Rheological Properties of Aqueous Polyacrylamide/NaCl Solutions

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ABSTRACT: Rheological properties of aqueous polyacrylamide-sodium chloride solutions are studied using RheoStress RS100. Polyacrylamide concentration was varied from 0.25 to 1.0% by weight, whereas sodium chloride ranged from 0.0 to 10 g L⁻¹. This range of concentrations is suitable to study many of the polyacrylamide-sodium chloride rheological properties. Steady flow parameters, yield stress, thixotropic behavior, creep recovery, and dynamic tests are covered in this study. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1905–1912, 1999

Key words: polyacrylamide; viscosity; yield stress; thixotropy; creep and recovery; complex modulus

INTRODUCTION

One of the important applications of the polyacrylamide (PAA) is in the enhanced oil recovery process, either to recover the oil remaining in a reservoir or to push surfactant solutions in the tertiary oil recovery stage.

A new well of oil first produces spontaneously, then by pumping system until the production rate becomes uneconomical. More oil can be produced by injecting water into the formation and pumping out a mixture of oil-water at other locations. Eventually, this injection process becomes uneconomical too. About 30-50% of the original oil remains in the well. Tertiary oil recovery is a process to discharge this residual oil. PAA also has several useful applications in our modern technology as a thickening agent, suspending agent, and turbulent reduction agent.

Numerous rheological studies have been conducted on the PAA solutions. These studies have shown unusual and complex behaviors: a significant pressure drop in porous media,^{1,2} mechanical degradation, 3,4 and macromolecule adsorption. 5

Li and McCarthy⁶ studied pipe flow of aqueous PAA solutions by nuclear magnetic resonance imaging. Flew and Sellin⁷ studied the non-Newtonian flow of PAA solutions in porous media. PAA solutions develop an extensional viscosity values many times those generated under simple shear flow for the same strain rate. The viscosity of the partially hydrolyzed polyacrylamide in mixtures of glycerol-water displays a transient regime with strong instability, followed by a steady state. Ait-Kadi et al.⁸ conducted an experimental study to investigate the effect of salt on viscoelastic properties of partially hydrolyzed PAA in aqueous solutions. They measured viscosity and primary normal stress differences using a Weissenberg rheogonimeter and a Contraves low-shear viscometer. They reported that the salt had a stabilizing effect on the solution viscosity. Several techniques, including continuum theories, mechanical models, and molecular theories, have been used to explain some of the reported phenomena. However, many of the reported observations are still not understood.

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Figure 1 Flow behavior of 0.25% PAA as a function of NaCl concentration.

Morawetz⁹ and Tanford¹⁰ reported that the PAA solutions are polyelectrolytes (i.e., materials containing a large number of electrostatic charges). The apparent size of the PAA macromolecules decreases by adding an electrolyte to the PAA solution. Therefore, the flow behavior and the macroscopic rheological properties of the PAA solution will be modified.⁸

The purpose of this work is to perform a wide variety of rheological tests to study the rheological behavior of aqueous PAA/sodium chloride (NaCl) solutions and to understand some of the observed phenomena.

EXPERIMENTAL

The rheometer RheoStress RS100 of Haake was used in all the rheological measurements of this study. Its operating modes include a controlled rate (CR) mode, a controlled stress (CS) mode, and an oscillation mode. The rheometer can switch between the CS and CR modes. It can also apply oscillating stress and frequency sweep. A variable left speed helps position the rheometer's cone on its plate. Air bearing is used to center the drive shaft to deliver an almost frictionless transmission of the applied stress. A digital encoder that processes 10^6 impulses per revolution is used to analyze deformations in the tested material. A special software package controls the operation of RS100, data evaluation, and analysis.

PAA is a white solid and water-soluble material from BDH Ltd. (Poole, UK). PAA with molecular weight of $5(10)^6$ is used. PAA solutions were prepared by adding a specific weight of PAA and NaCl to 1 L of double distilled water. Sufficient time was given to achieve homogeneous solution without external source of heat or power to prevent any cause for polymer network degradation. This study investigates a concentration range of 0.25-1.0% by weight of PAA, and 0-10 g NaCl L^{-1} of PAA solution to cover a wide range of the rheological behavior of the PAA/NaCl solutions.

A wide range of tests were conducted to observe the many possible phenomena of the PAA/NaCl solutions. These tests are steady-flow study, yield stress measurements, thixotropy study, creep recovery test, and dynamic test.

RESULTS AND DISCUSSION

Steady Flow Study

This study investigates the flow behavior of the 0.25-1.0% PAA solutions with 0, 2.5, 5, and 10 g NaCl L⁻¹ of PAA solution. Figures 1 and 2 show typical examples of the flow curve of shear stress-shear rate for 0.25 and 1.0% PAA with the effect of NaCl concentration. These figures show that the influence of NaCl in both cases of lower and higher concentration of PAA solutions is to reduce the values of shear stress significantly. This is due to the ability of the NaCl to decrease the apparent size of the PAA macromolecules and consequently to decrease the viscosity of PAA solutions is to reduce the values of shear stress the viscosity of PAA solutions are consequently to decrease the viscosity of PAA solutions is to reduce the viscosity of PAA solutions is to reduce the viscosity of PAA solutions of the PAA macromolecules and consequently to decrease the viscosity of PAA solutions is to reduce the viscosity of PAA solutions the viscosity of PAA solutions is to reduce the viscosity of PAA solutions is to reduce the viscosity of PAA solutions the viscosity of PAA sol



Figure 2 Flow behavior of 1.0% PAA with NaCl concentration.



Figure 3 Viscosity curves of 0.25% PAA as a function of NaCl concentration.

lutions. With concentration > 2.5 g NaCl L⁻¹, the effect of NaCl is less pronounced.

Under normal conditions, the amide groups (NH_2) of the PAA molecules are hydrolyzed to produce carboxyl groups (COO⁻) and ammonia. The degree of hydrolysis defined as the number of carboxyl groups substituted to the amide groups over the total number of the macromolecule groups is $\sim 2\%$. Once the polymer is hydrolyzed, the number of the negative charges on the polymer chain increases. Therefore, the network of PAA molecules in deionized water is stretched due to the repulsive forces of the negative charges on the carboxlic groups of the network.¹¹ Therefore, the hydrodynamic radius of the PAA network is large, which causes higher viscosity. By the addition of NaCl, sodium ion concentration in PAA solution increases. This reduces the repulsive forces of the network. Therefore, the hydrodynamic radius of the PAA network decreases and chain entanglement reduces. So, the addition of NaCl reduces the viscosity of PAA solution significantly. Figures 3 and 4 show the flow behavior of PAA/NaCl solutions in terms of viscosity. All solutions experience shear thinning behavior up to the critical shear rate. At this critical shear rate, the viscosity of all tested solution experiences a shear thickening behavior. The shear thickening behavior that appears at $\dot{\gamma}_c$ is generally observed for polymer solutions, and it also has been reported by several authors.^{8,12} Burow and colleagues¹³ reported a significant increase for shear stress greater than a critical value. They concluded that this behavior could be observed

only for high molecular weight polymers in viscous solvents. Ait-Kadi and colleagues⁸ concluded that the shear thickening phenomenon is reversible and independent of the geometry of the measuring device. They attributed this phenomenon to a flow-induced reversible structure that requires a certain time, depending on the imposed shear rate $(\dot{\gamma} > \dot{\gamma}_c)$. Figures 3 and 4 show the viscosity of PAA solutions is decreasing with NaCl concentration. Above the critical shear rate, in the case of 0.25-0.75% PAA, the viscosity is decreasing with NaCl concentration. However, in the higher concentration of 1.0% PAA, the effect of NaCl is completely diminished. The critical shear rate for unsalted PAA solutions is decreasing with PAA concentration. By adding NaCl, the PAA viscosity decreases due to the contraction of the polymer coils caused by the screening effect of NaCl. The critical shear rate, $\dot{\gamma}_c$, for unsalted 0.25% PAA is ~ 200 s⁻¹. By adding NaCl to PAA solution, the $\dot{\gamma}_c$ shifts to a higher shear rate of ~ 300 s⁻¹ and does not change with NaCl. For 0.5 and 0.75% PAA, increases in the critical shear rate were observed with NaCl. However, in the higher concentration of PAA of 1%, $\dot{\gamma}_c$ is constant with NaCl concentration.

The viscous behavior (Figures 3 and 4) can be described by a nonlinear regression of Carreau viscosity model as

$$(\eta - \eta_{\infty})/(\eta_0 - \eta_{\infty}) = [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}$$
 (1)

where η is viscosity, η_0 is zero shear rate viscosity, η_{∞} is infinite shear rate viscosity, λ is time constant, $\dot{\gamma}$ is shear rate, and *n* is fluid behavior



Figure 4 Viscosity curves of 1.0% PAA with NaCl.

| Solution Concentration | η_{c} | λ | |
|------------------------|------------|--------|--|
| PAA/NaCl | (mPa s) | (s) | |
| 0.25/0 | 78 | 0.0029 | |
| 0.25/2.5 | 300 | 0.0029 | |
| 0.25/5.0 | 140 | 0.0031 | |
| 0.25/10 | 110 | 0.0031 | |
| 0.50/0 | 150 | 0.0029 | |
| 0.5/2.5 | 1000 | 0.0031 | |
| 0.5/5.0 | 730 | 0.0029 | |
| 0.5/10 | 340 | 0.0029 | |
| 0.75/0 | 210 | 0.0031 | |
| 0.75/2.5 | 140 | 0.0031 | |
| 0.75/5.0 | 110 | 0.0031 | |
| 0.75/10 | 100 | 0.0029 | |
| 1.0/0 | 360 | 0.0031 | |
| 1.0/2.5 | 230 | 0.0031 | |
| 1.0/5.0 | 210 | 0.0029 | |
| 1.0/10 | 190 | 0.0031 | |

Table IRegression Coefficientsof Carreau Model

index. The parameters of this regression cover a shear rates range up to 700 s⁻¹ and are listed in Table I, where PAA concentration is in weight % and NaCl concentration is in g L⁻¹ of PAA solution. In Table I, the regression coefficient r equals 1, $\eta_{\infty} = 0$, and fluid behavior index n = 0.5 for all solutions. Table I shows that the zero shear rate viscosity is, generally, decreasing with NaCl concentration. However, for the 0.25–0.5% PAA solutions, the addition of 2.5 g NaCl increases the zero shear rate viscosity from the unsalted values.

Yield Stress Measurements

Yield stress measurements were conducted for all the tested solutions in the range of 0.25-1.0%PAA and from 0 to 10 g NaCl L^{-1} of PAA solution. CS mode was used to ramp stress until the applied stress surpasses the yield value and the sample starts to flow. The up-curve was established by ramping stress from 0.09 to 5 Pa; then, the assigned stress was instantaneously ramped down from 5 to 0.09 Pa to establish the downcurve. Figure 5 shows a typical example for the effect of NaCl concentration on the yield points measurement of the up- and down-curves. For all measurements, the up- and down-curve cycles are decreasing with NaCl concentration as in Figure 5. Table II reports the analysis results according to the Herschel-Bulkley model:

$$\tau = k \dot{\gamma}^n + \tau_0 \tag{2}$$



Figure 5 Yield stress response of 0.75% PAA.

where τ is shear stress, τ_0 is yield stress, and k is consistency index. The yield stresses τ_{01} and τ_{02} for the up- and down-curves are reported in Table II for all the tested samples. In general, Table II shows small values of yield stress for unsalted PAA solutions. Table II shows that the addition of 2.5 g NaCl to the unsalted PAA solution decreases the yield stresses τ_{01} and τ_{02} from their unsalted values. However, adding more NaCl to the PAA solution causes only slight change. Therefore, the effect of NaCl is to lower the yield stresses of the up- and down-curves.

Table II Yield Stress Values of τ_{01} and τ_{02}

| Solution Concentration | $	au_{01}$ | $	au_{02}$ | |
|------------------------|------------|------------|--|
| PAA/NaCl | (Pa) | (Pa) | |
| 0.25/0 | 0.36 | 0.34 | |
| 0.25/2.5 | 0.09 | 0.30 | |
| 0.25/5.0 | 0.09 | 0.28 | |
| 0.25/10 | 0.09 | 0.26 | |
| 0.5/0 | 0.60 | 0.35 | |
| 0.5/2.5 | 0.34 | 0.36 | |
| 0.5/5.0 | 0.09 | 0.34 | |
| 0.5/10 | 0.09 | 0.32 | |
| 0.75/0 | 0.86 | 0.61 | |
| 0.75/2.5 | 0.34 | 0.35 | |
| 0.75/5.0 | 0.34 | 0.35 | |
| 0.75/10 | 0.34 | 0.35 | |
| 1.0/0 | 1.1 | 0.61 | |
| 1.0/2.5 | 0.6 | 0.36 | |
| 1.0/5.0 | 0.34 | 0.35 | |
| 1.0/10 | 0.34 | 0.35 | |

| 10.0 | 5.0 | 2.5 | 0.0 | PAA/NaCl |
|--------|--|-------------------------|----------------------------|---------------------|
| | _ | 51.8 | 60.8 | 0.25 |
| 190.2 | 440.5 | 725 | 2077.4 | 0.50 |
| 700 | 1705 | 2046.4 | 5272.6 | 0.75 |
| 3200.7 | 3722.6 | 4314.7 | 6111.2 | 1.0 |
| | $\begin{array}{c} 440.5 \\ 1705 \\ 3722.6 \end{array}$ | $725 \\2046.4 \\4314.7$ | 2077.4 5272.6 6111.2 | 0.50 0.75 1.0 |

Table IIIHysteresis Area (Pa s⁻¹)

Thixotropy

Measurements of the thixotropy test were conducted using controlled rate mode of Haake RS100. The assigned shear rate was programmed from 0.15 to 700 s⁻¹ over a certain period of time to establish the up-curve. Whereas, the gradual decrease of shear rate provided the down-curve. The up-curve is different from down-curve for thixotropic solutions. The up- and down-curves form a hysteresis process of area A. It has the dimension of energy per volume (i.e., the energy required to break down the thixotropic structure of the sample).

The total break down of the solution structure may not be reached in 1 cycle of up- and down-curves. To completely destroy the solution structure, a number of up- and down-cycles may be needed before the up- and down-curves coincide. A different technique could be used to destroy the PAA solution structure. It consists only of 1 cycle of up-curve from 0.15 to 700 s⁻¹, followed by constant shear at 700 s⁻¹ for a certain time, and finally a down-curve from 700 s⁻¹ to 0.15 s⁻¹.

Five different tests were designed to find out the sufficient approach able to completely destroy the PAA solution structure. Test 1 consists of 1 cycle of an up-curve from 0.15 to 700 s⁻¹, and a down-curve back to 0.15 s⁻¹; each curve lasts 2 min. Test 2 consisted of 3 cycles of test 1. Test 3 consisted of a three-part cycle of an up-curve from 0.15 to 700 s⁻¹, a constant shear at 700 s⁻¹, and a down-curve back to 0.15 s⁻¹. The duration of each part was 1 min. Tests 4 and 5 repeated test 3 with a time period of 2 and 3 min, respectively.

Thixotropic analysis of all unsalted PAA solutions were conducted using the five different tests. Test 4 provided the highest thixotropic area for most samples of the unsalted PAA solutions. It also appears that a test according to the second technique, which includes a constant shear time, was essential to make sure that the gel structure of the PAA solutions has been completely destroyed.

Test 4 was performed for all the PAA/NaCl solutions, and the thixotropic analysis results are

reported in Table III in terms of area Pa s⁻¹. Table III reports a higher thixotropic area for a higher concentration of PAA. Therefore, the thixotropic behavior of PAA solutions builds up with increasing concentrations. Thixotropic analysis for the effect of NaCl shows that the NaCl has a great ability to lower the up- and down-curves significantly from the unsalted position. The thixotropic area of the unsalted PAA solution in the concentration range of 0.25–1.0% PAA decreased gradually with NaCl concentration. The effect of NaCl is more pronounced with a higher concentration of PAA. This conclusion can be attributed to the ionic strength of NaCl on the polyelectrolyte behavior of PAA molecules.

Creep Recovery Test

The creep recovery test was conducted on all the examined samples to reveal the viscoelastic behavior of the PAA/NaCl solutions. The deformation response, in a pure elastic material, to a constant applied shear stress is linearly proportional to the stress. The deformation is maintained as long as the stress is applied. The deformation disappeared completely when the stress was removed. In the case of viscoelastic materials, the deformation response to an applied stress is a function of time. Initially, the network deforms within its mechanical limits. This is followed by dismantling of the network, and finally the liquid starts to flow. When the applied stress is removed, the total deformation includes a permanently maintained viscous part and a recovery elastic part.

High values of applied stress usually cause a nonlinear viscoelastic response. Consequently, the material deformation depends on test conditions and system parameters. However, lower applied stress usually provides a linear viscoelastic response. Therefore, the material compliance is independent of the applied stress. The importance of linear viscoelasticity is in providing a nondestructive test of measuring the rheological behavior of a sample. Consequently, it is necessary to define the linear viscoelastic range by applying different values of constant shear stress for 300 s. In the linear viscoelastic range, the compliance results, J(t), at different values of shear stress, should coincide. In the nonlinear viscoelastic range, the compliance data curve separates significantly from the linear data. So, the creep test was conducted to determine the linear viscoelastic range for all the unsalted PAA solu-



Figure 6 Viscoelastic response of 0.25 and 1.0% PAA.

tions. It was found that the linear viscoelastic ranges for 0.25, 0.5, 0.75, and 1.0% PAA were 0.5, 1.0, 1.5, and 2.0 Pa, respectively.

The creep recovery test was conducted by applying a constant stress within the linear viscoelastic range for 300 s, then the stress was set to zero to record the response over 300 s. The feature of an almost frictionless air-bearing of the RS100 is important for the creep recovery test with shear stress set at zero. Figure 6 shows the compliance data J(t) for unsalted 0.25 and 1.0% PAA solutions at different values of applied shear stress. At lower applied shear stress, a noticeable time dependence is reported in the creep and recovery phases (i.e., elastic recovery in addition to its viscous response). Figure 6 also shows that the compliance of the PAA solutions increases with increasing applied shear stress and decreasing PAA concentration. Figure 7 shows the effect of the addition of 5 g NaCl on the compliance behavior at different values of shear stress. NaCl has a strong influence to significantly reduce the viscoelastic behavior of the solutions over the examined range of concentration of 0.25-1.0% PAA. Figure 7 shows that the compliance of the salted PAA solutions increases by \sim 100 times of the unsalted PAA solutions due to the ability of NaCl to reduce the PAA molecular size, and consequently change the behavior of the PAA solutions from viscoelastic to almost viscous behavior.

Dynamic Test

The dynamic test studies the viscoelastic behavior in a way different from the creep recovery test. Both tests are important, because some features of viscoelasticity are better described by the creep recovery test and others by the dynamic test. In the CS mode, the stress may be applied as a sinusoidal time function,

$$\tau = \tau_0 \sin(wt) \tag{3}$$

where τ_0 is stress amplitude and w is frequency. The substance complex modulus, G^* , can be separated into two parts as,

$$G^* = G' + iG'' \tag{4}$$

where G' is storage modulus and G'' is loss modulus. Complex viscosity, η^* , represents the total resistance against dynamic shear as

$$\eta^* = G^*/w. \tag{5}$$

Dynamic test must start with a stress sweep to determine the linear viscoelastic range to run the further test of frequency sweep. The linear viscoelastic range for the unsalted 0.25–1.0% PAA was found to be ~ 4 Pa.

Figure 8 shows the behavior of the complex modulus of PAA solutions *versus* frequency as a function of PAA concentration. The complex modulus for unsalted PAA solution increases gradually with frequency from 0.1 to 10 rad s⁻¹. The complex modulus increases with PAA concentration up to frequency of 10 rad s⁻¹. Figure 8, also displays the effect of the solution ionic strength in terms of 5 g NaCl (black symbols). The complex



Figure 7 Viscous response of 0.25 and 1.0% PAA with 5 g NaCl L^{-1} .



Figure 8 Complex modulus-frequency of PAA/NaCl solutions.

modulus of the PAA solution decreases significantly with NaCl. The effect of frequency sweep on the loss modulus, G'', of the PAA solution as a function of PAA concentration is displayed in Figure 9. G'' gradually increases with both PAA concentration and frequency sweep up to 10 rad s⁻¹. However, the ionic strength of the 5 g NaCl (black symbols) decreases G'' significantly. Studying the storage modulus response of the unsalted and salted PAA solutions reveals that the PAA/NaCl solutions developed only viscous behavior over the range of 0–10 rad s⁻¹.

Figure 10 shows the complex viscosity, η^* , *versus* frequency as a function of PAA concentration. Complex viscosity decreases with frequency for



Figure 9 Loss modulus of PAA/NaCl solutions.



Figure 10 Complex viscosity-frequency of PAA/NaCl solutions.

all the PAA solutions of 0.25–1.0% up to 10 rad s⁻¹ providing a shear thinning behavior. Figure 10 shows that 5 g NaCl (black symbols) reduce the complex viscosity of all the PAA solutions up to 10 rad s⁻¹. The reduction of G^* , G'', and η^* for the PAA solutions by the addition of 5 g NaCl can be attributed to the role of NaCl to change the molecular size and consequently the network behavior.

CONCLUSIONS

The addition of NaCl to the PAA solutions decreases the shear stress and viscosity. The effect of NaCl is less pronounced with concentration $> 5 \text{ g L}^{-1}$. The viscosity of all tested solutions experiences a shear thickening behavior at a critical shear rate. For unsalted PAA solutions, the critical shear rate decreases with the PAA concentration. However, the addition of NaCl increases the critical shear rate of the PAA solutions. The up- and down-curves of the PAA solutions and their yield points are decreasing with NaCl concentration. The thixotropic area of the unsalted PAA solutions decreases gradually with NaCl.

NaCl has a strong influence to reduce the viscoelastic behavior of the 0.25–1.0% PAA solutions to an almost viscous behavior. The addition of 5 g NaCl L^{-1} increases the compliance of the unsalted 0.25–1.0% PAA solutions by ~ 100 times.

The complex modulus of the unsalted PAA solution decreases significantly by the addition of 5 g NaCl up to frequency of 10 rad s⁻¹. Dynamic test of the PAA/NaCl solutions reveals that these solutions developed only viscous behavior. NaCl showed a significant effect to lower the complex viscosity of all PAA solutions up to frequency of 10 rad s⁻¹.

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