RHEOLOGICAL PROPERTIES OF VISCOELASTIC POLYMER SOLUTIONS

A Thesis

by

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ABSTRACT

Rheological property study of polymer solutions plays an important role in mobility control for chemical enhanced oil recovery. This study evaluated the rheological behavior of viscoelastic polymers by various factors by a series of experiments.

Rheological properties of polymer solutions are usually effect by several factors such as polymer type, polymer concentration, salt type, salinity, temperature, shear rate and functional groups in the polymer chain. This research studied four effects: polymer concentration, temperature, salinity and salt type for copolymer and terpolymer. Viscosity measurements measured the apparent viscosity of solutions as a function of shear rates at a range of 0.1-935.3 1/s. And the oscillation tests were conducted to evaluate the viscoelastic properties of polymer solutions.

Results show that SAV 10 solutions have strong shear-thinning behavior than SAV 333. Increasing polymer concentration causes the growth of apparent viscosity, elastic modulus, viscous modulus and relaxation time. Increasing temperature declines the viscosity, level of shear thinning behavior, G’, G”, and relaxation time. Increasing salinity indicates more significant reduction in apparent viscosity, G’, G” and relaxation time at low salinity. Salt type plays different roles on SAV 10 and SAV 333.

DEDICATION

To my family

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my committee chair, Dr. Hisham Nasr-El-Din, for his patience, guidance and support throughout the course of this research. And I would also extend my appreciation to Dr. Zoya Heidari and Dr. Mahmoud El-Halwagi for spending their precious time to review my research work.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Polymer

Polymer flooding is one of the most widely applied chemical EOR methods, which firstly began in the early 1960s after water flooding to continently improve oil recovery (Manning et al., 1983). One potential mechanism widely accepted for the polymer flooding is viscosity improvement of liquid by expansion of polymer, and further to decline the water/oil mobility ratio (Samanta et al., 2010). The other method is fluid diversion effect generating cumulative force to overcome the resistance in the reservoirs, then to inject solutions into the areas which are not swept in water flooding (Needham and Doe, 1987).

Hydrolyzed polyacrylamide (HPAM) is one of synthetic polymers widely used in the oilfield and it can be used up to about 185F according to the brine hardness. Another type of polymer is biopolymer, and the main polymer studied by a lot of researchers in EOR is xanthan gum. The polymers used in the EOR flooding are usually HPAM, biopolymers and copolymers.

Rheological Models of Polymer Solutions

A lot of rheological properties studies were finished on polymer flooding. In the early 1960s, experimental study was conducted in conventional water flooding by adding 0.05 percent polymer additives to 50,000 ppm brine solution (Clay and Menzie, 1966). The rheological behavior investigation was studied on polymer solutions in sand packs (Chauveteau and Kohler, 1974). The effect of salt concentration, polymer concentration and slug size was analyzed on polymer flooding in different permeability sand packs (Szabo, 1975). Although the study of ideal elastic (Boger) fluid showed elasticity played an unimportant role on macroscale, it still assumed a vital part at the microscale (Allen and Boger, 1988). Screening Criteria for polymer flooding and basic mechanisms how polymer solution acting as the mobility control additives can achieve better oil displacement effectiveness were discussed by comparison of different EOR field case studies (Taber et al., 1997). The effect of polymer type for effective viscosity was investigated at low velocities (Seright et al., 2010).

Shear viscosity is one of the most important rheology factors measuring polymer solutions, which is used to describe whether the fluid type is non-Newtonian fluid or Newtonian fluid. Polymer solution is shear-thinning fluid which shows lower viscosity while the shear rate increases.

Various researches studying the effect of polymer injection brought by elastic properties have been conducted. Individual effect of elasticity study showed that polymer with higher value of elasticity improved volumetric sweep productivity and decreased oil trapped in the pores by offering high resistance force to the solution

(Urbissinova et al. 2010). Viscoelastic property is significantly effected by average molecular weight, polymer type, polymer concentration and hydrophobicity, however, it is vaguely influenced by temperature and salt concentration (Wilton and Torabi, 2013). Elasticity value and relaxation time are shown as functions of elastic properties.

Different types of fluids are depended on the general relationships between shear stress and shear rate (Bröckel et al., 2013). Newtonian fluid, such as water, displays a linear association between shear rate and shear stress. With the increment of shear rate, shear stress of Newtonian fluid increases linearly regardless of other factors. Both shear thinning and shear thickening fluids present non-linear connections of shear stress as the function of shear rate. The trend of slope for the shear thinning curve decreases with the growth of shear rate, however, the shear thickening curve performs the opposite tendency. The relationship of shear rates and viscosity offers the basic foundation to distinguish the brands of fluids in the laboratory tests. The viscosity of Newtonian fluid stays at a constant value with the change of shear rate. Polymer solutions usually exhibit as shear thinning fluid, which means the apparent viscosity of polymer solutions decreases with the accumulative shear rate. The reasons of shear thinning occurrence are widely studied but not fully comprehended. Most explanations are related to the realignments of chemical structures of molecules when shear rate changes. The apparent viscosity of shear thickening fluid, which rises with the increasing shear rate, has a reverse trend against the shear thinning fluid. Those theories are used in the tests of rheological properties to indicate the fluid behavior.

The log to log figure of shear rates and viscosity describes the common rheological behavior for most polymer solutions Green and Willhite, 1998). The apparent viscosity stays at the highest constant value at very low shear rate, which is similar to the rheological phenomenon of Newtonian fluids. As the shear rate increases, the viscosity of polymer solution sharply decrease as shear thinning fluid. And when shear rate arrives at very high value, the solution begins to remain a constant viscosity value as Newtonian fluid. This is because at very low shear rates, the shear stress can not disrupt the steady relationships between polymer and solvent molecules. While at very high shear rates, the solution Newtonian behavior is mainly decided by solvent molecules and the polymer particles don't have enough effect on shear viscosity. The log-log plot of the polymer solution rheological behavior contains three regions, including lower Newtonian region, shear thinning region and upper Newtonian region.

There are two common typical models widely used in the polymer rheological behavior (Sorbie, 1991). Power-law model and Carreau model are both non-Newtonian models concluded from the data of experiments. Power-law model can be used to explain the shear-thinning region of polymer solutions. For whole range of shear rate, Carreau model is used to describe both Newtonian regions at very low or high shear rates and shear-thinning region at the medium shear rates.

Power-law model is the experimental model plot the shear stress and shear rate data in log-log scale, which can be practiced on either shear thinning or shear thickening fluids:

$$\tau = K\dot{\gamma}^{n} \tag{1}$$

where

τ is the shear stress

K is the flow consistency index

$\dot{\gamma}$ is the shear rate

n is the flow behavior index

Power-law model also can describe the relationship of apparent viscosity and shear rate:

$$\mu = K\dot{\gamma}^{n-1} \tag{2}$$

where

μ is the fluid viscosity

The type of fluids can be divided by the value of index n. When n < 1, the fluid is pseudoplastic, or shear thinning fluid. When n = 1, the fluid is Newtonian fluid. When n >1, the fluid is dilatant, or shear thickening fluid.

Compared with power-law model, Carreau model is not limited to a specific range of shear rates (Carreau et al., 1979; Green and Willhite, 1998; Nasr-El-Din et al., 1991). It can commonly fit different regions of shear rates to describe the rheological behavior of pseudoplastic fluid:

$$\frac{\mu-\mu_\infty}{\mu_0-\mu_\infty} = [1 + (\lambda\dot{\gamma})^2]^{(n-1)/2} \tag{3}$$

where

μ is the steady viscosity at shear rate $\dot{\gamma}$

μ_∞ is the constant viscosity at high shear rate in upper Newtonian region

μ_0 is the constant viscosity at low shear rate in lower Newtonian region

λ is the time constant

$\dot{\gamma}$ is the shear rate

n is the flow behavior index

Viscoelastic Properties of Polymer Solutions

Viscoelastic fluids have viscous and elastic properties at the same time. Some polymers like HPAM with viscoelastic properties were researched. The curve of HPAM viscosity as the function of strain rate has three regions (Sochi, 2009). At low shear rates, the viscoelastic fluid shows Newtonian behavior first, then shear thinning behavior. These two regions are similar with the viscous fluid without elasticity. However, when shear rates rise continuously, the viscoelastic polymer starts to show shear thickening behavior. This is caused by elastic structures in the polymer chains are stretched at high shear rates. Stretching expand the chain size of polymer, and hence the viscosity increases. The extension-dominated region in the figure is the indication of the effect described above, and this region is also known as the shear thickening zone. If the shear rates cumulatively increase over the largest shear rate of the shear thickening zone, the mechanical degradation will cause the polymer chains breaking and the rheological properties can not return to the original status (Corapcioglu, 1996). Laboratorial rheological characteristics of polymer solutions were studied by different researchers (Mungan, 1969; Kreiba, 2010; Bataweel, 2011; Shedge, 2011; Gao, 2014; Larsen, 2014; Koh, 2015).

Viscoelastic fluids flow in the porous media by expansion and contraction (Urbissinova, 2010). Viscoelastic polymer solutions combine the advantages of viscous behavior and elastic behavior together. Viscous behavior gives the ability of polymer chains to coil up and entangle, and elasticity makes the molecules stretching. As the consequence, the viscoelastic solutions can expand and contract. The solutions can enter the pore as far as possible to improve the sweep area by the expansion and contraction phenomena. In this way, the sweep efficiency is improved.

CHAPTER II

EXPERIMENTAL STUDIES

The objective of the experimental study is to evaluate the rheological properties of viscoelastic polymer samples under different conditions and study the effect of temperature, polymer concentration, salt type, and salinity on polymer rheological behavior. The following procedures were followed:

1. Prepare different concentration (1,000 ppm, 3,000 ppm, 5,000 ppm) polymer solutions using De-Ionized (DI) water.
2. Prepare different polymer concentration for solutions using different salt (Na^+, Ca^{2+}) types and with different salinity.
3. Study the effect of temperature, polymer concentration, salt type and salinity on polymer rheological properties.

Materials

De-ionized (DI) water was used to prepare polymer solutions for all measurements. NaCl and $CaCl_2.2H_2O$ were used as salts to provide Na^+ and Ca^{2+} for study the effect of salt type.

The two polymers used in the laboratory tests are supplied in powder form from SNF holding company. Superpusher SAV 10 is copolymer with functional groups of acrylamide (AM), Acrylamido-Tert-Butyl-Sulfonate (ATBS) and N-Vinyl-Pyrrolidone (NVP). Superpusher SAV 333 are new water soluble anionic terpolymers with N-Vinyl-

Pyrrolidone (NVP) and Acrylamido-Tert-Butyl-Sulfonate (ATBS), which are more expensive than common HPAM but it can also stand higher temperature. Superpusher SAV 10 with higher level of ATBS than SAV 333 and the composition of NVP in Superpusher SAV 333 both can show good performance with temperature reach up to 284°F (Gaillard et al., 2015). The structures of SAV 10 and SAV 333 clearly show the difference of their functional groups (Quadri et al., 2015).

Equipment

Grace M5600 high pressure / high temperature (HP/HT) Rheometer was used in all measurements for rheological properties. The Grace Instrument M5600 HP/HT rheometer is an Couette, coaxial cylinder, rotational, high pressure and temperature rheometer (up to 1,000 psi and 500 °F). All measurements were conducted at a constant psi of 300 psi and temperature varied from 75 to 250°F.

Procedures

Viscosity Measurements

Steady rate sweep test shows the apparent viscosity of solutions as the function of shear rates. All tests were conducted at at a constant psi of 300 psi and the range of shear rate was from 0.01 to 935.3 1/s. Five different temperature (75°F, 100°F, 150°F, 200°F and 250°F) are repeated for all testes. Test steps at 75°F are shown in **Table 1**.

Oscillation Tests

The oscillation tests measure viscoelastic properties of elastic modulus G’ and viscous modulus G” related to frequency varying from 0.01 Hz to 5 Hz and various temperature from room temperature to 250°F.

Table 1—Viscosity measurement steps at 75°F.

Shear rate, 1/s	Times, s
0.1	90
0.3	90
0.5	90
0.7	90
1	90
3	90
5	90
7	90
10	90
30	90
50	90
70	90
100	90
300	90
500	90

Table 1—Continued.

Shear rate, 1/s	Times, s
700	90
935.3	90

CHAPTER III

RESULTS AND DISCUSSION

Two different kinds of rheological property experiments were conducted to evaluate both viscous and elastic characteristics of copolymer SAV 10 and terpolymer SAV 333 solutions, including viscosity measurements and dynamic rheological measurements. The shear viscosity tests of polymer solutions were piloted under growing shear rates from 0.1 to 935.3 1/s at constant pressure of 300 psi. The dynamic rheological tests were measured as a function of viscoelastic performance under increasing frequency between 0.01 to 5 Hz with pressure of 300 psi. As we know, several factors may affect the rheological properties of the polymer fluid, like temperature, shear rate, polymer concentration, salinity, salt type, etc. Here, all influence brought by above factors will be examined and discussed in details. These rheological measurements were examined at different polymer concentrations (1,000 – 5,000 ppm), temperature (75 - 250°F), with and without salt (DI water, NaCl, $CaCl_2$), various salinity (0.5 – 5 wt%) to study the influence brought by these factors.

Viscosity Measurements of Polymer Solutions

Effect of Polymer Concentration

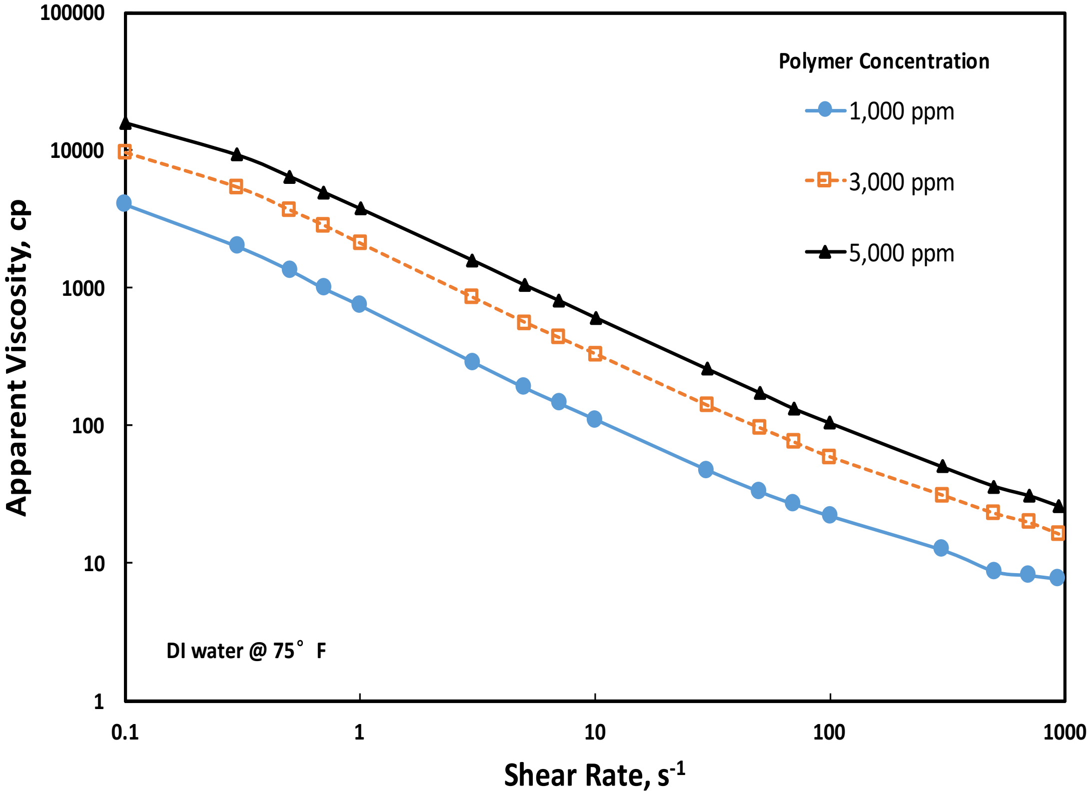

Fig. 1—Apparent viscosity of SAV 10 solutions in deionized water at 75°F.

Fig. 1 and **Fig. 2** show obvious shear thinning phenomenon of SAV 10 and SAV 333 solutions made by deionized (DI) water under 1,000 ppm, 3,000 ppm, and 5,000 ppm polymer concentrations at room temperature (75°F) and continuous pressure (300 psi). In theses measurements, shear rate starts at 0.1 1/s, and ends at 935.3 1/s. The rheological behaviors at various concentrations are schemed in a log-log scale to fit the power-law model of fluid. The curves are close to linear shapes by observation and present characteristics of shear thinning fluid. The samples display an obviously drop of viscosity with the increasing shear rates. The polymer viscosity diminution behavior is caused by uncoiling and unentangling effect of polymer molecules and they are stretched in the flow. The upper Newtonian region and lower Newtonian region are not shown in the figures, and the possible reason is the shear rate range is not wide enough.

Table 2—Power-law parameters for SAV 10 for polymer concentrations.

Concentration, ppm	K, cp	n
1000	693.92	0.286
3000	1929.9	0.275
5000	3451.1	0.264

Table 3—Power-law parameters for SAV 333 for polymer concentrations.

Concentration, ppm	K, cp	n
1000	522.41	0.4
3000	1114.3	0.438
5000	1689.2	0.446

Table 2 and **Table 3** list the power-law factors for the SAV 10 and SAV 333 solutions used in **Fig. 1** and **Fig. 2**. Power-law index, n values are all less than 1, which indicate shear thinning behavior. The n value of SAV 10 is smaller than SAV 333 at the

same conditions. It might result from the component difference in polymer backbone. SAV 10 is copolymer made of acrylamide (AM) and acrylamide-tertio-butyl sulfonate (ATBS), and SAV 333 has compositions of acrylamide (AM), acrylamide-tertio-butyl sulfonate (ATBS) and N-vinyl pyrrolidone (NVP). The level of NVP in SAV 333 is high (30-45 mol%), whereas SAV 10 has no NVP component. The level of ATBS in SAV 333 varies from 25-35 mol%, while SAV 10 has higher level of ATBS than SAV 333. For individual SAV 10 and SAV 333, the level of shear thinning behavior is nearly independent on polymer concentrations since the power-law indexes are almost the same even the polymer concentration change.

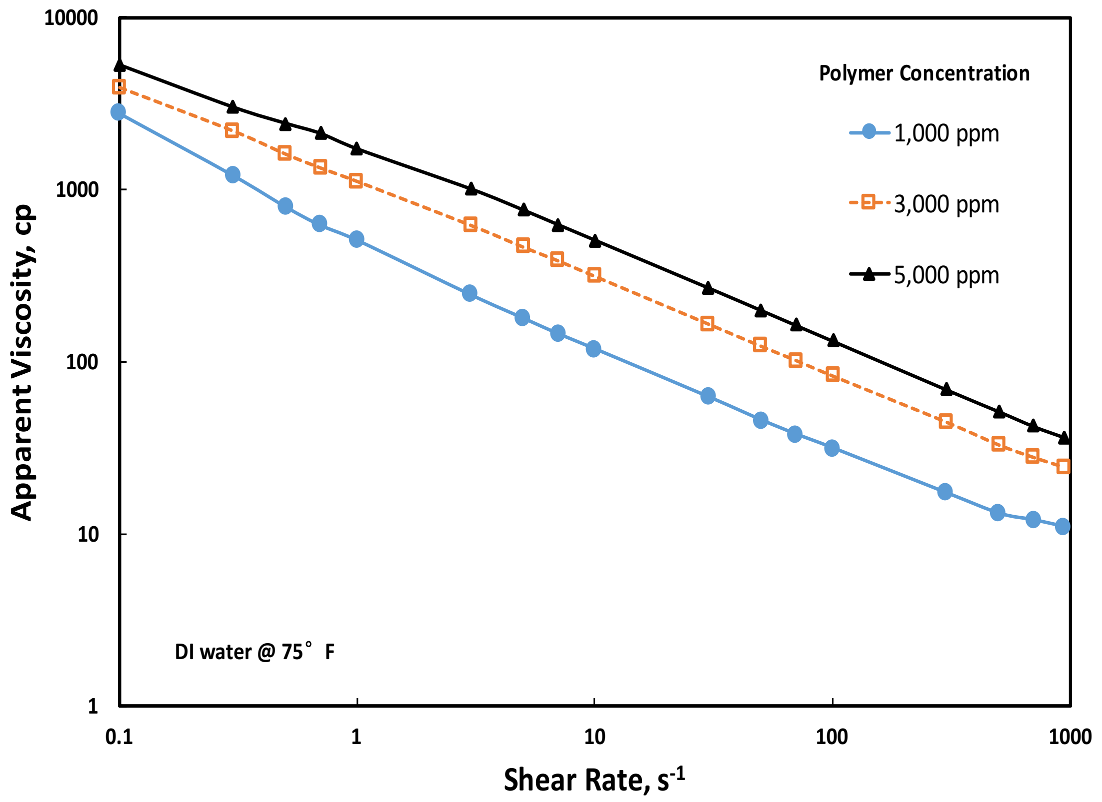

Fig. 2—Apparent viscosity of SAV 333 solutions in deionized water at 75°F.

Fig. 3 and **Fig. 4** use the logarithmic diagrams to study the effect of polymer concentration to shear-viscosity of solutions with different salinity at 75°F and the value chosen to study is at the shear rate of 10 1/s. You can see a clear tendency that shear-viscosity increases when more polymer is added inside the solution. This viscosity increment behavior results from the polymer molecules coiling and entangling effect when more polymers are dissolved and aggregated in the solution. Viscosities of two polymer solutions both increase more significantly than the solutions in brine, furthermore, higher salinity will induce smaller increasing slope. The effect of salt and salinity on polymer viscosity will be discussed in later sections. We can also observe that SAV 10 has a clearer inclination than SAV 333 when salt is added.

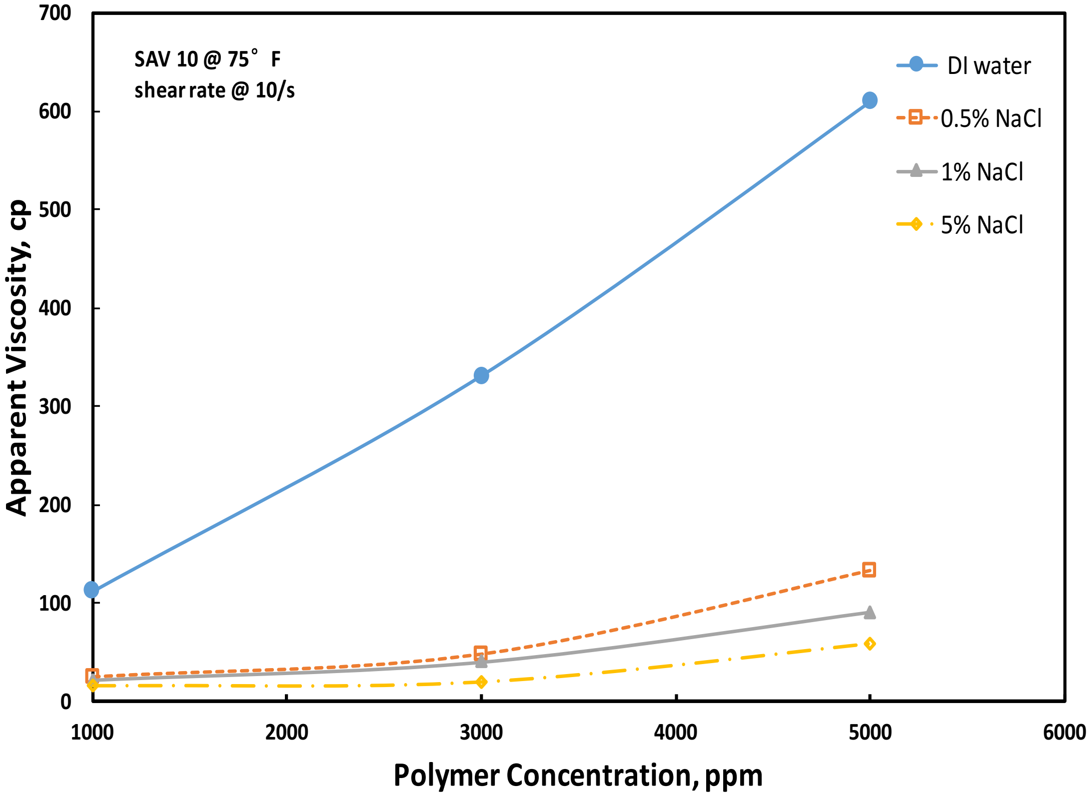

Fig. 3—Apparent viscosity of SAV 10 with polymer concentration.

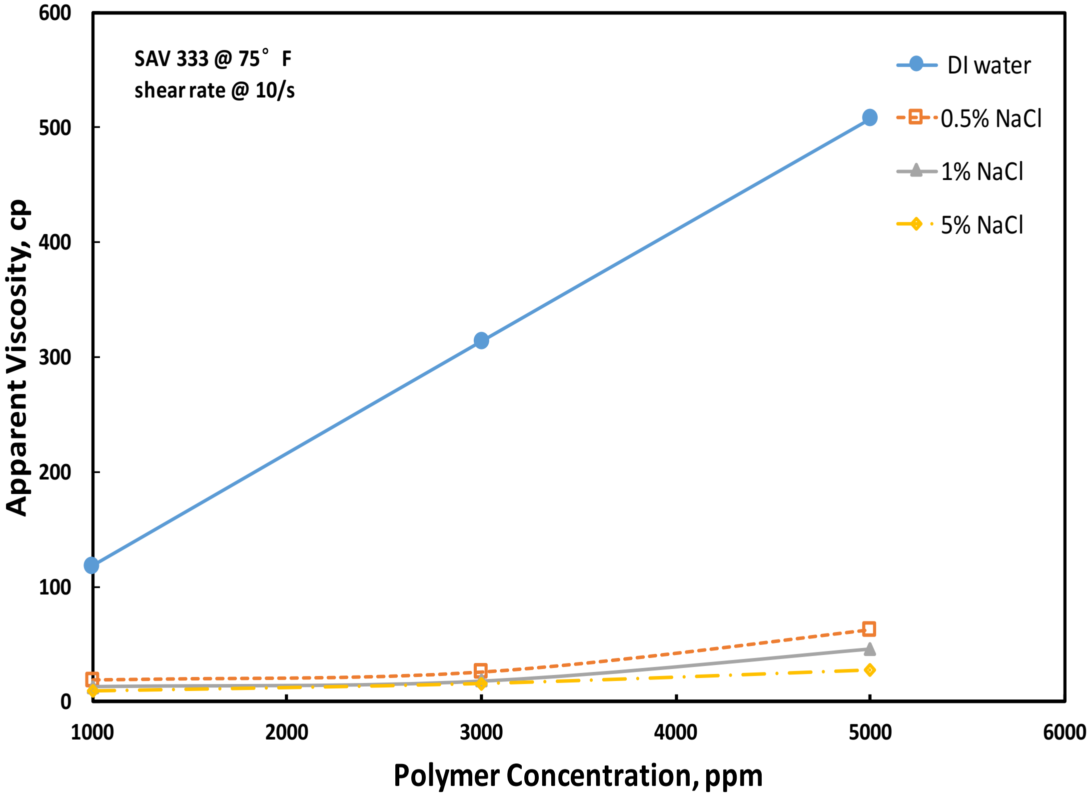

Fig. 4—Apparent viscosity of SAV 333 with polymer concentration.

Fig. 5 is the comparison diagram of shear-viscosity of copolymer SAV 10 and terpolymer SAV 333 as the function of polymer concentration. The tests shown in the figure are solutions testing at 75°F at a constant shear rate of 10 1/s. The increasing trend paths of two polymers are close to each other. From the comparisons of the rheological behaviors of two polymers, both of the polymers display similar shear-thinning behavior. The apparent viscosities of SAV 10 and SAV 333 are almost same range. This results from the similar molecular weight (M_W). The SAV 10 is a copolymer that has a molecular weight within the range of 4-6 MDa and SAV 333 is a terpolymer that contains NVP and has a molecular weight within the range of 3-5 MDa.

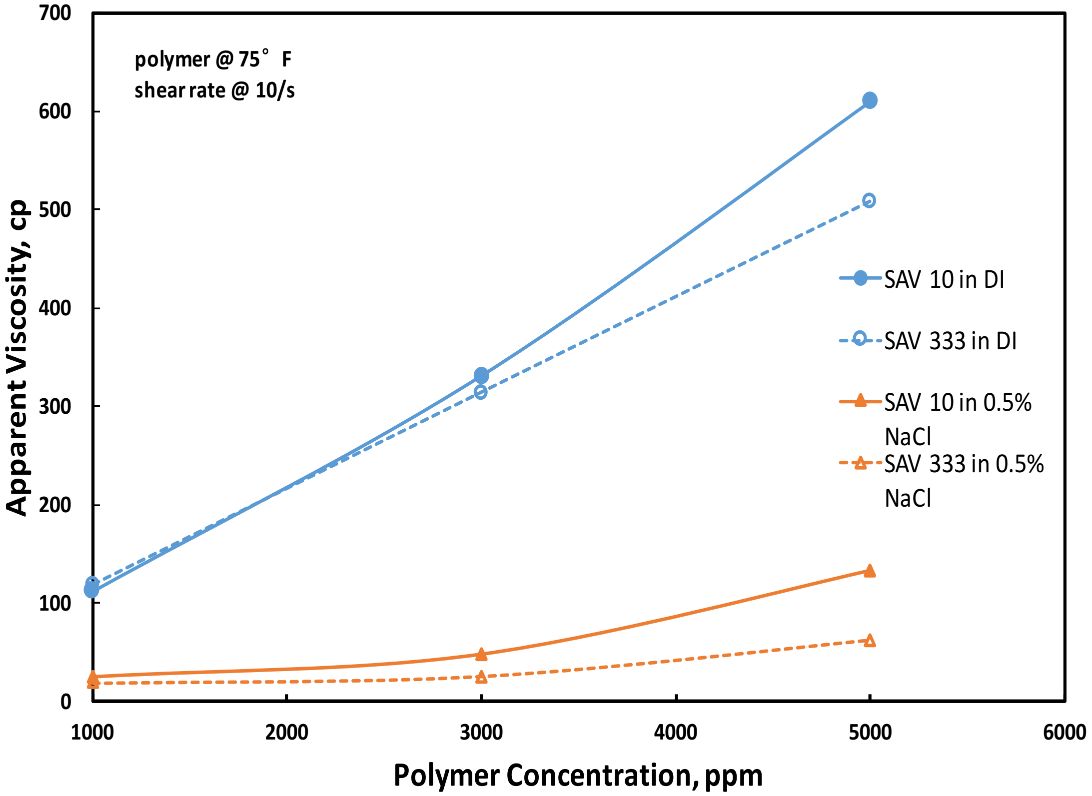

Fig. 5—Effect of polymer concentration on apparent viscosity.

Effect of Temperature

Fig. 6 and **Fig. 7** perform the apparent viscosities of 3,000 ppm SAV 10 and SAV 333 solutions prepared in DI water against shear rate ranging from 0.1 to 935.3 1/s at various temperatures (75, 100, 150, 200 and 250°F). For polymer SAV 10, all curves show shear thinning behavior at major range of shear rates, while the curve at 250°F has a small range of upper Newtonian region. SAV 333 has the same situation at 200°F 250°F when shear rate is smaller than 1 1/s. It seems that very low shear rates affect the fluid rheological performance more significantly at high temperature.

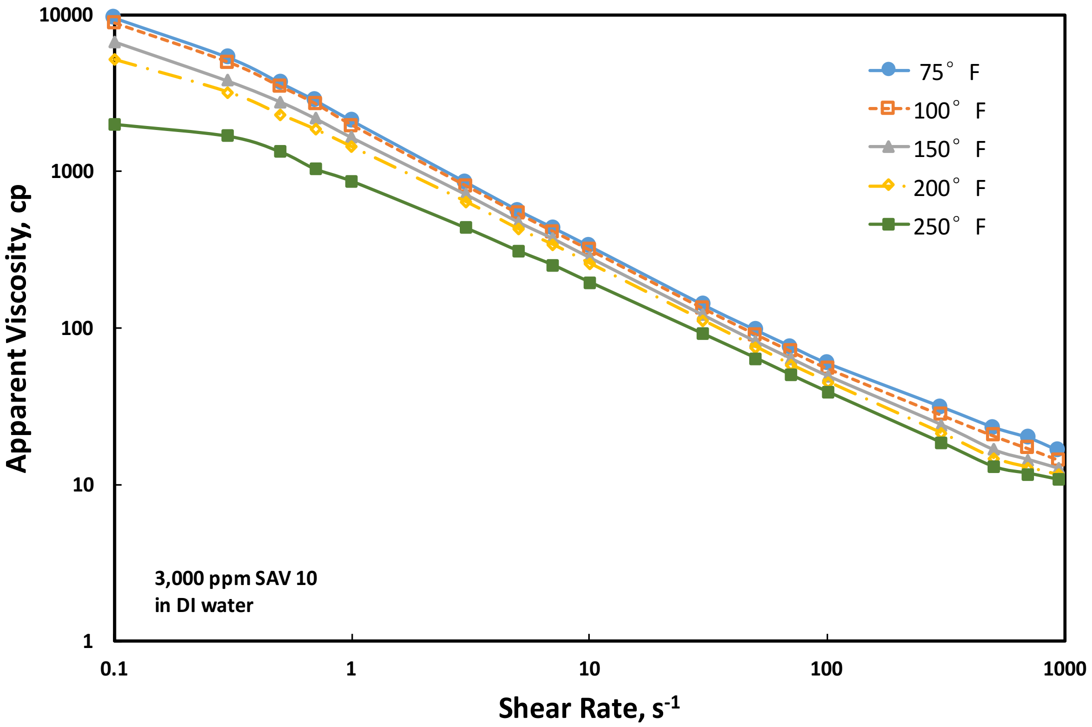

Fig. 6—Apparent viscosity of SAV 10 at different temperatures.

The power-law parameters of samples applied in **Fig. 6** and **Fig. 7** are recorded in **Table 4** and **Table 5**. The power-law index performs a constantly growing tendency with the increasing temperature. It is known that larger power-law index value equals to weaker level of shear thinning behavior. The samples at lower temperature have the stronger pseudoplastic behavior.

Table 4—Power-law parameters for SAV 10 at different temperatures.

Temperature, °F	K, cp	n
75	1929.9	0.275
100	1818	0.267
150	1511.3	0.278
200	1290.9	0.289
250	842.62	0.343

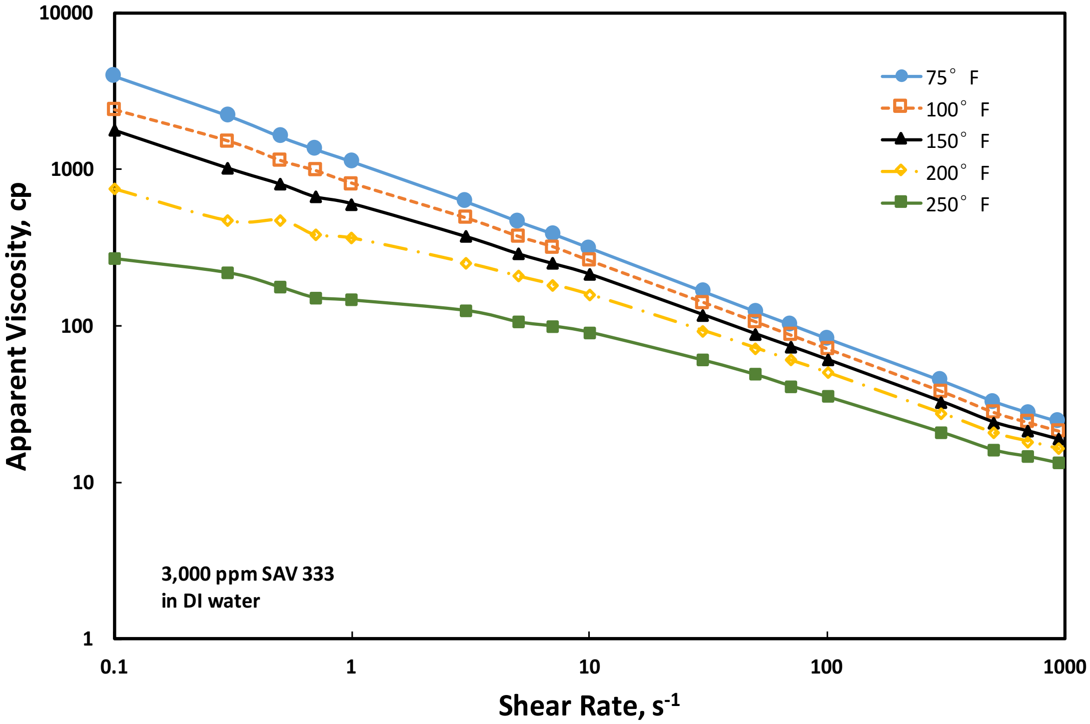

Fig. 7—Apparent viscosity of SAV 333 solutions at different temperatures.

Table 5—Power-law parameters for SAV 333 at different temperatures.

Temperature, °F	K, cp	n
75	1114.3	0.438
100	810.3	0.472
150	594.6	0.499
200	346.9	0.571
250	155.4	0.664

The neutral amide groups in the polymer chain can hydrolysis and turn to carboxylate groups (COO-) with negative charges. High temperature can produce more negative charges from hydrolysis process. The repulsions between negative charges in the molecular chains stretch the polymers and hence the larger hydraulic radius which indicates higher viscosity is formed. So increasing temperature can enhance viscosity by aggravating the hydrolysis level. In conclusion, the effect of thermal kinetics progresses viscosity, while the hydrolysis decreases viscosity. The diminished viscosity with temperature at all concentrations proves that the first mechanism is principal.

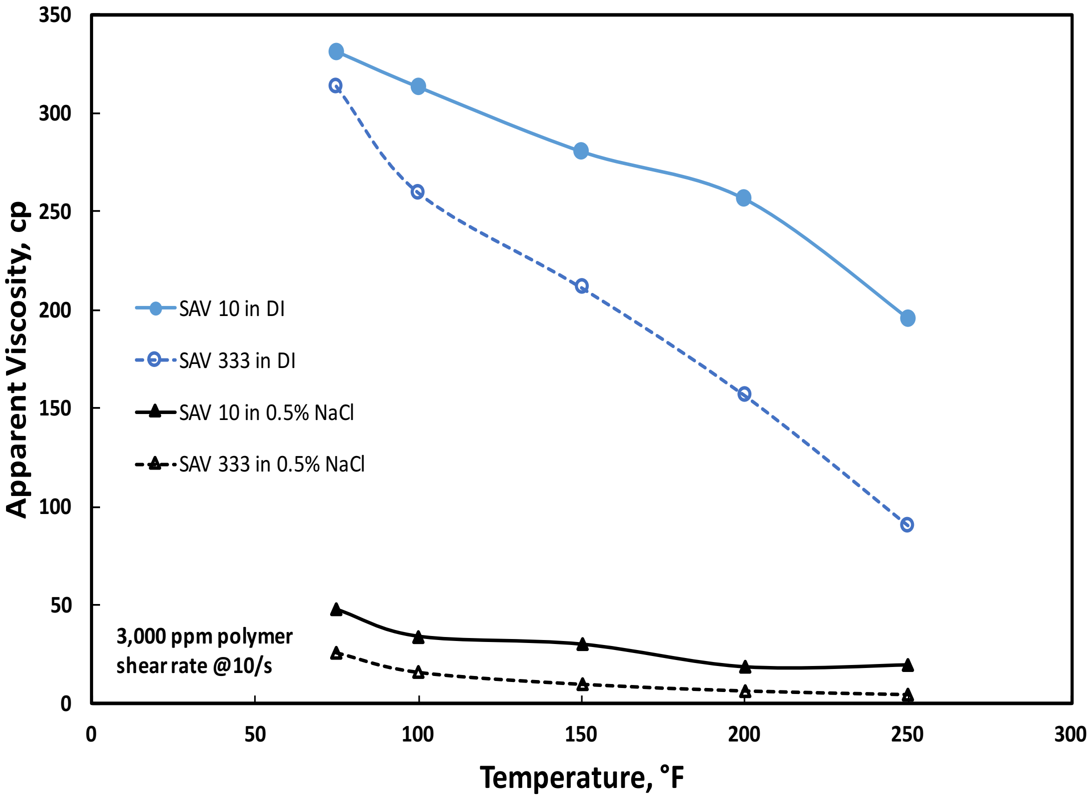

Fig. 8—Effect of temperature on apparent viscosity.

Fig.8 compares the SAV 10 and SAV 333 together to study the temperature effect. It can be observed that the viscosities of SAV 10 and SAV 333 in DI water are close to each other at low temperature, while the differences become bigger with increasing temperature. This is the indication of SAV 333 is more sensitive to temperature than SAV 10. However, for the solutions with salt, the viscosity differences between two polymer solutions are almost the same even if temperature rises. The observations indicate that viscosity is more sensitive to salt and salinity than temperature factor.

Effect of Salinity

Fig. 9 and **Fig. 10** perform the the shear rate-viscosity curve of 3,000 ppm SAV 10 and SAV 333 solutions added with different NaCl concentrations (0, 0.5, 1 and 5 wt%). The shear rates of the measurements vary from 0.1 to 935.3 a/s and the temperature used is 75°F.

Table 6 and **Table 7** claim the power-law index of solutions used above. For SAV 10, the power-law index significantly falls with the decreasing salinity. But the situation for SAV 333 is different. Except the n index of SAV 333 solutions in DI water is clearly smaller than other, the salinity change is almost independent of salinity.

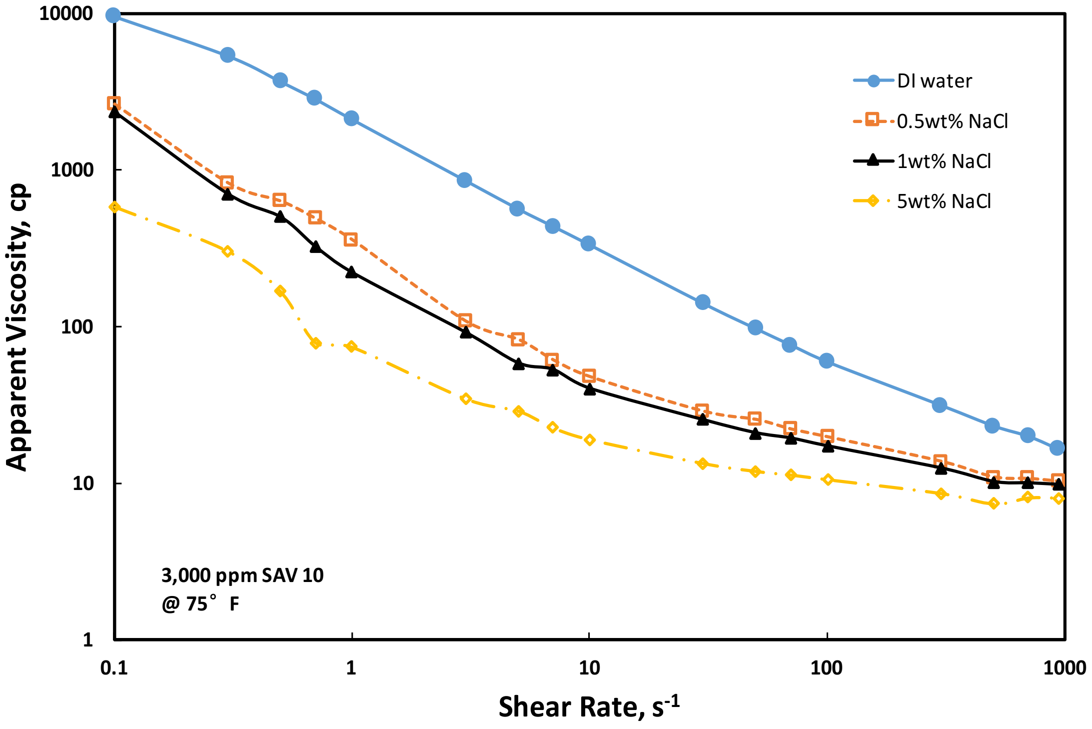

Fig. 9—Effect of salinity on apparent viscosity of SAV 10 at 75°F.

The overall influence of salinity on viscosity is that the growing salinity will bring dropping viscosity. It can be deduced from the hydrolysis and charge shielding mechanism. The hydrolysis of polymer solutions made in DI water induces high viscosity of solutions in DI water due tot the large chain size. When salts are added into solutions, the sodium ions (Na^+) with positive charges will moderate the negative charges produced by hydrolysis and this can be called charge screening effect or charge shielding effect. As a result, the repulsive forces declines and the polymer chains coil up. Consequently, the hydraulic radius of the polymer chain is reduced and hence the viscosity decreases (Nasr-El-Din et al., 1991). More salts dissolved, the declining extent is larger.

Table 6—Power-law parameters for SAV 10 at different salinity.

Salinity, wt%	K, cp	n
0	1929.9	0.274
0.5	344.87	0.29
1	272.72	0.305
5	95.859	0.426

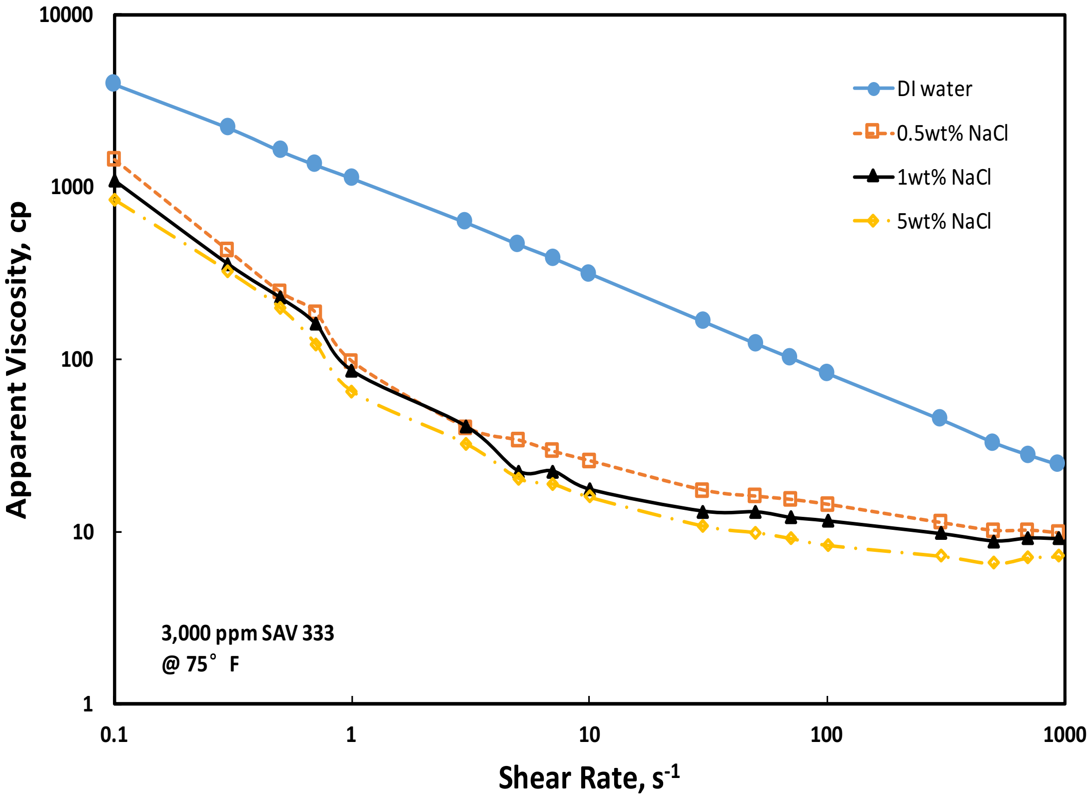

Fig. 10—Effect of salinity on apparent viscosity of SAV 333 at 75°F.

Table 7—Power-law parameters for SAV 333 at different salinity.

Salinity, wt%	K, cp	n
0	1114.3	0.438
0.5	150.65	0.366
1	123.85	0.353
5	102	0.344

The **Fig. 11** and **Fig. 12** input the NaCl concentration and apparent viscosity relationships of SAV 10 and SAV 333 with different polymer concentrations. Shear rate is fixed at 10 1/s and temperature is 75°F.The difference in viscosity is distinct between solution in DI water and solution with salt. The viscosity dissimilarities between the SAV 333 solutions under various NaCl concentrations from 0.5 wt% to 5 wt% are negligible compared with SAV 10.

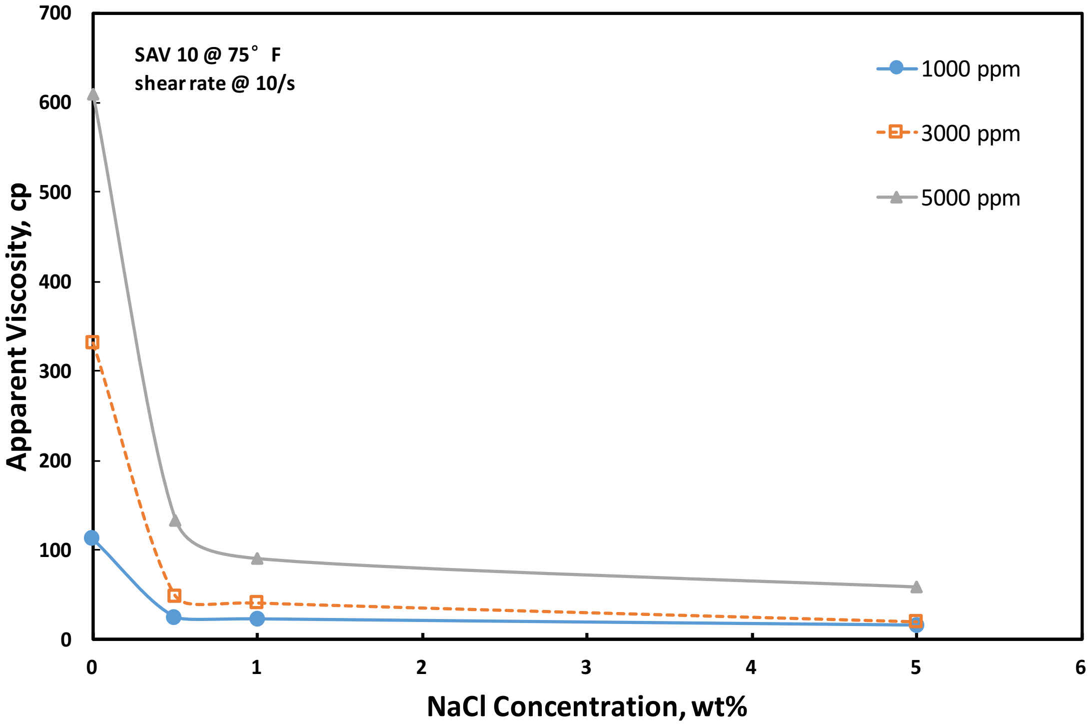

Fig. 11—Effect of salinity on apparent viscosity of SAV 10 solutions.

The apparent viscosity tendencies of SAV 10 and SAV 333 are very close to each other. The apparent viscosity of these two polymers both decrease very sharply when salt is added. However, when salt concentration increases, the viscosity slightly decreases. This phenomenon can explain that salt effect the viscosity a lot and the impact of salt is larger than the impact of polymer concentration.

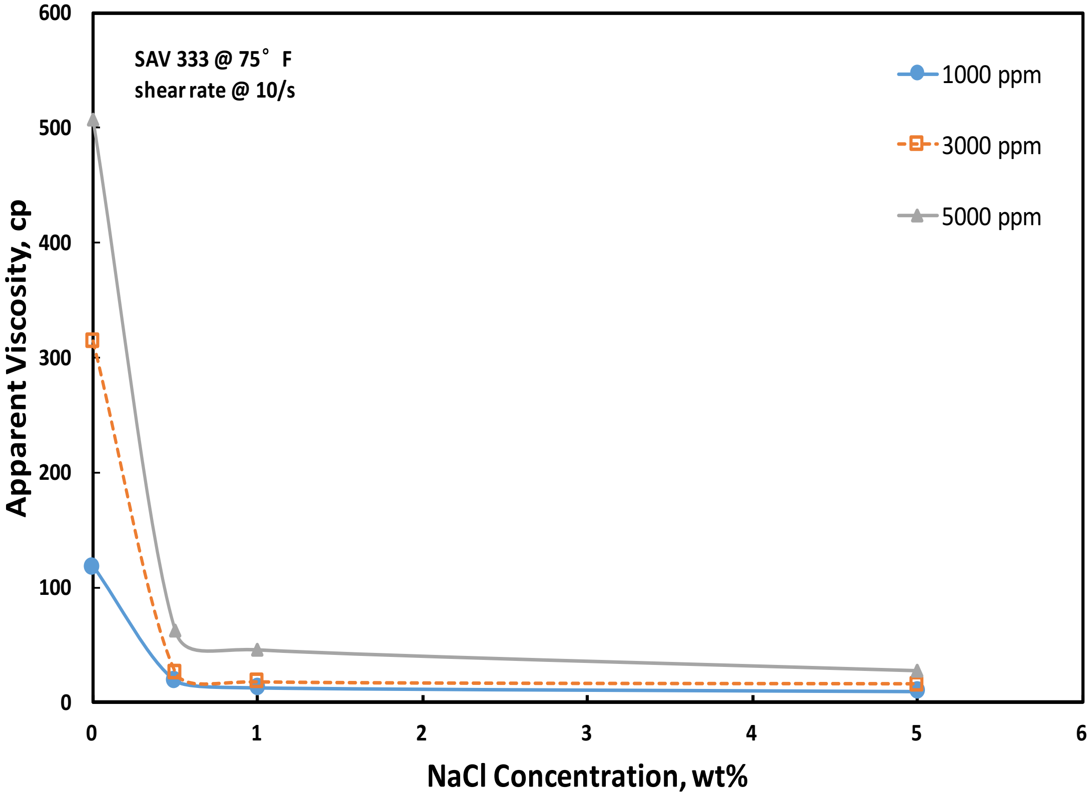

Fig. 12—Effect of salinity on apparent viscosity of SAV 333 solutions.

Fig. 13 compares the effect of salinity on viscosity of SAV 10 and SAV 333. We can see that the viscosities are close for the solutions in DI water. The differences become bigger after adding salts, however, the variances decrease with the salinity rises. And after adding salt, SAV 333 drops more significantly than SAV 10 even at low salinity, which can draw the conclusion that SAV 333 is more sensitive to salt concentration than SAV 10.

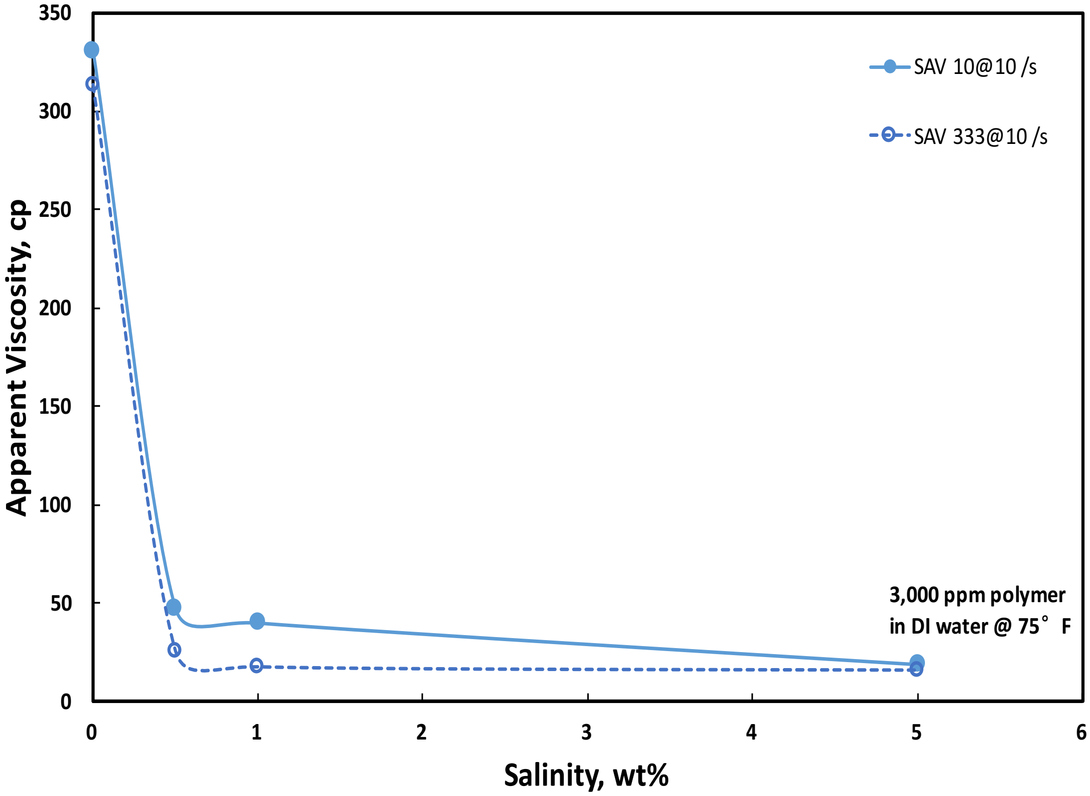

Fig. 13—Effect of salinity on apparent viscosity.

Effect of Salt Type

Fig. 14 and **Fig. 15** perform the effect of cation type on the viscosity of 3,000 ppm SAV 10 and SAV 333 solutions. The measurements were tested at 75°F and shear rates are at the range of 0.1 to 935.3 1/s. Three types of polymer solutions are measured, including solution made in DI water, solution with 0.5 wt% NaCl and solution with 0.5

wt% $CaCl_2$. For SAV 10, the solutions in DI water has shear thinning behavior all the time while the solutions added with salts (NaCl and $CaCl_2$) have shear thinning performance at the shear rates from 0.1 to 500 1/s and Newtonian behavior at the shear rates larger than 500 1/s. As can be seen from the figures, $CaCl_2$ reduce viscosity of solutions prepared in DI water more significantly than NaCl with the same salt concentration at most range of tested shear rates. The possible explanation is related to bridging effect of divalent cations. Since calcium ions (Ca^{2+}) have higher positive charges, $CaCl_2$ is more effective in shielding the negative charges than NaCl (Nasr-El-Din et al., 1991). As a consequence, divalent cations like Ca^{2+} can decrease viscosity more obviously than monovalent cations as Na^+.

Table 8 and **Table 9** show the power-law factors of solutions used in **Fig. 14** and **Fig. 15.** It can be seen that the power-law index of solutions prepared in $CaCl_2$ is smaller than the ones made by NaCl.

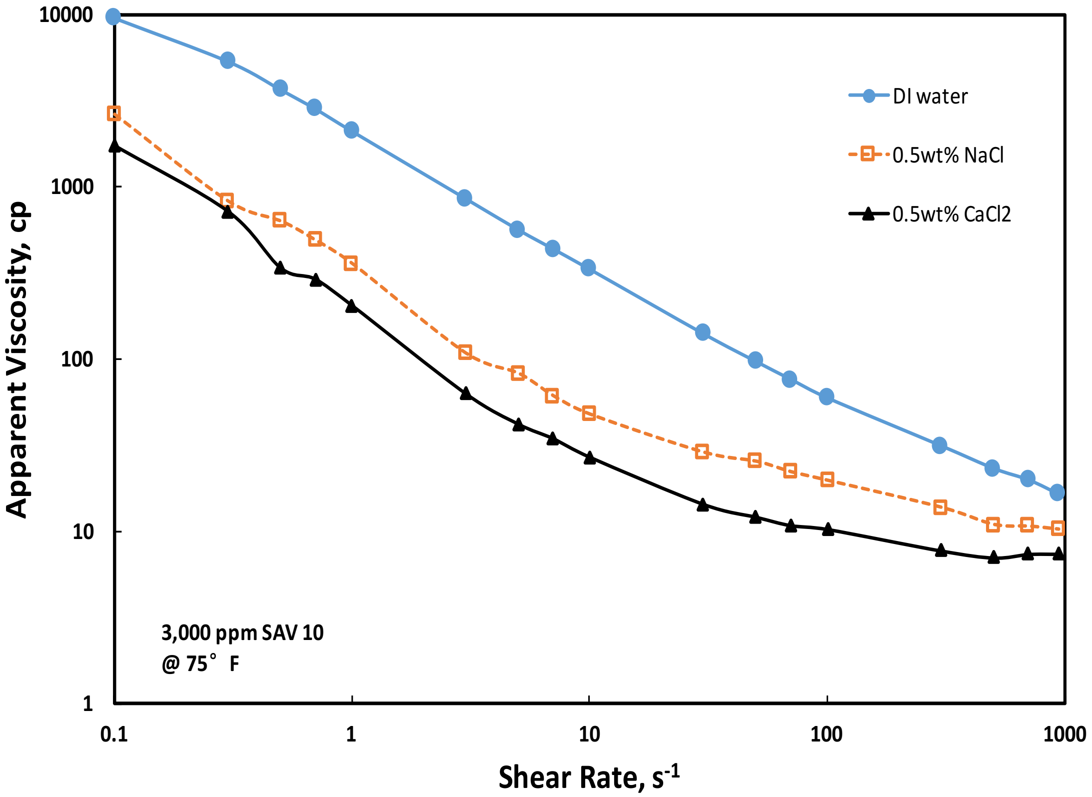

Fig. 14—Effect of salt type on apparent viscosity of SAV 10 solutions.

Table 8—Power-law parameters for SAV 333 with different salts.

Salt type	K, cp	n
DI water	1929.9	0.274
0.5wt%NaCl	344.87	0.29
0.5wt%$CaCl_2$	210.74	0.238

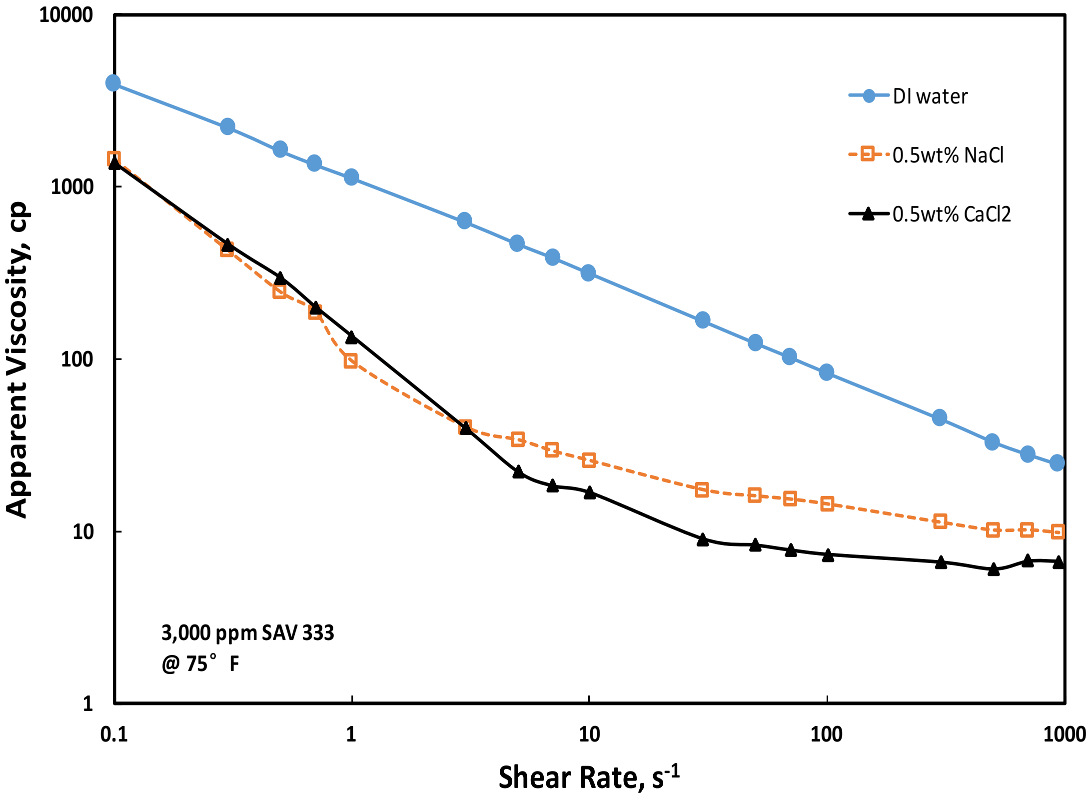

Fig. 15—Effect of salt type on apparent viscosity of SAV 333 solutions.

Table 9—Power-law parameters for SAV 333 with different salts.

Salt type	K, cp	n
DI water	1114.3	0.438
0.5wt%NaCl	150.65	0.366
0.5wt%$CaCl_2$	142.35	0.223

Fig. 16 and **Fig. 17** are the diagrams of CaCl2 concentration versus apparent viscosity of SAV 10 and SAV 333 chemical solutions with different polymer

concentrations at 75°F. The measured shear rate is 10 1/s. After adding $CaCl_2$, the viscosity variance of chemical solutions is obvious at very low salt concentations (< 0.5 wt%). However, the effect of salt concentration and effect of polymer concentraion decline with salinity increasing.

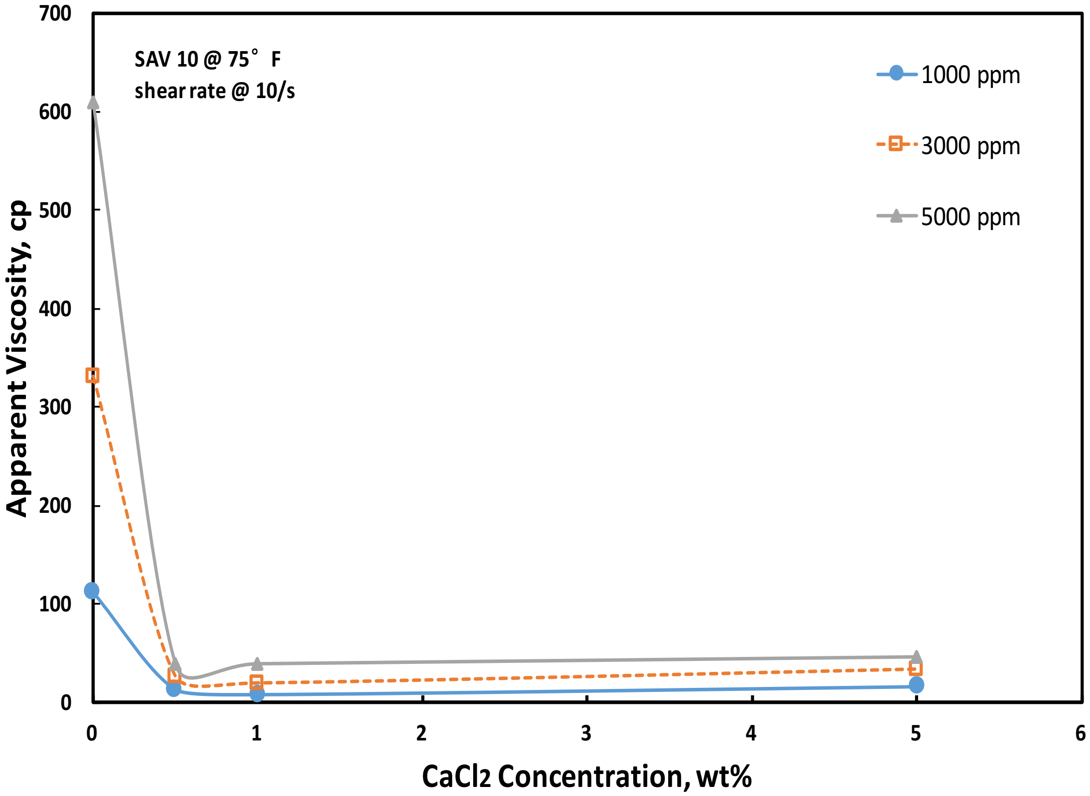

Fig. 16—Effect of $CaCl_2$ concentration on apparent viscosity of SAV 10.

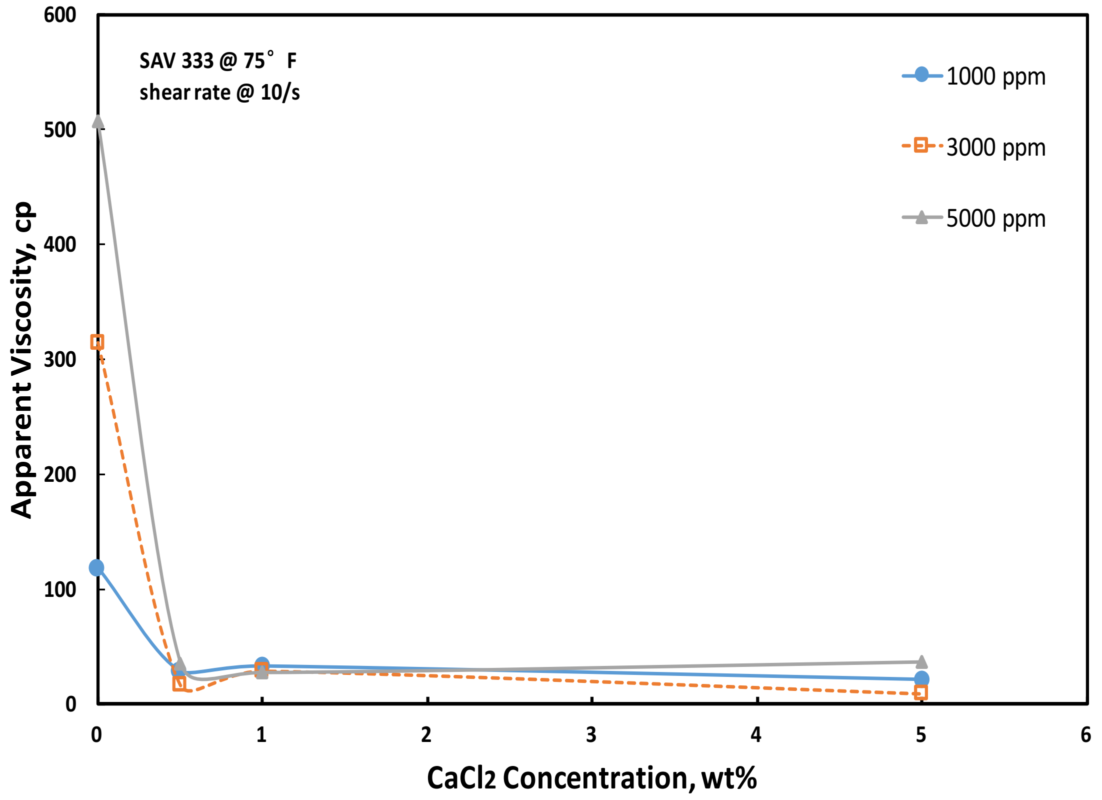

Fig. 17—Effect of $CaCl_2$ concentration on apparent viscosity of SAV 333.

Fig. 18 associates the effect of salt type and salinity on viscosity of SAV 10 and SAV 333 with the polymer concentration of 3,000 ppm at 75°F and the shear rate of 10 1/s. For SAV 10, the solutions made in $CaCl_2$ shows higher viscosity decreasing rate with salinity at low salt concentrations < 1 wt%. But the differences of the decreasing rates become small at salt concentrations > 1 wt%. The reason as mentioned before is related to bridging effect of Ca^{2+}. For SAV 333, the difference taken by cation types is not obvious. The possible illumination is related to the function of NVP in SAV 333 polymer chain. NVP functional groups offer tolerance to divalent ions as well as protect from hydrolysis (Gaillard et al., 2014).

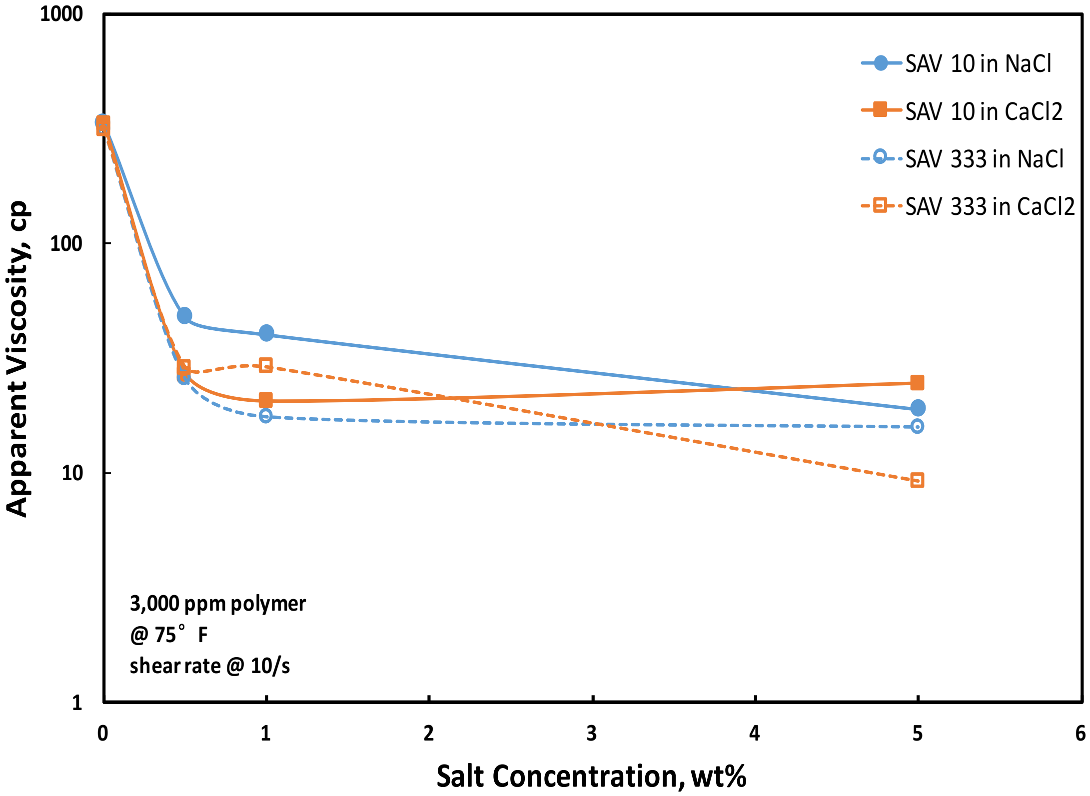

Fig. 18—Effect of salt type on apparent viscosity.

Viscoelastic Property Measurements of Polymer Solutions

Oscillation tests are taken to measure the viscoelastic properties of elastic modulus (G') and viscous modulus (G") as the function of frequency (Veerabhadrappa et al., 2013). Two polymer (SAV 10 and SAV 333) solutions are measured at different factors, including polymer concentrations (1,000, 3,000 and 5,000 ppm), temperature (75-250°F), salinity (0.5 and 1 wt%) and salt type (DI water, NaCl and $CaCl_2$). All measurements are happened at the frequency range of 0.1-5 Hz.

Effect of Polymer Concentration

Fig. 19 shows G' and G" values of SAV 10 chemical solutions diluted in DI water under different polymer concentrations (1,000, 3,000 and 5,000 ppm). It is shown that G' and G" both increase with the increasing polymer concentration. The crossover point show dependence on polymer concentration. When polymer concentration rises, the crossover frequency diminishes and hence the relaxation time which is inverse of crossover frequency increases. The relaxation time which is the time for the stretched elastic properties in the fluid to turn to the original status, is considered as an important factor to describe the viscoelastic property behavior (Castelletto et al., 2004). The crossover point is also a signal of entanglement coupling starting up. This obvious changes in the relaxation variety is a result of strong entanglement coupling of neighboring molecules to transfer along the chain (Kim et al., 2010). Increasing polymer concentration causes stronger entanglement and hence more time is needed for the chain to relax.

As shown in the figure, G’ value is higher than G” value when the frequency is larger than the critical frequency, while the G” value is higher at the low frequency. This is the typical viscoelastic fluid behavior. Elastic behavior is dominated at most tested frequency.

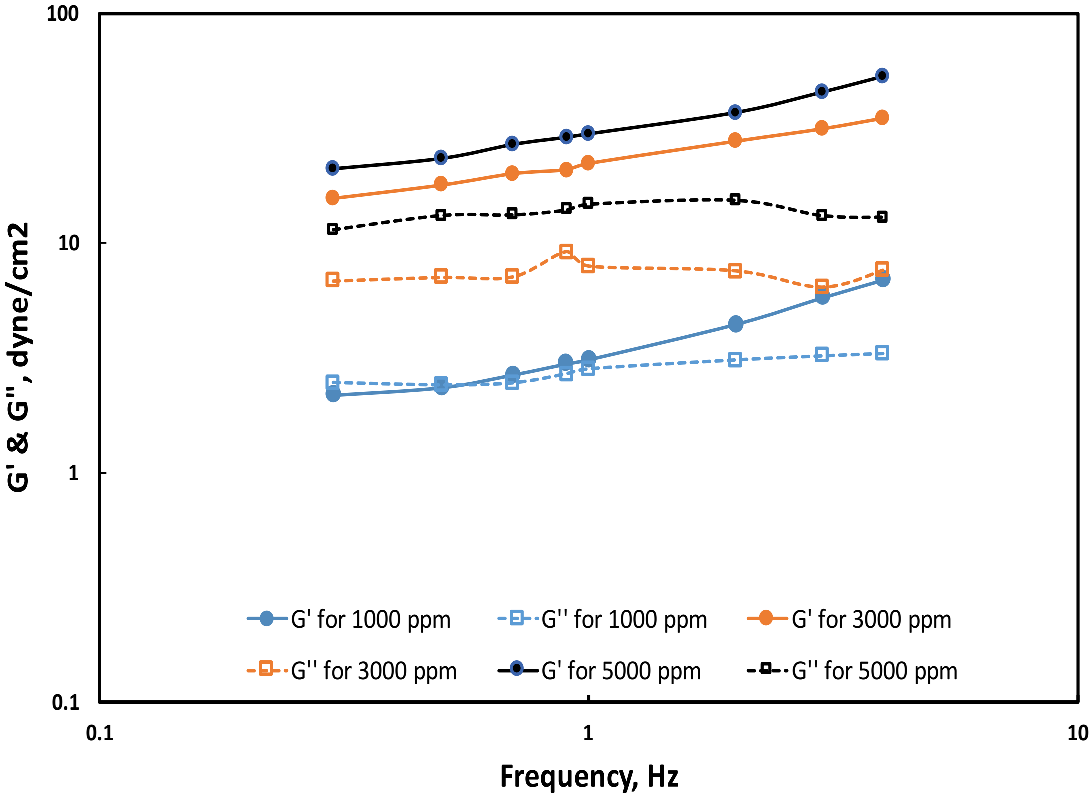

Fig. 19—Effect of polymer concentration on G’ and G” of SAV 10.

Fig. 20 displays G’ and G” values of SAV 333 solutions in DI water under different polymer concentrations (1,000, 3,000 and 5,000 ppm). The critical frequency slightly decreases with the increasing polymer concentration, indicating the same relaxation time dependence of polymer concentration. Different from SAV 10, the G” value is larger than the G’ value at the most tested frequency range, presenting viscous behavior is principal. Furthermore, the relaxation time for SAV 333 is smaller than SAV 10.

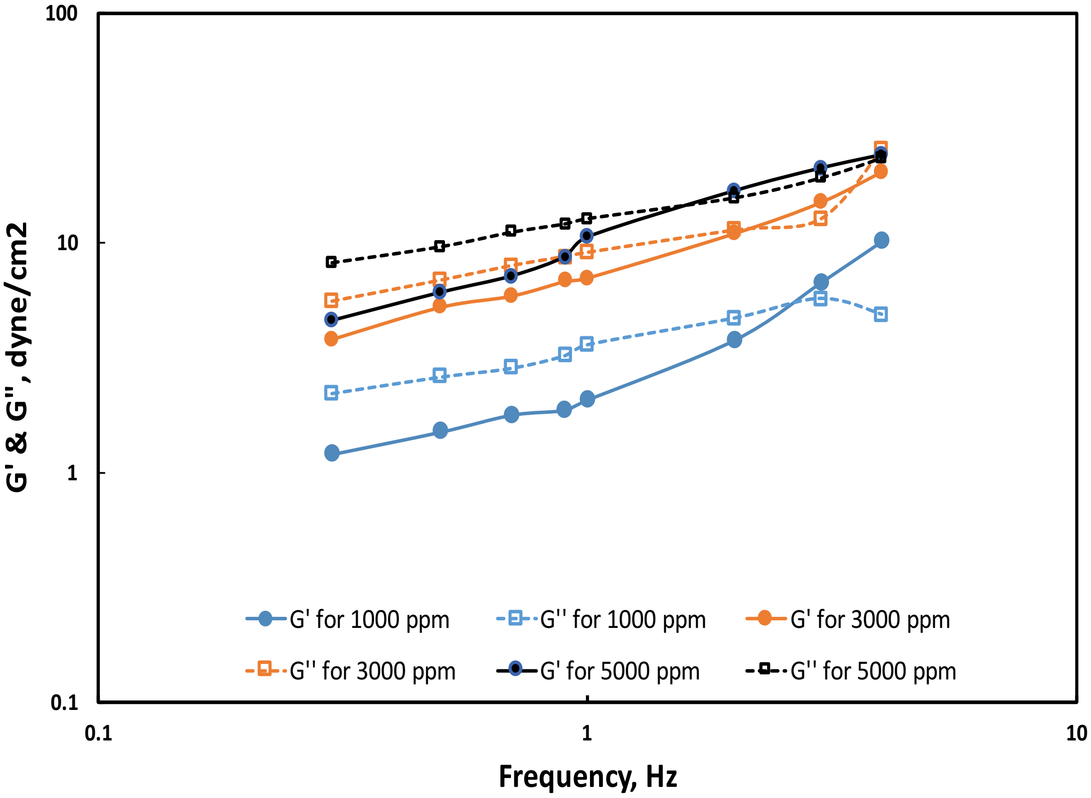

Fig. 20—Effect of polymer concentration on G’ and G” of SAV 333.

As shown in **Fig. 21**, the elastic modulus of samples of SAV 10 are higher than SAV 333 samples, which is result from the differences of the solution polydispersity exponents. It can be concluded that SAV 10 is more elastic than SAV 333 solutions by the method of higher G' value implying stronger elastic behavior.

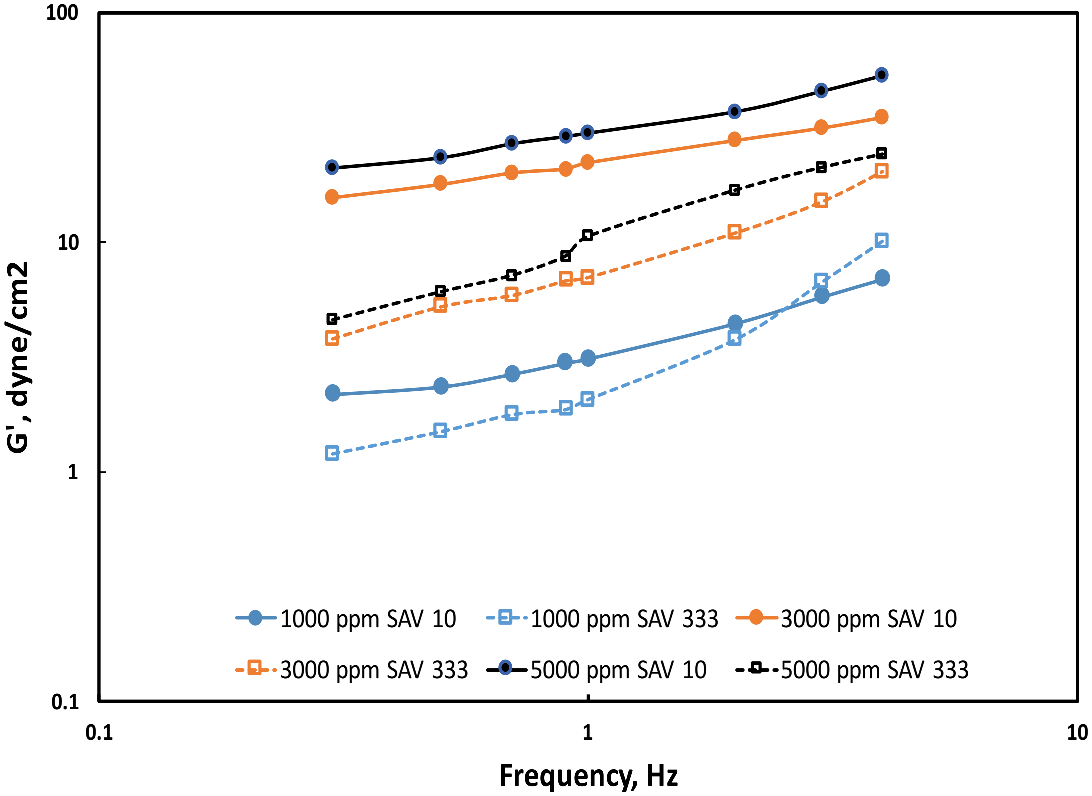

Fig. 21—Comparison of G' values of SAV 10 and SAV 333 solutions.

As shown in **Fig. 22**, the general viscous modulus of SAV 10 samples are close to SAV 333 solutions, which can be explained by the similar molecular weight of two polymers. At polymer concentration of 1,000 ppm, G" value of SAV 333 is higher than SAV 10, showing stronger viscous characteristics of SAV 333 solutions. With polymer concentration increasing, the G" value of SAV 333 become lower than SAV 10 at the polymer concentration of 5, 000 ppm. This changing tendency of two samples is in support of the effect of polymer concentrations on apparent viscosity as shown in **Fig. 5**.

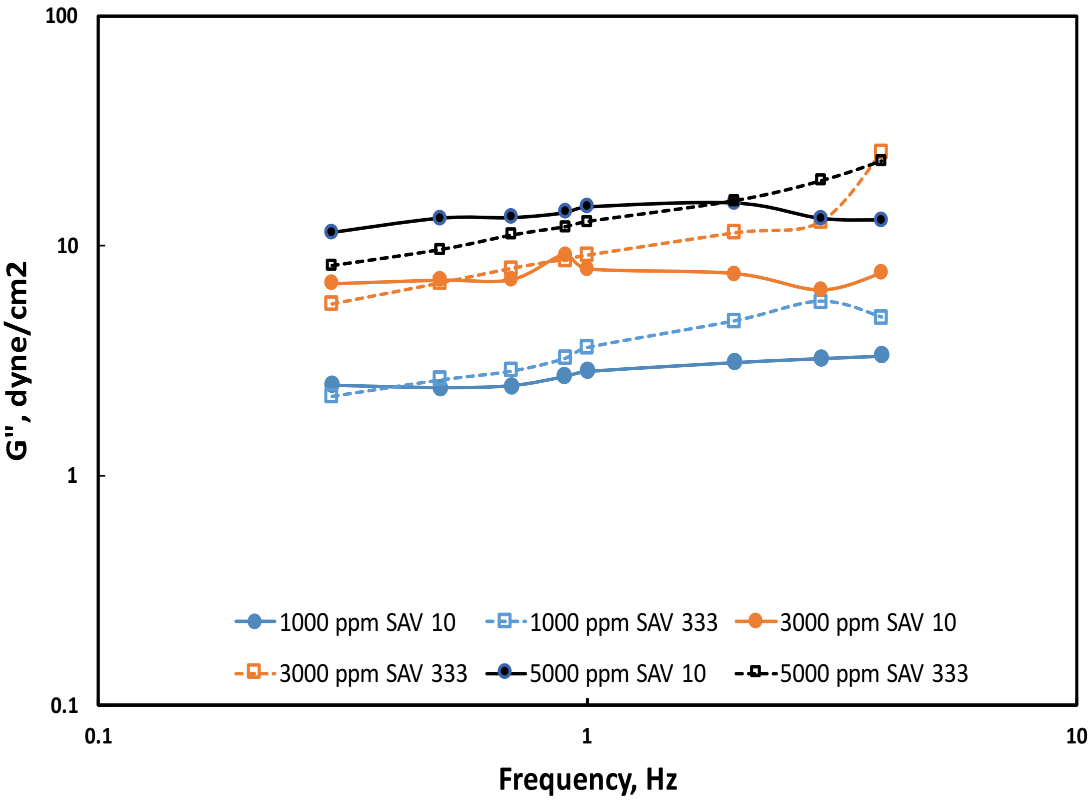

Fig. 22—Comparison of G” values of SAV 10 and SAV 333 solutions.

Effect of Temperature

Fig. 23 shows both G’ and G” values are dependent of temperature for polymer SAV 10 solutions in DI water. The growing temperature brings the lower elastic modulus, which means elasticity is weaken by high temperature. This behavior can be caused by the effectiveness of entanglements. The viscous modulus also decreases when temperature inclines, supported by the **Fig. 8** which describes the effect of temperature on apparent viscosity. Another thing can be observed from the figure is that the critical frequency identically increases with the upward temperature, revealing that the relaxation time is negatively related to temperature for SAV 10.

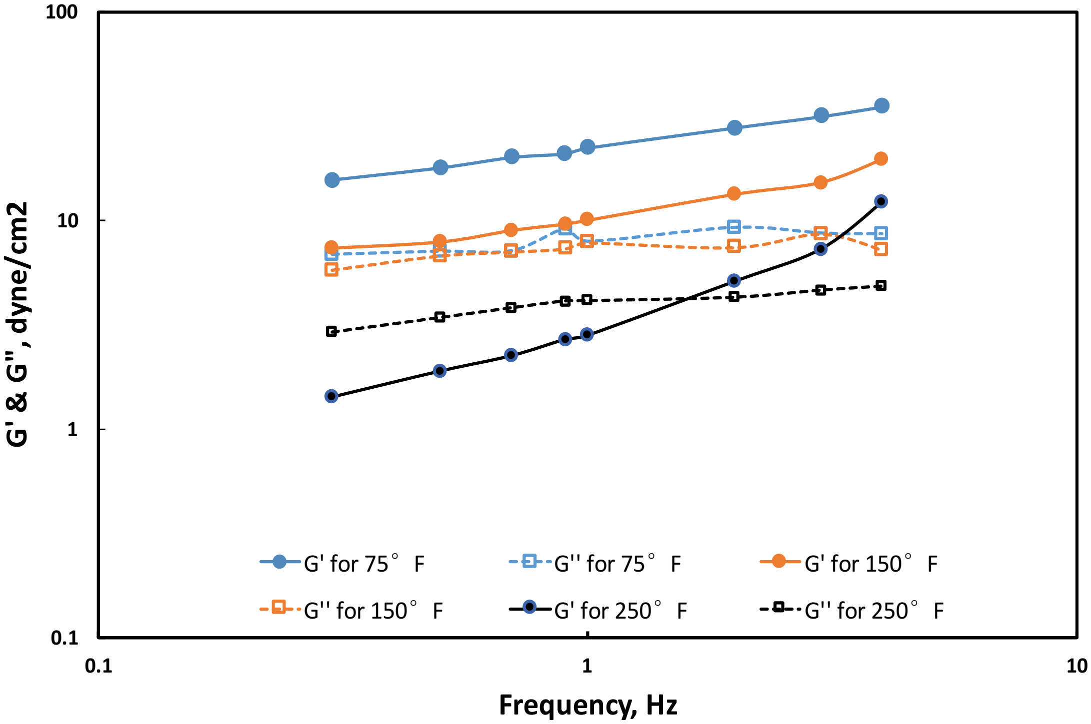

Fig. 23—Effect of temperature on G' and G" of 3,000 ppm SAV 10.

The same relationship between temperature and viscoelastic properties are observed on SAV 333 samples as shown in **Fig. 24**. **Fig. 8** can also offer the prove for the trend. The relaxation time of SAV 333 is smaller than SAV 10 at the whole tested temperature range. And the relaxation time slightly decreases with higher temperature.

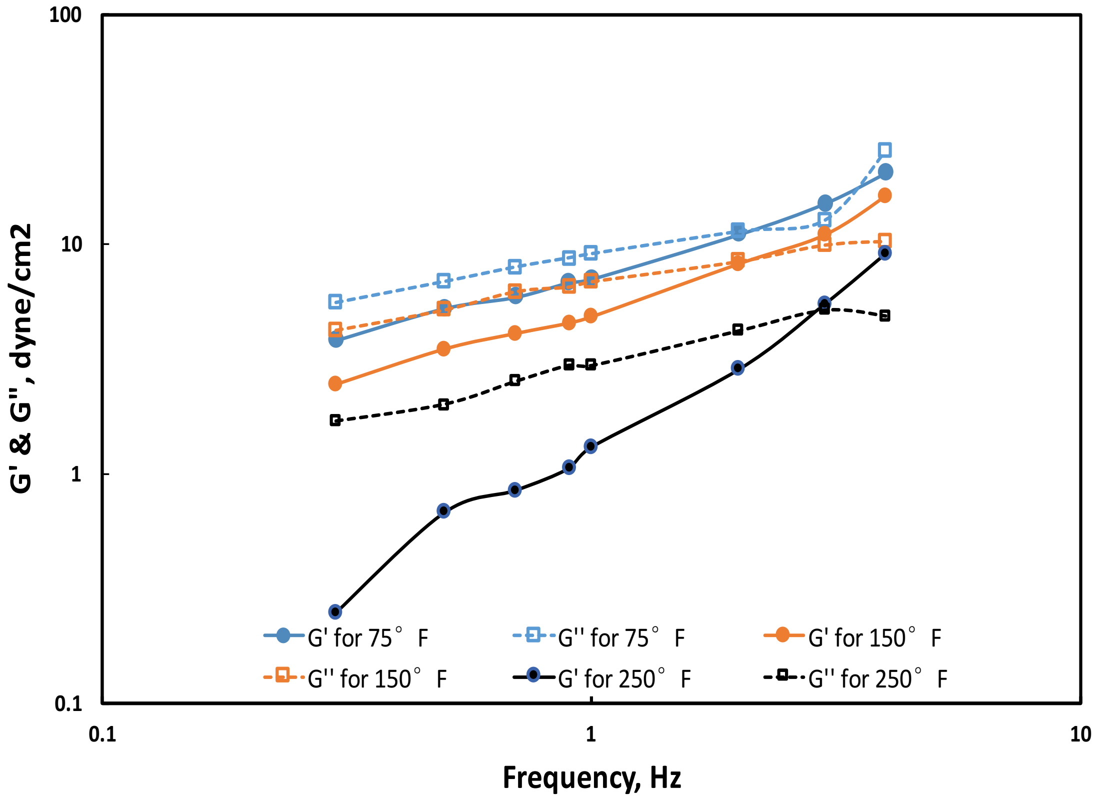

Fig. 24—Effect of temperature on G' and G" of 3,000 ppm SAV 333.

Fig. 25 and **Fig. 26** compares the G' and G" value individually for SAV 10 and SAV 333. It is shown that elastic modulus of SAV 10 is always higher than it of SAV 333 at different temperature. This phenomenon indicates SAV 10 has larger elasticity even at higher temperature. The viscous modulus of two polymers are closer to each other at lower temperature. This viscosity behavior was also shown previously in **Fig. 8**.

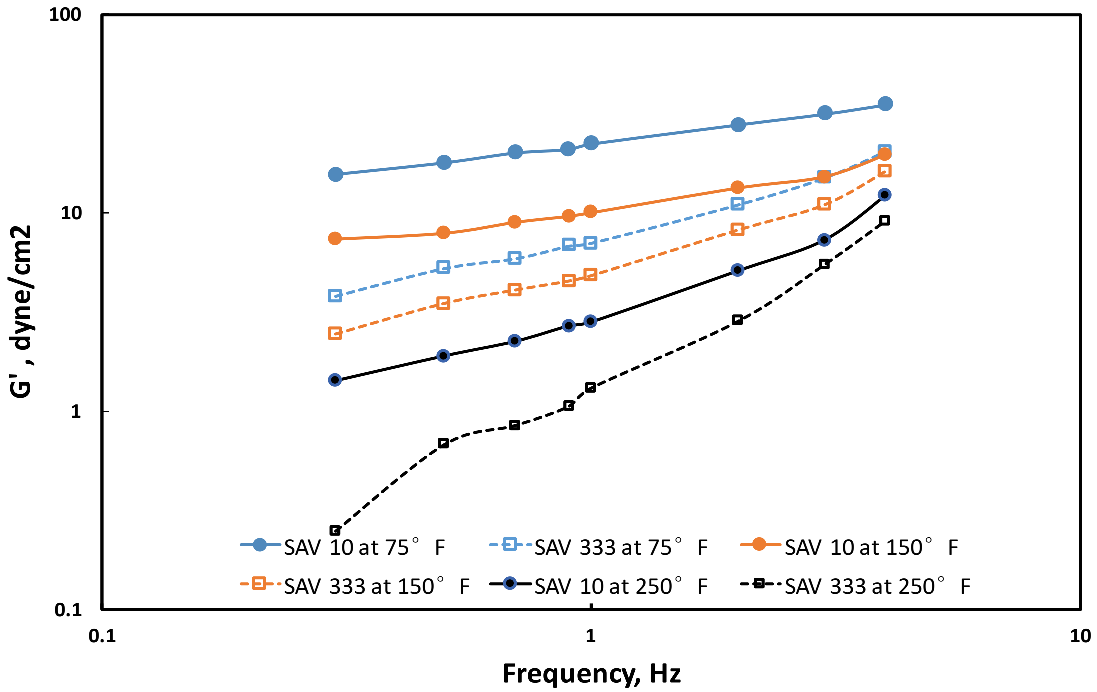

Fig. 25—Comparison of G' values of SAV 10 and SAV 333 for temperatures.

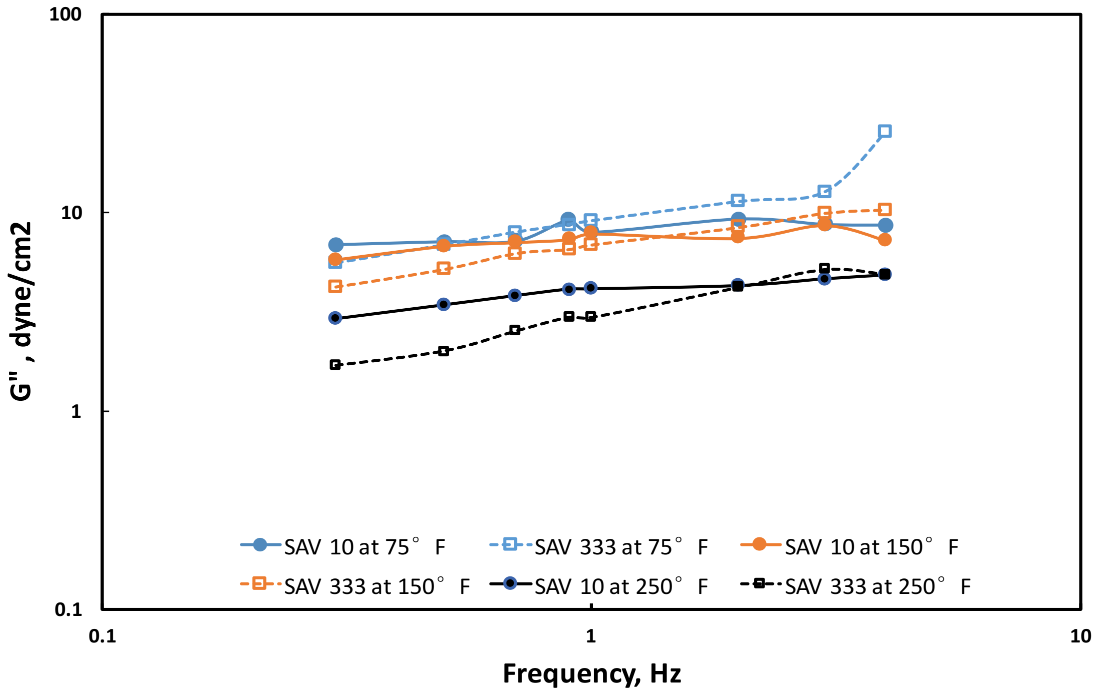

Fig. 26—Comparison of G" values of SAV 10 and SAV 333 for temperatures.

Effect of Salinity

Fig. 27 shows the significant reduction of G' and G" values when salt is added into the solution. However, the salinity slight effects the viscoelastic properties and relaxation time. **Fig. 11** supports that difference between the viscosity of SAV 10 with 0.5 wt% NaCl and 0.1 wt% NaCl is small. When salt is added, the dominant behavior of fluid transfers from elastic behavior to viscous behavior and the relaxation time decreases significantly.

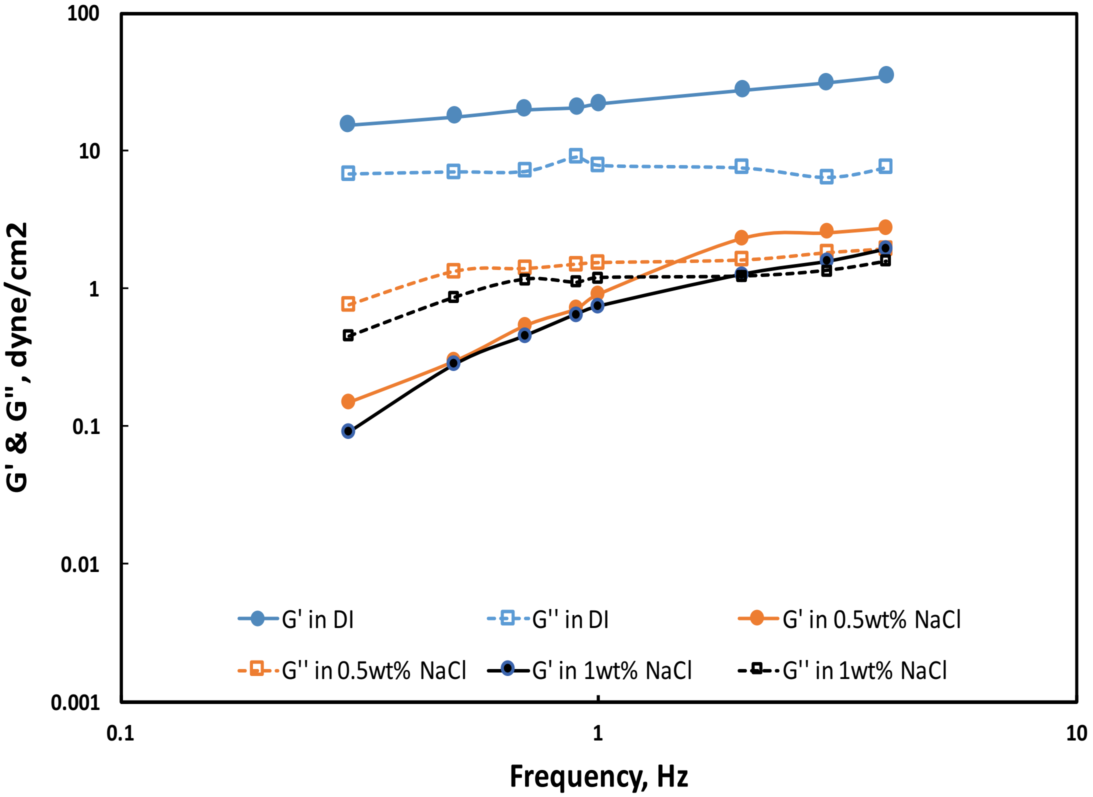

Fig. 27—Effect of salinity on G' and G" of 3,000 ppm SAV 10 at 75°F.

The effect of salinity on viscoelastic characteristics is not obvious for SAV 333 samples as shown in **Fig. 28**. SAV 333 shows the dominate viscous behavior, which can be the result of screen shielding. The relaxation time and G’ and G” values of three sample solutions slightly decrease with higher salinity.

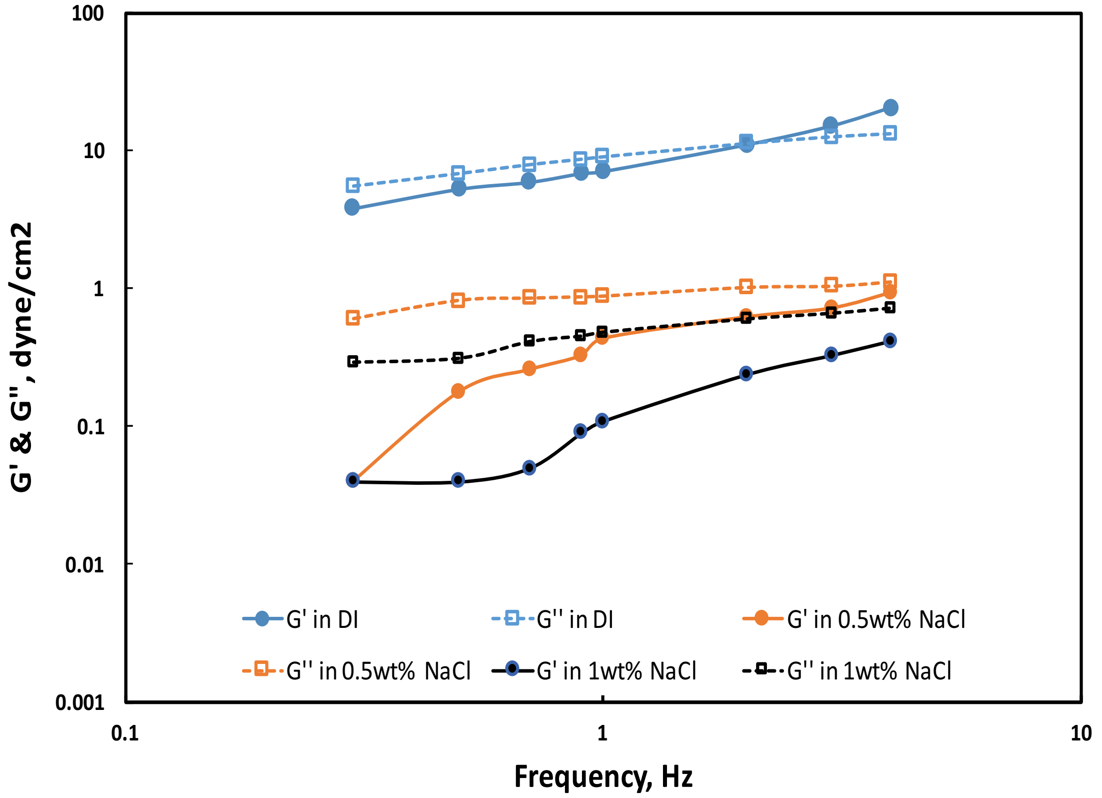

Fig. 28—Effect of salinity on G’ and G” of 3,000 ppm SAV 333 at 75°F.

<u>Effect of Salt Type</u>

Viscoelastic properties of SAV 10 is dependent on salt type from the observation of **Fig. 29**. At the frequency from 0.1 to 5 Hz, SAV 10 has major elastic behavior in DI water and the main behavior changes from elastic to viscous for brine with NaCl. When salt type turns to $CaCl_2$, domination of viscous behavior is shown. So the viscoelastic properties (G', G" and relaxation time) are adversely associated with the charge number of salt. This behavior can be caused by charge shielding.

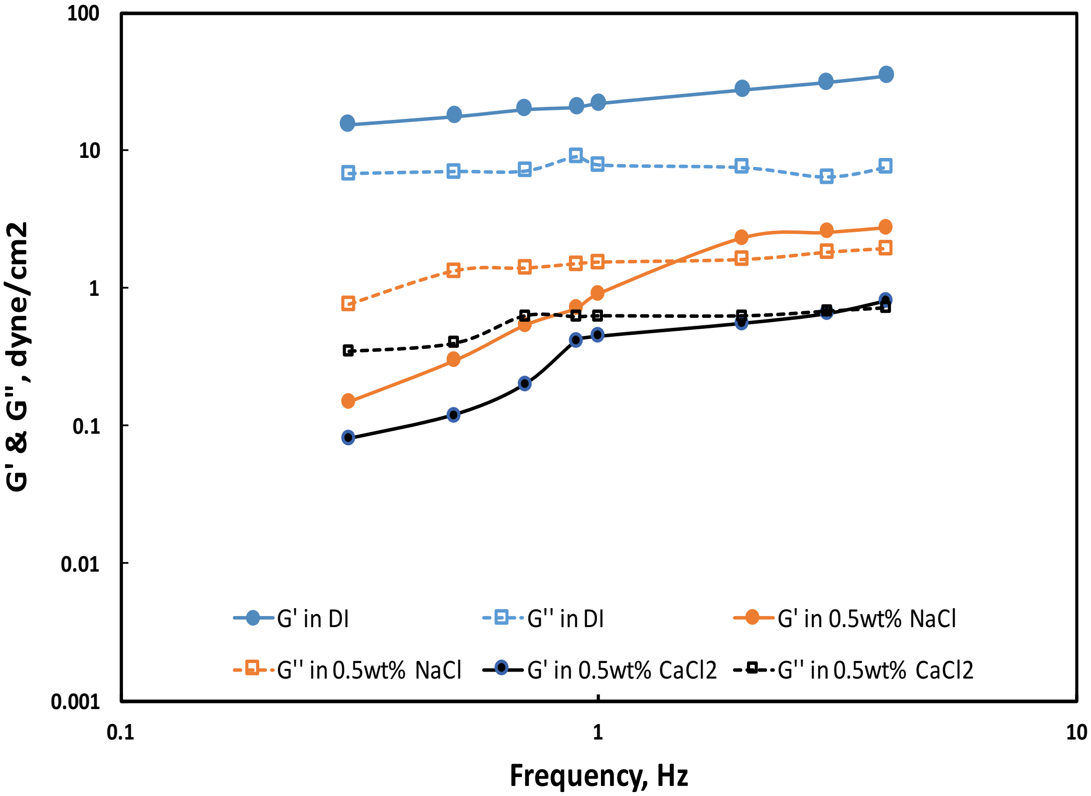

Fig. 29—Effect of salt type on G' and G" of 3,000 ppm SAV 10 at 75°F.

As is shown in **Fig. 30**, viscous behavior is always the major fluid behavior. For salt type of NaCl and $CaCl_2$, the elastic modulus and viscous modulus has very small value which is resulted from the salt adding. The G’ and G” values and relaxation time slightly differ from solutions prepared in different salt types.

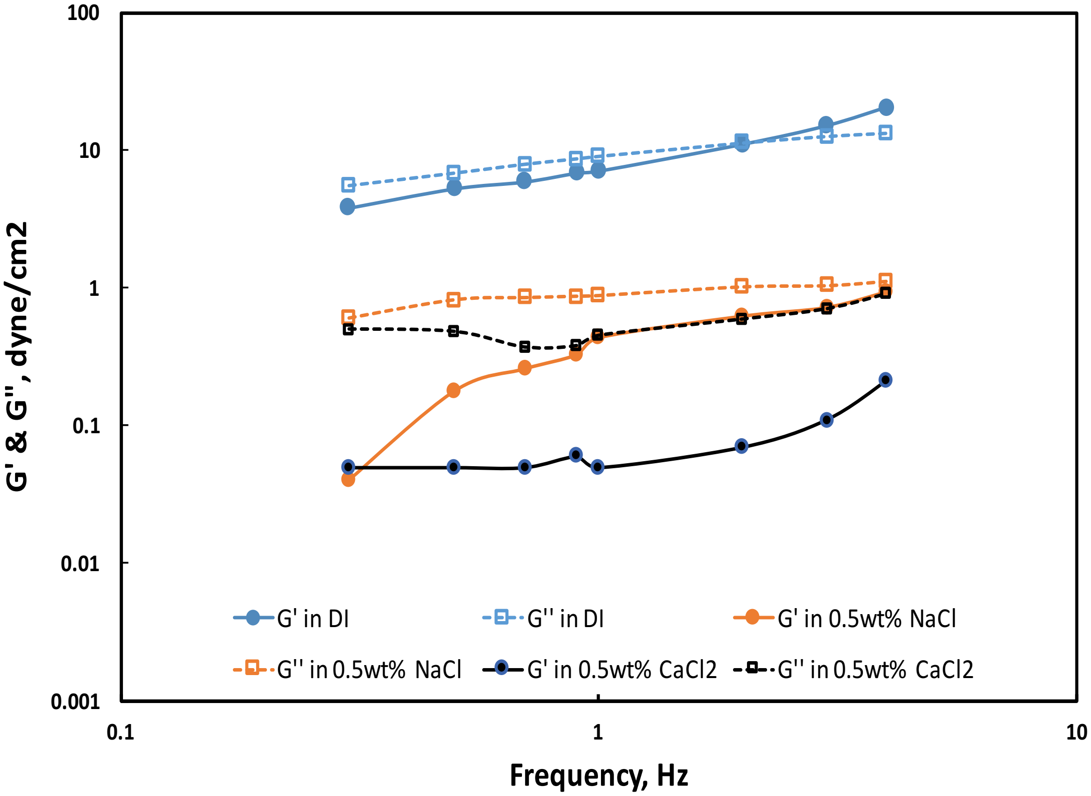

Fig. 30—Effect of salt type on G’ and G” of 3,000 ppm SAV 333 at 75°F.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Steady state test and oscillation test were conducted to evaluate rheological characteristics of two types of polymer solutions under different conditions, including polymer concentration, temperature, salinity and salt type. The two polymers used in the experiments are the co-polymer SAV 10 with functional groups of acrylamide (AM) and acrylamide-tertio-butyl sulfonate (ATBS), and the ter-polymer SAV 333 with N-vinyl pyrrolidone (NVP), AM and ATBS in the polymer chain. Based on the results gained, the following conclusions can be made:

1. The apparent viscosity versus shear rate relationship shows a shear thinning behavior at the most tested shear rates and a Newtonian behavior at very high shear rates.
2. SAV 10 solutions prepared in DI water show strong shear-thinning behavior than SAV 333.
3. Increasing polymer concentration causes the growth of apparent viscosity, G', G" and relaxation time.
4. Effect of polymer concentration on apparent viscosity of SAV 10 is stronger than it on SAV 333.
5. Increasing temperature declines the viscosity, level of shear thinning behavior, G', G", and relaxation time.

6. The apparent viscosity of SAV 333 in DI water decrease more sharply than SAV 10 with higher temperature.
7. Increasing NaCl concentration indicates more significant reduction in apparent viscosity, G', G" and relaxation time at low salinity.
8. Effect of NaCl concentration on apparent viscosity and viscoelastic properties of SAV 333 is stronger than it on SAV 10.
9. Effect of $CaCl_2$ concentration on apparent viscosity of SAV 333 is stronger than it on SAV 10.
10. For the solutions with same salt concentration, effect of salt type on apparent viscosity of SAV 10 is significant at low salinity while the effect at high salinity can be neglected.
11. Effect of salt type on apparent viscosity of SAV 333 can be ignored.
12. $CaCl_2$ slightly decreases G', G" and relaxation time compared with the solutions prepared with NaCl with same salt concentration.
13. SAV 10 solutions show stronger elastic behavior than SAV 333 solutions.
14. Viscous behavior of SAV 10 and SAV 333 are close to each other.

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