow curves prepared sample of polymer was run through the rheometer, the shear rate varying from 0 to 1,000 s⁻¹, with a sufficient time measurement (10 min). It permitted reaching the equilibrium state and measuring every point accurately.

3. Results and discussions

3.1. Effect of concentration on rheological behavior of PAM-ATBS-NVP

The variations of viscosity with respect to the shear rate with different polymer concentrations were assessed. The maximum concentrations were employed to ensure the maximum viscosity and get then to obtain the best sweep. However, there were two concerns with this. The first one was economic as the polymer was expensive to use any concentration. The second was technical: the porous rock can be clogged resulting in reduced permeability if the polymer concentration was too high [1]. Thus, the need to optimize the concentrations.

To assess the effect of PAM-ATBS-NVP polymer concentration on its rheological behavior, the evolution of apparent viscosity for different polymer concentrations are presented in Fig. 1. Five samples were prepared with
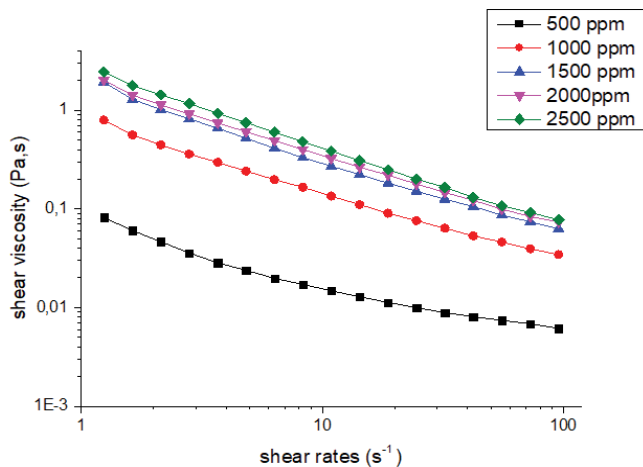
Fig. 1. Effect of polymer concentration on its apparent viscosity, $T = 25°C$.

Fig. 2. Effect of temperature on the viscosity of 2,000 ppm polymer.

different concentrations from 500 ppm to 2,500 ppm at a temperature of 25°C and with shear rates between 0.1 to 100 s^{-1}. The time of analyses was 10 min.

Fig. 1 revealed that the higher the concentration of the polymer, the more viscous were the solutions. The terpolymer exhibited a typical shear thinning behavior where the viscosity decreased exponentially with respect to the shear rate. The viscosity also increased with an increase in polymer concentration. But the variation was not linear; it slowed down with higher concentrations. It appeared that for the concentrations 1,500; 2,000 and 2,500 ppm, the viscosity of the polymer varied very little. As an example, for a shear rate of 10.9 s^{-1}, the viscosity varied from 0.27 to 0.38 Pa·s. In contrast, for low concentrations (500 and 1,000 ppm) the viscosity varied in the shear range of 0.1– 10 s^{-1} was noted that the viscosity of the 1,000 ppm solution was 10 times higher than a solution with 500 ppm. Above 10 s^{-1}, the ratio changed from 10 to 5.

The choice of the optimal concentrations will depend on the rock characteristics of the reservoir, that is, permeability, porosity, and oil viscosity. In the literature, a 2,000 ppm concentration of polymer solution was widely used in the polymer sweep [16,18]. This concentration will be employed in the rest of the paper.

3.2. Effect of temperature on rheological behavior of PAM-ATBS-NVP

Since the polymer solutions would be injected into reservoirs that were at high temperatures, it was important to know the temperature of the reservoir and to choose a polymer that was resistant to the temperature of the reservoir to avoid thermal degradation. It was therefore essential to study the effect of temperature on the rheological behavior of the polymer used for enhanced oil recovery. Fig. 2 represents the evolution of the apparent viscosity of PAM-ATBS-NVP at 2,000 ppm as a function of temperature.

It was noticed that the temperature had no to little effect on this polymer for temperatures between 25°C and 65°C (the identical observations have been made for the concentration of 1,000 ppm, Fig. 3). This result seemed
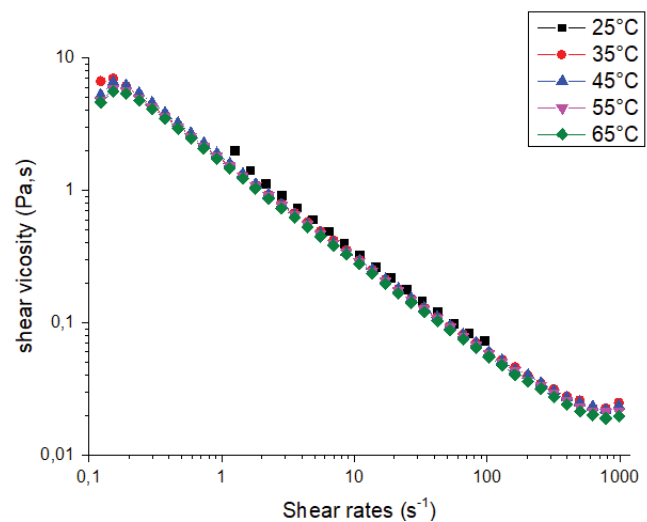
logical considering that the polymer contained 40% ATBS and 30% of NVP which conferred very good thermal stability [1,19].

3.3. Effect of salinity on the rheological behavior of PAM-ATBS-NVP

Salts have an influence on the rheology of polymers and since they are always present elements within a reservoir, it was important to study their effect on enhanced oil recovery (EOR) operations. The water salt concentrations in reservoirs varied from field to field. The influence of salinity at different concentrations from 1,000 to 150,000 ppm were investigated on the rheological behavior of the polymer (Fig. 4). The reduction in viscosity was very pronounced as the salinity of the solutions increased and this was due to the shrinkage of the polymer in the presence of Na$^+$ and Cl$^-$ ions. It should be noted that the viscosity decrease slowed down and eventually stabilized for shear rates higher than 616 s^{-1}. The viscosity at different salinities was close to 0.02 Pa·s. The main reason for this behavior was that almost all charges in the polymer chain had been neutralized by Na$^+$ counterions [20].

3.4. Effect of hardness on rheological behavior of PAM-ATBS-NVP

The viscosity of polymers was influenced by the salt content of the injection water and the salinity of the reservoir and particularly by the content of divalent cations (calcium, magnesium) [1]. According to the properties of the existing rocks in the southern Algerian sites, the Ca^{2+} concentrations was varied between 0 and 5,000 ppm for polymer solutions at 2,000 ppm and in the presence of 50,000 ppm of NaCl. The objective of this part of the study was to evaluate the effect of ionic species on the viscosity of the polymer solution. Several authors and in particular Sheng [21] have shown that the presence of ionic species can reduce the molecular size of polymers, reverse the
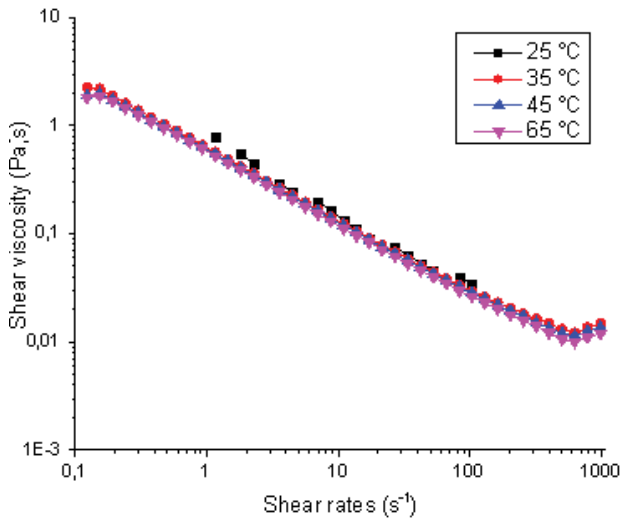
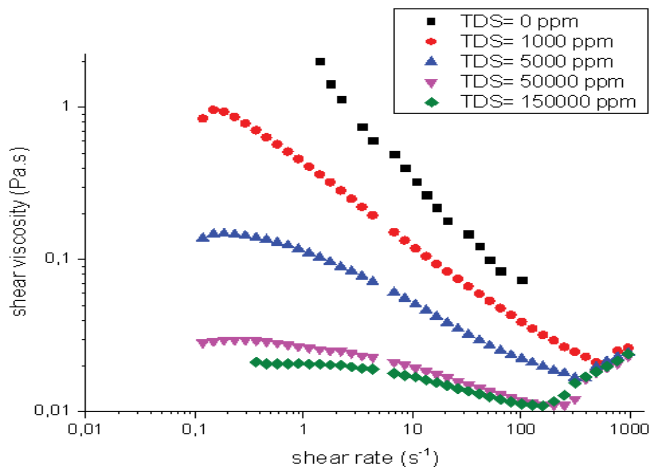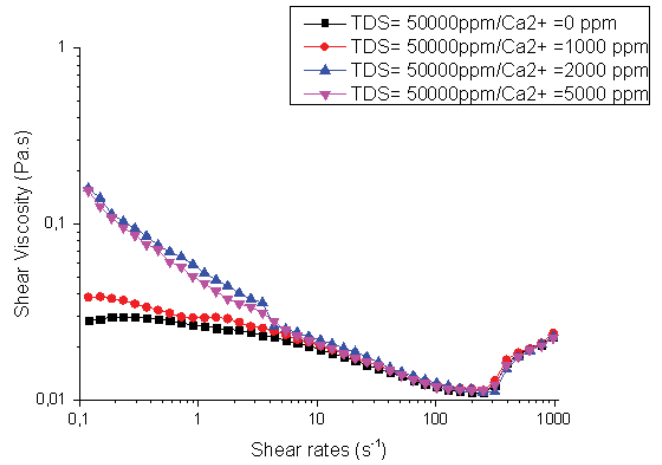Fig. 3. Effect of temperature on the viscosity of 1,000 ppm polymer.

Fig. 5. Effect of hardness on the viscosity of 2,000 ppm polymer in the presence of 50,000 ppm of NaCl.

viscosity has been underestimated. This was due to low friction between the sample and the wall to support the applied stress.

3.5. Effect of nanoparticle concentration on rheological behavior of PAM-ATBS-NVP

Recent developments in nanotechnology showed that the addition of nanoparticles in the polymer injection process can change wettability and improve the oil recovery factor [22]. The effect of three types of nanoparticles was investigated on the rheological behavior of PAM-ATBS-NVP terpolymer (Figs. 6 and 7). The nanoparticles were alumina, nanosilica, and titanium dioxide in polymer solutions of 2,000 ppm at 25°C.

3.6. Effect of the type of nanoparticles on rheological properties of PAM-ATBS-NVP

It was observed that the viscosity of the silica-polymer mixture (Fig. 7) was lower than the original 2,000 ppm polymer solution. We observed also that it was concentration dependent: the viscosity of the mixture was lower when the concentration of the silica NP was higher. The addition of titan and alumina NPs (Figs. 6 and 8) had little to no effect on the rheology of the 2,000 ppm polymer solution, even when the concentration was changed the viscosity of the mixtures did not change.

A comparative rheological study was done between the different mixtures at all concentrations from 500 to 2,000 ppm and 2,000 ppm of NP at a temperature of 25°C (Fig. 9). It could be seen that the viscosity of two mixtures alumina-polymer and titanium-polymer did not change compared to the original viscosity of the 2,000 ppm polymer solution. However, the viscosity of the silica-polymer decreased in comparison with the original 2,000 ppm polymer solution. As mentioned above, the loss in viscosity was concentration dependent on the silica-polymer mixtures.

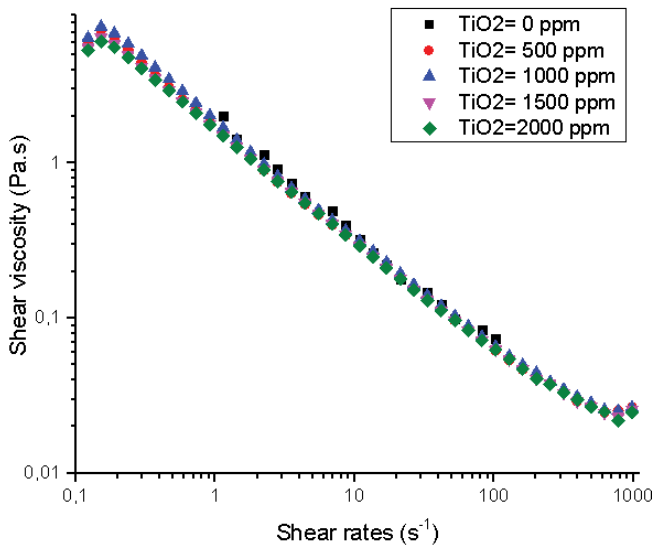Zeyghami et al. [23] reported similar results where they studied the HPAM and silica NP interaction. They

Fig. 4. Effect of salinity on polymer viscosity at 2,000 ppm.

charges, and affect the relationship between viscosity and shear rate, leading to a lower efficiency during the recovery production process.

Fig. 5 shows the apparent viscosity of the polymer over a shear range of 0.1–1,000 ppm and at a temperature of 25°C. It was quite clear that the solutions had a viscosity that decreased by increasing the brine concentration. It was also noted that the effect was very apparent at low shear rates. For shear rates higher than 10 s^{-1}, the hardness did not affect the viscosity of the polymer, which was favorable and logical at the same time, because the molecule contained about 40% ATBS which makes it not too affected by the hardness, which allowed for the conclusion that the polymer had resistance in difficult reservoir conditions. For shear rates above 550 s^{-1}, the polymer stabilized and the viscosity turned around 0.02 Pa·s. We noted a certain difference at low shear rates. Since we used the cup and bob geometry, we can explain this difference at weak shear rates (from 0.1 to 8 s^{-1}) by the "wall slip" phenomena where the

Fig. 6. Evaluation of apparent viscosity as a function of shear rate for different concentrations of titanium dioxide at 2,000 ppm of PAM-ATBS-NVP, T = 25°C.
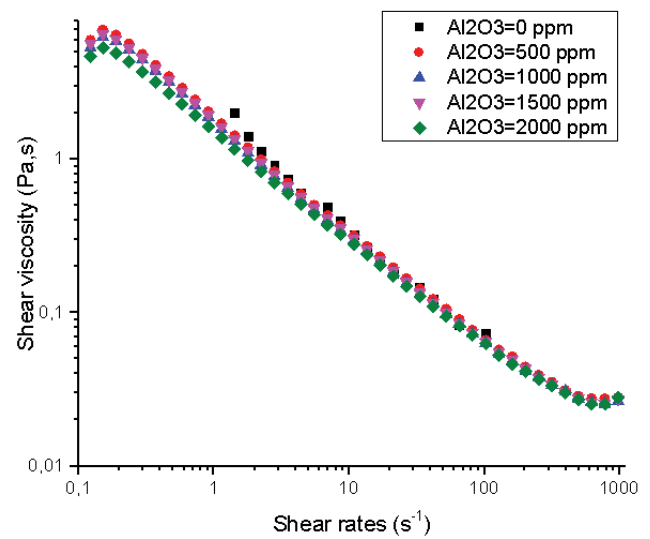

Fig. 8. Evaluation of apparent viscosity as a function of shear rate for different concentrations of alumina at 2,000 ppm of PAM-ATBS-NVP, T = 25°C.
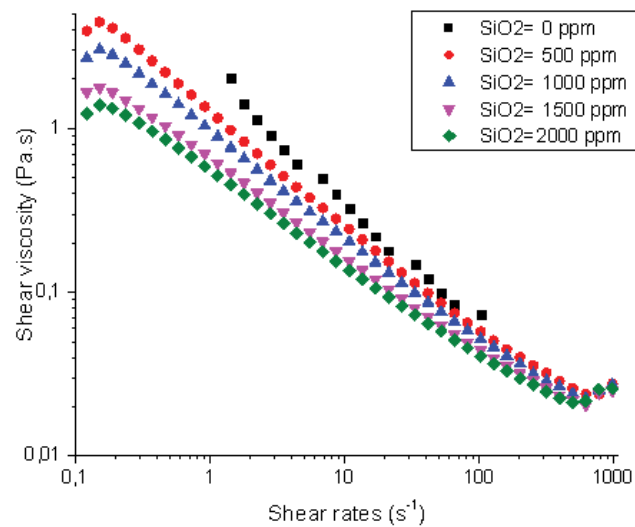

Fig. 7. Evaluation of apparent viscosity as a function of shear rate for different concentrations of nanosilica at 2,000 ppm of PAM-ATBS-NVP, T = 25°C.

Fig. 9. Type effect of 2,000 ppm NPs on the rheological properties of PAM-ATBS-NVP at 25°C.

found that the polymer molecules dissolved in the solution adsorbed to the silica NP surface. This would cause a decrease in the concentration (i.e., number of molecules) in the solution and thus decrease the mixture rheology. This fit perfectly with the current results where the viscosity of the mixture solution decreased with an increase in the concentration of silica NP. Hence, it can be said that PAM-ATBS-NVP molecules adsorbed onto the silica NP surface. Furthermore, no change was seen in the viscosity of the alumina NP-polymer and the titan NP-polymer mixtures. This led to the conclusion that there was no adsorption of the polymer molecules on alumina NP or titan oxide NP
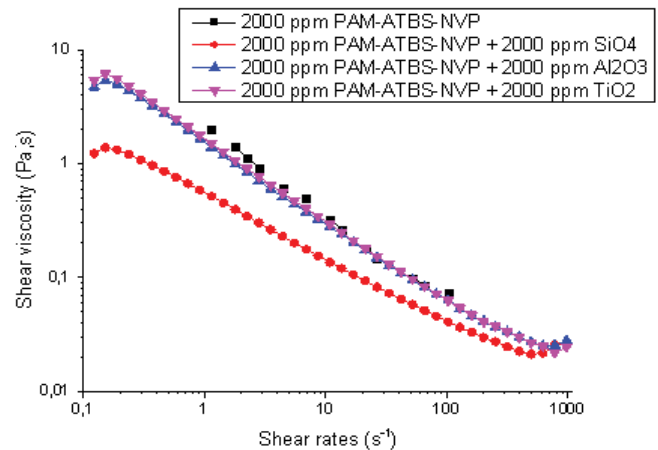
surface and thus there was no interaction between the NP surface and the polymer molecules.

The use of the two NPs (aluminium oxide and titan) was thus more advantageous for an enhanced oil recovery application since the viscosity stayed the same. The silica NP caused a loss in viscosity and thus more polymer must be used to get the same initial viscosity. The economic cost would then be more important. Different papers in the literature tried to explain the adsorption of the HPAM molecules on silica NP surface (Kawaguchi [24], Samoshina et al. [25]). Adsorption was caused by the hydrogen bond between the acrylamide molecules and the NP surface. It could also have been due to electrostatic adsorption where there was an attraction between PAM molecules and the negative surface of silica NP. Another possibility was hydrophobic adsorption.

4. Conclusion

The rheological behavior of solutions of a polyacryl-amide-based terpolymer (PAM-ATBS-NVP) were successfully studied at different concentrations, temperatures, and salinities, and in the presence of three different types of nanoparticles. There was a loss of viscosity in the shear range examined which indicated a shear thinning behavior. An increase in the polymer concentration allowed for higher viscosities with a good thermal resistance. The presence of mono- and divalent cations caused the apparent viscosity to be reduced when the ion concentration increased. Finally, it was noticed that the results were approximately the same for alumina and titanium dioxide as with nanoparticles while where their addition did not affect the original solution. In contrast, the viscosity of the polymer solution decreased when using silica nanoparticles.

Acknowledgments

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