

## Rheological properties of a hydrophobically modified anionic polymer: Effect of varying salinity and amount of hydrophobic moieties

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**ABSTRACT:** Hydrophobically modified polyelectrolytes have been suggested as an alternative to the more commonly used polyelectrolytes in enhanced oil recovery (EOR) applications involving polymers. Compared to regular polyelectrolytes, the hydrophobically modified polyelectrolytes are known to be more stable at high salinities. In this study, we have investigated the influence of brine salinity and ionic composition for a series of six hydrophobically modified polyelectrolytes with the same polymer backbone, but with an increasing average number of hydrophobic groups per polymer molecule. Polymer characterization has been performed using a combination of steady-state shear viscosity and dynamic oscillatory measurements. Hydrophobic interactions leading to a change in rheological properties was only observed above a threshold value for the concentration of hydrophobe. At the threshold value, salt-induced hydrophobic interactions were observed. For higher concentrations of hydrophobe, high salinity solutions showed one order of magnitude increase in viscosity compared to the polymer without hydrophobic groups. This could partly be explained by an increase in elasticity. These findings have important implications for polymer selection for EOR. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43520.

**KEYWORDS:** oil and gas; polyelectrolytes; properties and characterization; rheology; viscosity and viscoelasticity

Received 28 September 2015; accepted 4 February 2016

DOI: 10.1002/app.43520

### INTRODUCTION

In a chemical flooding process, a polymer solution with high viscosity is injected to improve the mobility ratio in the water flood and increase the recovery in the reservoir.<sup>1</sup> The polymers injected have to withstand high salinity, high temperature, and long injection times without decreasing in viscosity.<sup>1,2</sup> High-molecular-weight polyelectrolytes, for instance partially hydrolyzed polyacrylamide (HPAM), are frequently used in oil field applications due to their relatively low cost and high viscosifying ability. However, at high salinities, particularly in the presence of divalent cations,<sup>3</sup> their viscosity decreases significantly due to coiling of the polymer as a result of electrostatic shielding. As an alternative, the use of hydrophobically modified versions of these polyelectrolytes has been suggested as a mean of maintaining high viscosity at high salinity. Associative polymers differ from hydrolyzed polyacrylamide, mainly due to the hydrophobic groups attached to the backbone of the associative polymer. The polymers still experience shielding of the polyelectrolyte backbone; however their viscosity does not decrease in concentration above critical overlap concentration,  $c^*$ , due to interaction between the hydrophobic groups.<sup>4,5</sup> In aqueous solutions, above  $c^*$ , the associative polymers form hydrophobic

intermolecular interactions between the side groups. This leads to the formation of a three-dimensional network,<sup>6</sup> and enhances the viscosity and gives unique rheological properties. Petit-Agnley *et al.*<sup>7</sup> has demonstrated that only a fraction of hydrophobic groups contributes to microdomain formation. Observations have shown that with increase in hydrophobic groups, one get better thickening capability. However, the presence of hydrophobic groups impairs the solubility of the polymer and can lead to solubility issues.<sup>8</sup>

### BACKGROUND

#### Polymers in Solution

The behavior of associative polyelectrolytes is due to two effects, the repulsive interaction between the negatively charged ions in the backbone, and the attractive interactions of the hydrophobic groups. By adding salt in the polymer solution, the charged backbone will be shielded, and the repulsive electrostatic interaction is cancelled out.<sup>9</sup> This results in a reduction in the hydrodynamic radius of the polymer, and a reduction in viscosity. An associative polymers response to salinity is different from that of polyelectrolytes like HPAM. Although a viscosity loss by charge screening is seen, the hydrophobic interactions will be even stronger in more polar, high salinity solutions;

both because of the lack of repulsion and the hydrophobic groups will be less hindered to make intermolecular interaction.<sup>10</sup> According to Reichenbach-Klinke *et al.*,<sup>10</sup> the viscosity increase due to the polar solvent is going to counteract the weakening repulsion between the anionic groups. The intermolecular interactions are dominant rather than the electrostatic repulsions.<sup>11</sup> The interaction due to polarity of the solvent can be explained by the Hofmeister series. The Hofmeister series is a classification of ions due to their ability to salt-in or salt-out proteins. For anions, the Hofmeister series the typical order is  $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^{2-} > \text{SCN}^-$ . The anions on the right have a salting-in effect which increases the solubility and decreases the hydrophobic interaction while the anions on the left can lead to a decrease in solubility, that is, salting-out, and strengthens the hydrophobic interactions.<sup>12</sup> Although similar effect and ordering is found for cations, the effect for anions is more pronounced. The thickening ability of the associative polymer can be controlled by changing the content of the hydrophobic group<sup>13</sup> and arrangement on the backbone,<sup>13,14</sup> the molecular weight,<sup>15</sup> and degree of hydrolysis.

The viscosity of hydrophobically modified polyelectrolytes depends strongly on the polymer concentration. With increasing concentration the viscosity increases as more interchain association takes place and a transient network is formed.<sup>16</sup> For a non-associative polymer, the increment in viscosity due to increasing concentration is caused by an onset of overlapping polymer at the critical overlap concentration,  $c^*$ , and related to the molecular size.<sup>4</sup> The concentration contains three different regimes: the dilute ( $c < c^*$ ), the semidilute ( $c > c^*$ ), and concentrated regime,<sup>17</sup> the border lines between the regimes can be diffuse.<sup>4</sup> For associative polymer, the chain overlap at the same molar mass cause formation of aggregates and form associating network at a concentration, CAC, which will be lower than  $c^*$ . As previously mentioned, formation of this network enhances the viscosity of the solution significantly.<sup>18</sup>

In the dilute region, below  $c^*$ , the polymers flow freely in the solution and are not in contact with each other. Here, the intramolecular association dominates<sup>19</sup>; which gives a low hydrodynamic volume, and a low viscosity. With an increase in the salinity for associative polymers in the dilute regime, the hydrophobic groups associate to minimize their exposure to water and more associations occur between hydrophobic groups of the same chain, which leads to tighter coil contraction and decrease in viscosity.<sup>20</sup> In the semidilute region, above  $c^*$ , the polymers start to overlap, and in the associating polymers the intermolecular interactions start to dominate, which leads to an increase in viscosity due to network formations.<sup>14,19</sup> Penott-Chang *et al.*<sup>21</sup> showed that hydrophobically modified HPAM (HMPAM) with concentration under  $c^*$ , had a lower viscosity than the original non-associating polymer. With higher polymer concentrations ( $>2000$  ppm), the HMPAM had a steeper increase in viscosity which got more significant with an increase in hydrophobic groups.

### Viscoelasticity

The materials viscoelastic properties are measured with an oscillatory test, where one apply sinusoidal strain, resulting in a shear stress response, which is shifted by the angle  $\delta$ .<sup>22</sup> The elas-

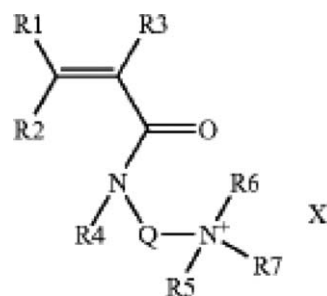


Figure 1. The backbone structure of polymer A.

tic (storage) modulus,  $G'$ , is a measure of the deformation energy stored by the sample during the shear process, while viscous (loss) modulus,  $G''$ , is the deformation energy used up by the sample during the process and thereafter lost.<sup>23</sup> The loss factor,  $\tan \delta$ , is defined as the ratio between viscous and elastic modulus of the viscoelastic behavior.<sup>23</sup>

$$\tan \delta = \frac{G''}{G'}$$

Ideal elastic or viscous behavior is characterized by frequency independent elastic and viscous moduli.  $G'$  completely dominates  $G''$ , and thus  $\delta = 0^\circ$  and  $\tan \delta = 0$ . On the other hand, for a fluid with ideal viscous behavior,  $G''$  dominates  $G'$ , and thus  $\delta = 90^\circ$  and  $\tan \delta = \infty$ .<sup>23</sup> For viscoelastic fluids, the storage modulus is higher than the loss modulus at high frequencies, and lower at low frequencies. At some intermediate frequency, referred to as the crossover frequency,  $\omega^*$ ,  $G' = G''$ , and thus  $\tan \delta = 1$ .

This article presents how the shear viscosity and the viscoelasticity of the polymers change due to increasing amount of hydrophobic groups in the structure in different salt solutions. The polymers contain the same backbone chain, the same degree of hydrolysis, the same type of hydrophobe, and they differ in the degree of hydrophobicity.

Previous studies by Kujawa *et al.*<sup>24</sup> have shown that the onset of the association in a polyelectrolytic associative polymer shifts toward lower concentration by increasing the length of the hydrophobic groups. The aim for this series was to give an indication at what the threshold value for the degree of hydrophobicity for the onset of association for this polymer is, and how the hydrophobicity affects the concentration of the onset.

As mentioned earlier, to enhance the recovery by polymer flooding, one needs a polymer which can tolerate high salinities and the presence of divalent cations. The salinity in this study has been varied from an ionic strength of 0.086 to 1.72 mol/L. The experimental study was conducted to examine the impact of salinity has on the threshold value towards the increment in viscosity and if it affects the concentration of the onset of association. In addition, the viscoelasticity has been a feature that still lack understanding concerning the behavior of the hydrophobic groups in solvents containing divalent cations.

## EXPERIMENTAL

### Materials and Preparation

In this study, we used an anionic polyacrylamide based polymer with different degree of hydrophobic monomer content

**Table I.** Relative Hydrophobicity of Polymer A

Product	Relative hydrophobicity based on A100
A0	0
A25	0.25
A33	0.33
A50	0.50
A75	0.75
A100	1

provided by SNF Floerger.<sup>25</sup> The polymer backbone is obtained by random polymerization with 83% acrylamide and 17% sodium acrylate, corresponding to a charge density of 17%. The molecular weight is between 8 and 12 MDa. The hydrophobic monomer is an acrylamide derivative (Figure 1), with 6–16 carbon atoms in the hydrocarbon chain (R7, Figure 1). As can be seen from the figure, the monomer is cationic, making the polymer amphoteric. The total hydrophobic monomer content varies from 0 to 0.3 mol % for the six polymers studied here. The polymer series differ only in the amount of hydrophobic groups distributed along the backbone. The relative amount of hydrophobe in the six polymers is presented in Table I.

The solvents used were four different salt aqueous solutions; composition of the different brines is provided in Table II. Three of the solvents were NaCl brines with different concentration, 0.5, 5, and 10 wt % NaCl with ionic strength of 0.086, 0.86, and 1.71M, respectively. The last brine is similar to synthetic seawater and is a mixture of five different salts (NaCl, CaCl<sub>2</sub>, KCl, Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub>) with a total ionic strength of 1.72M. All of the brines were filtered through a 0.45- $\mu$ m filter before use. The stock solutions were made according to API stock solution procedure. All polymer solutions were prepared in stock solutions of 5000 ppm. A vortex was established with a magnetic stirrer in the relevant solvent; the polymer powder was poured slowly into the vortex. The solution was stirred at 150 rpm for 12 h. The stock solution was diluted to the desired concentrations. After each preparation and dilution, the polymer solution was left un-agitated in an air tight container for

24 h before starting any measurements. The pH of the solutions was measured to a constant value of  $6.7 \pm 0.5$ .

### Rheology

Rheological measurements were performed using Malvern Kinexus pro rheometer, equipped with a cone-plate geometry (angle = 4°, diameter = 40 mm). The temperature was maintained at  $22 \pm 0.1$  °C. For the shear-dependent behavior, the viscosity measurements were carried out at shear rates ranging from 0.001 to 1000 s<sup>-1</sup>. This range was changed to 0.05 to 1000 s<sup>-1</sup> for low concentrations (below 1000 ppm) because the sensitivity of the sensor did not allow getting accurate values at very low shear rates.

Linear viscoelasticity experiments were performed on stock solutions samples that provided significant viscosity to get accurate data. Frequency sweeps were performed in the of 0.01–10 Hz frequency range of, at a constant strain of 10%. The strain was picked to lie in the LVE range based on amplitude sweeps. The latter were performed at a frequency of 1 Hz.

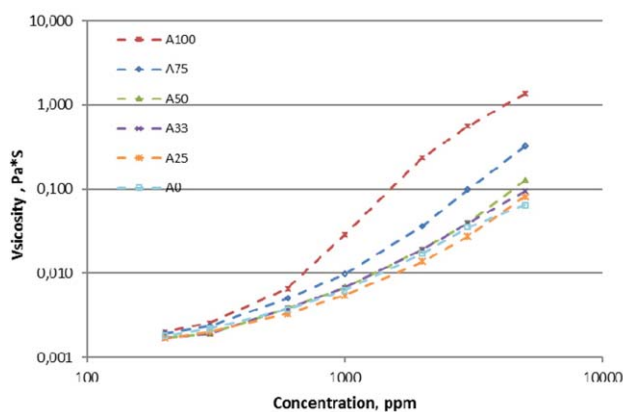
## RESULTS AND DISCUSSION

### Degree of Hydrophobe

**Steady Shear Flow Measurements.** Figure 2 shows the shear viscosity as a function of concentration for polymer A in 0.085M NaCl at increasing relative hydrophobicity. At low polymer concentration, below 600 ppm, which can be assumed as the dilute concentration regime, the effect of relative hydrophobicity on solution viscosity is limited. However, above 600 ppm, behavior of A100 starts to deviate from the other polymer solutions with a steep increase in viscosity as a function of concentration. This gives rise to the assumption that the polymer solution has reached a critical overlap concentration ( $C^*$ ), where the individual polymer molecules start to overlap in the semidilute regime. For associative polymers, this overlap of individual polymer molecules may give rise to intermolecular interactions between the hydrophobic groups, and thus to a steep increase in viscosity. By increasing the polymer concentration to a concentration in the semidiluted regime, the associative polymers exhibit a higher viscosity increase compared to the standard equivalent (A0),<sup>19</sup> and the crossover becomes sharper as the relative hydrophobicity increases from A25 to A100. Earlier, it has

**Table II.** Composition of Brines

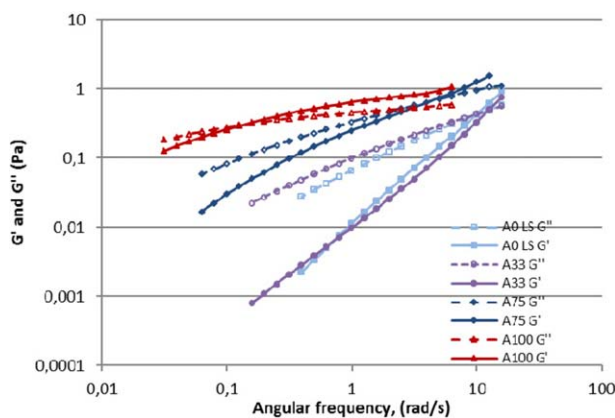
Component	Molecular weight (g/mol)	Composition at 1 kg solution							
		Low salinity (M)	Low salinity (ppm)	5 wt % (M)	5 wt % (ppm)	10 wt % (M)	10 wt % (ppm)	High salinity (M)	High salinity (ppm)
Na <sup>+</sup>	22.99	0.086	1967	0.856	19,670	1.71	39,340	1.14	26,198
Ca <sup>2+</sup>	40.08	-	-	-	-	-	-	0.10	4089
K <sup>+</sup>	39.10	-	-	-	-	-	-	0.27	10,489
Cl <sup>-</sup>	35.45	0.086	3033	0.856	30,330	1.71	60,660	1.58	56,174
HCO <sub>3</sub> <sup>-</sup>	61.02	-	-	-	-	-	-	0.024	1453
SO <sub>4</sub> <sup>2-</sup>	96.07	-	-	-	-	-	-	0.0035	338
TDS (ppm)	-	-	5000	-	50,000	-	100,000	-	98,742
Ionic strength (M)	-	0.086	-	0.856	-	1.71	-	1.72	-



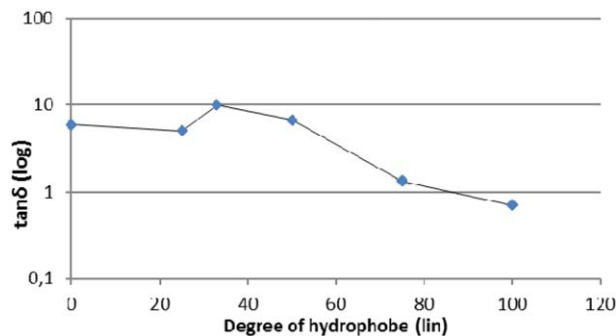
**Figure 2.** Shear viscosity as a function of concentration for polymer A series in 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

been shown that the viscosity increase is sharper for polymers with longer hydrophobic groups.<sup>9</sup> Martinez *et al.*<sup>26</sup> found that a chain length of minimum of six carbon atoms were necessary to see an associative effect of the hydrophobic groups. From Figure 2, one can draw the conclusion that to get a strong effect of the associative polymer with regard to viscosity enhancement, one need to cross a threshold value of the amount of hydrophobic groups present in the polymer.<sup>9,24</sup> For A0 to A75, there is typical polyelectrolyte behavior in 0.086M NaCl, with a steady increase in viscosity with increase in concentration. For A100, however, there is a sharp increase in viscosity with concentration at polymer concentrations above 600 ppm, due to the formation of intermolecular hydrophobic interactions.

**Viscoelasticity.** We have shown that the viscosity increases in the polymer solutions with addition of hydrophobic groups in modified polyacrylamide. However, the viscoelasticity is also strongly influenced by the addition of hydrophobic groups.<sup>27</sup> From Figure 3, the loss modulus ( $G''$ ) and the storage modulus ( $G'$ ) are plotted against angular frequency for 5000 ppm solution of A0, A33, A75, and A100 in 0.086M NaCl. The slopes of the  $G'$  curves change when increasing hydrophobicity. The solu-



**Figure 3.** Frequency sweep of 5000 ppm solutions of A0, A33, A75, and A100 in 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.**  $\tan \delta$  as a function of degree of hydrophobe at 1 rad/s and 1% strain for 0.086M NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

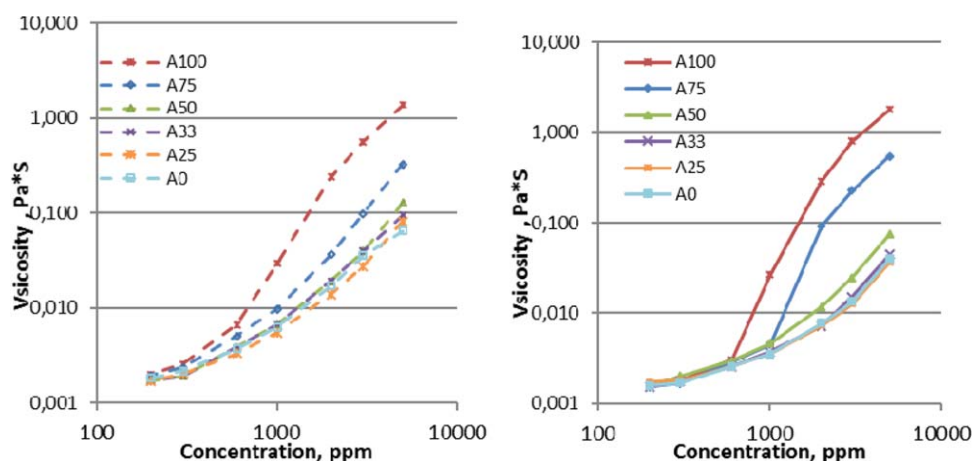
tions of A0 and A33 show a steep increment of  $G'$  when increasing the frequency with a  $\omega^*$  around 10 rad/s. The slope for A75 solution is less steep, however the value of  $G'$  is higher and  $\omega^*$  is shifted to lower values. For A100 solution,  $\omega^*$  is much lower, and  $G'$  does not change much with frequency, which implies that A100 has a more gel like structure than the polymers with lower degree of hydrophobicity. A25 and A50, although not shown, have a similar behavior as A0 and A33.

The loss tangent ( $\tan \delta$ ), obtained at a frequency of 1 Hz and 1% strain, is plotted against the degree of hydrophobe at 0.086M NaCl in Figure 4. With increasing the hydrophobicity, the loss tangent decreases towards a  $\tan \delta$  close to 1. At this frequency, only the solution of A100 shows an elastic behavior with a  $\tan \delta$  value below 1. The error in each of these points is about 3%.

### Effect of Salt

**Steady Shear Flow Measurements.** Figure 5, viscosity as a function of concentration at different salinities, shows a significant change in behavior for A75 solution, with an increase in salinity. At 0.086M NaCl brine, is the slope of the viscosity versus concentration plot for A75 similar to the polymers with lower hydrophobicity, in the semidilute regime ( $>600$  ppm). With addition of salt and increase in the ionic strength, there is a significant change in the slope of the viscosity versus concentration plot starting at a polymer concentration around 1000 ppm. This indicates the onset of significant intermolecular hydrophobic interactions due to the aqueous phase becoming a poorer solvent for the hydrophobic groups at increasing ionic strength.<sup>11</sup> In addition to having higher ionic strength, the high salinity aqueous phase also contains divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and anions different from  $\text{Cl}^-$  ( $\text{HCO}_3^-$ ,  $\text{SO}_3^{2-}$ ). Thus, whether the observed response is due to specific ion effects or ionic strength is not clear. To further investigate this, A0, A75, and A100 were used further in two NaCl brines, 0.86 and 1.71M NaCl (Figures 6 and 7). The 1.71M NaCl has the same ionic strength as the high salinity brine, and thus serves as a direct comparison of ionic strength versus specific ion effects.

The hydrophobe-free polymer, A0, behaves as can be expected from a polyelectrolyte in saline solution. In the dilute regime the polymer chains do not entangle, and the ionic units within the polymer backbone lead to repulsion and expansion of the

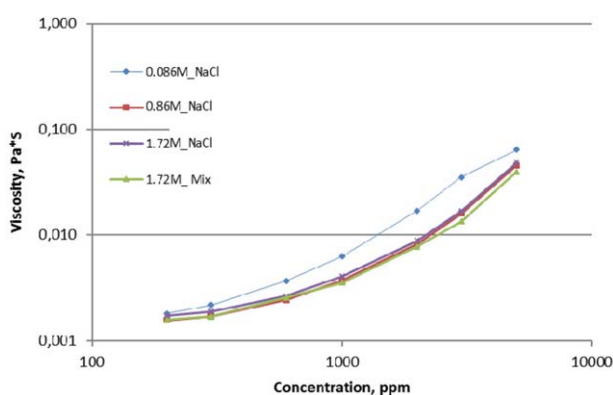


**Figure 5.** Concentration as a function of shear viscosity at  $10 \text{ s}^{-1}$  for polymer A in  $0.086 \text{ M NaCl}$  (left) and  $1.72 \text{ M}$  mixed solution (right). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

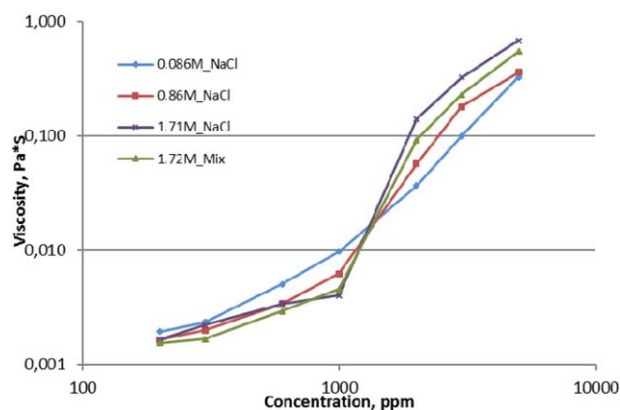
polymer coils. This gives a high hydrodynamic radius for each coil, which leads to higher viscosity. Addition of salt to the polymer solution, leads to electrostatic screening of the charges within the polymer chain, and the Coulomb repulsion becomes less effective<sup>10</sup> (Figure 6). This leads to contraction of the chains, a reduction in the hydrodynamic radius and thus a decrease in viscosity. In Figure 6, the viscosity of A0 in different solvents is plotted against the concentration at  $10 \text{ s}^{-1}$ . The  $0.086 \text{ M NaCl}$  has a higher viscosity all over compared to the other brine. From  $0.086 \text{ M NaCl}$  to  $0.86 \text{ M NaCl}$ , the viscosity of the polymer decreases. The viscosity measurement with  $1.71 \text{ M NaCl}$  and HS is almost the same at  $0.86 \text{ M NaCl}$ , and it seems to be little effect of adding salt beyond  $0.86 \text{ M NaCl}$ . All the charges within the solution are here already screened and there is little or no effect of adding more salt to the solvent. This result is in accordance with Levitt *et al.*'s<sup>3</sup> viscosity study, which showed that above 3% NaCl in the solvent there is no significant difference in viscosity in HPAM solutions.

From Figure 7, the shear viscosity at  $10 \text{ s}^{-1}$  is plotted against the concentration of the polymer solutions. In the dilute area ( $c < 600 \text{ ppm}$ ), the A75 behaves like a polyelectrolyte: the low

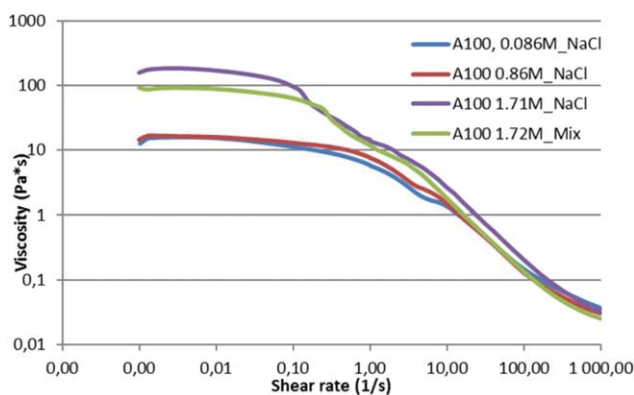
salinity solution has the highest viscosity, and viscosity is reduced with addition of salt.<sup>3,28</sup> In the dilute regime the coils are not in contact with each other, and interaction between hydrophobic groups is mainly intramolecular. Addition of salt screens the electrostatic charges along the backbone chain of the polymer and gives tighter intramolecular interactions. The effect increases with higher ionic strength of the solvent. Above a polymer concentration of  $1000 \text{ ppm}$ , there is a change in viscosity response to salinity and, at polymer concentrations above  $1000 \text{ ppm}$ , the lowest viscosities are found for the  $0.086 \text{ M}$  solution. The viscosities increase in the order  $0.086 \text{ M NaCl} < 0.86 \text{ M NaCl} < 1.72 \text{ M mixed} < 1.71 \text{ M NaCl}$ . While the increase in viscosity with increasing NaCl concentration from  $0.086 \text{ M NaCl}$  to  $1.71 \text{ M NaCl}$  is in accordance with previous observations for associative polymers,<sup>11</sup> and can be attributed to enhanced intermolecular hydrophobic associations, the reason for the difference in viscosity between the  $1.72 \text{ M mixed}$  and  $1.71 \text{ M NaCl}$  brine is not clear. The brines have the same ionic strength but differ in ionic composition. The high salinity brine contains five different salt, and among them,  $\text{CaCl}_2$ . The presence of the  $\text{Ca}^{2+}$  ion leads to lower viscosity in HPAM, and might be the



**Figure 6.** Viscosity A0 at constant shear rate of  $10 \text{ s}^{-1}$ , as a function of concentration. Measured in  $0.086 \text{ M NaCl}$ ,  $0.86 \text{ M NaCl}$ ,  $1.71 \text{ M NaCl}$ , and  $1.72 \text{ M}$  mixed solution solvents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



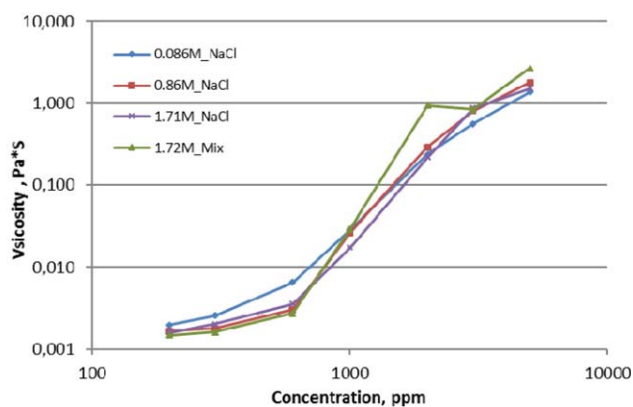
**Figure 7.** Viscosity of A75 solutions at constant shear rate of  $10 \text{ s}^{-1}$ , as a function of concentration. Measured in  $0.086 \text{ M NaCl}$ ,  $0.86 \text{ M NaCl}$ ,  $1.71 \text{ M NaCl}$ , and  $1.72 \text{ M}$  mixed solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Shear viscosity of stock solutions (5000 ppm) of A100 in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

reason that the high salinity brine also has lower viscosity in the associative polymer, although other effects cannot be excluded due to competition between hydrophobic and electrostatic interaction.

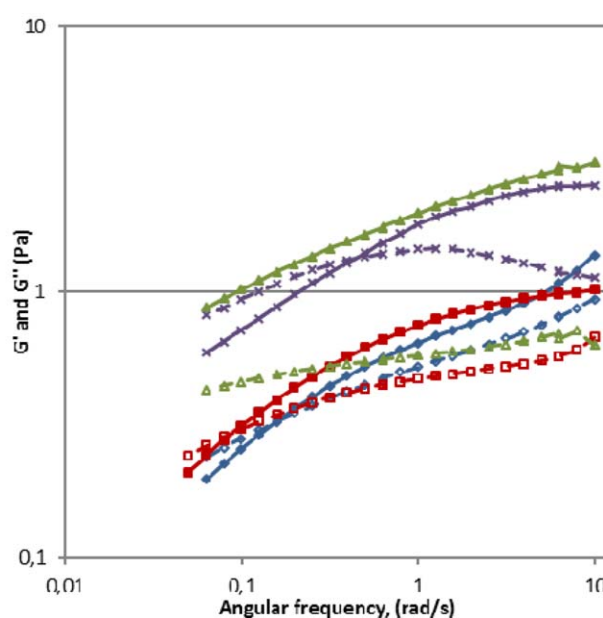
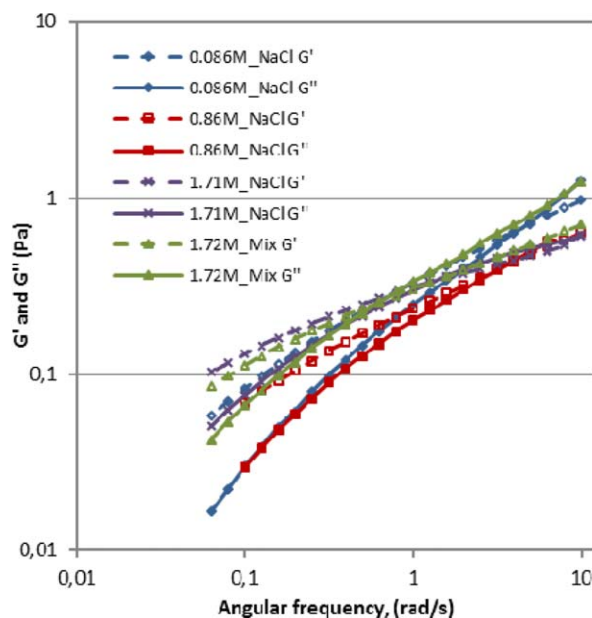
Variation in viscosity depends significantly on the polymer concentration.<sup>9</sup> While viscosity curve of A75 solution showed a significant change of behavior from 0.086M to 0.86M NaCl in the impact of salinity on viscosity profile of A100 is only observed for salt concentration above 0.86M NaCl (Figure 8). The increase in viscosity is more evident in the low shear rate area, and shows a steep increase in viscosity above 0.86M NaCl, this effect is not as obvious at  $10 \text{ s}^{-1}$ . In 0.086M NaCl, the polymer behaves like an associative polymer; however, this trend is enhanced with an increase in salinity (Figure 9). The sudden change in slope at  $c^*$  (600 ppm) is more distinct and gives a higher increase in viscosity from 600 to 2000 ppm. In the dilute



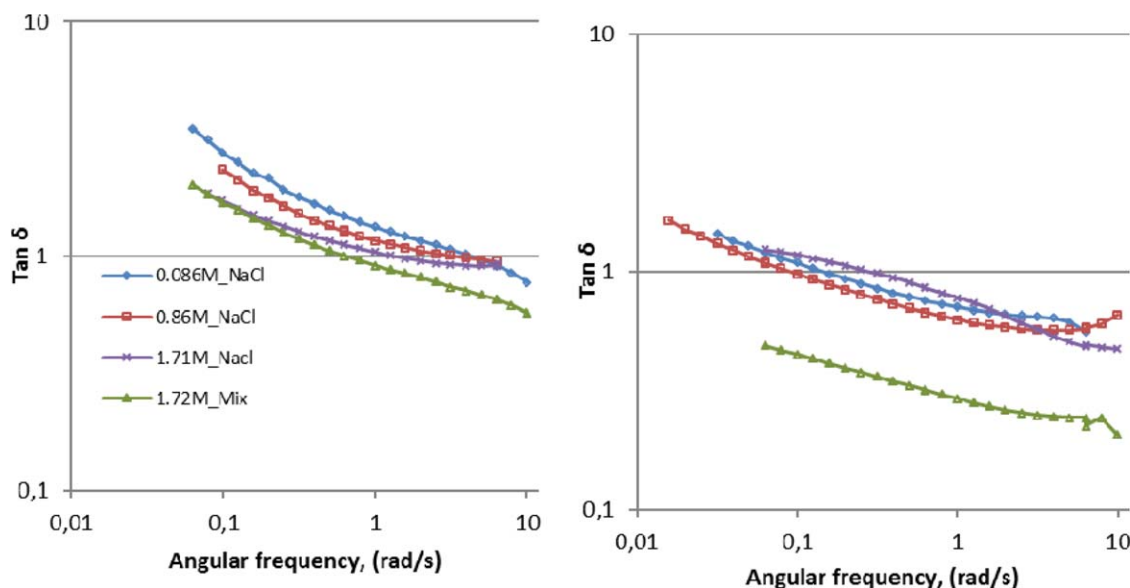
**Figure 9.** Shear viscosity at  $10 \text{ s}^{-1}$  against concentration for A100 in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

regime is the viscosity for the higher salinity solutions lower than for 0.086M NaCl, this is due to the intramolecular interactions within the coils, which are strengthened with the addition salt.

**Linear viscoelasticity.** Loss modulus ( $G''$ ) and storage modulus ( $G'$ ) are plotted against angular frequency for A75 and A100 in the four brines (Figure 10). For the A75 solutions, the 0.086M and 0.86M NaCl has a small deviation in the elastic modulus at high frequencies, and viscous modulus is higher for 0.086M NaCl than for 0.86M NaCl. The  $\omega^*$  shift is at the same angular frequency, however with a lower value of  $G'$  and  $G''$ . The 1.72M mixed solution has a both higher storage modulus and loss modulus than the 1.71M NaCl solution, and a shift in  $\omega^*$  toward the left.



**Figure 10.**  $G'$  and  $G''$  for stock solution (5000 ppm) of A75 (left) and A100 (right) in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11.** Loss tangent ( $\tan \delta$ ) for stock solution (5000 ppm) of A75 (left) and A100 (right) in 0.086M NaCl, 0.86M NaCl, 1.71M NaCl, and 1.72M mixed solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

For A100 solutions,  $G'$  and  $G''$  are much lower for 0.086M NaCl and 0.86M NaCl brines than for the 1.71M NaCl and 1.72M mixed brines. The  $\omega^*$  shift toward the left from 0.086M NaCl to 0.86M NaCl, and the storage modulus decreases. From 0.86M to 1.71M NaCl, the  $\omega^*$  increases and shift toward the right. For the mixed high salinity solution,  $G'$  is above  $G''$  for all the frequencies indicating that  $\omega^*$  is shifted far to the low values.

1.71M NaCl and 1.72M mixed brines have the same ionic strength but the second ones contain divalent cations. The 1.72M mixed solution contributes to a higher elastic effect in the polymers with relative high hydrophobicity, "... which might be due to the presence of divalent cations or be a Hofmeister effect: in the mixed solutions  $\text{SO}_4^{2-}$  ions, which can strengthen the hydrophobic interactions, are present." This effect is more evident in A100 with a high elastic modulus within the whole frequency sweep. In Figure 11, the polymer solutions from Figure 10, is presented as loss tangent as a func-

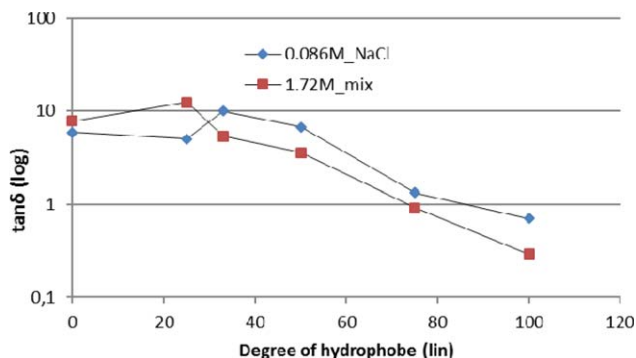
tion of angular frequency. The difference in elasticity is more evident as regards to the loss tangent. 1.72M mixed solution is the brine that contributes most to the elasticity with the presence of divalent cations, and the effect is enhanced with an increase in hydrophobicity. Increasing salinity induces a shift towards more elastic behavior of the solutions of associative polymers. Divalent cations enhance this effect.

In Figure 12, the loss tangent is plotted as a function of the degree of hydrophobe in 0.086M NaCl and 1.72M mixed solution. The polymers with no or relative low hydrophobicity, A0 and A25, has a higher elasticity in the 0.086M NaCl than in the 1.72 M mixed solution. However, this change as the hydrophobicity increases, and around 0.33 relative amount of hydrophobic groups (polymer A33), the highest elasticity in the two brines is found for the polymer solutions with the mixed brine. This is likely due to the onset of intermolecular hydrophobic associations as the polarity of the solvent is increased in the presence of a sufficient amount of hydrophobic groups. In the mixed high salinity brine, the polymer with more than 0.75 relative amount of hydrophobic groups present an elastic behavior, whereas for the 0.086M NaCl solution, the level of hydrophobic moieties has to be raised to at least 0.9.

## CONCLUSIONS

The effect of degree of hydrophobicity on shear viscosity and viscoelasticity for an associative polymer was investigated and correlated with the presence of salt at different ionic strengths and ion compositions.

Regardless of ionic strength, there is significant increase in shear viscosity at polymer concentrations above 600 ppm with increasing degree of polymer hydrophobicity from 50 to 75% relative hydrophobicity. At lower relative hydrophobicity, the degree of hydrophobicity only has a limited effect on shear viscosity. Thus, one needs to cross a threshold value of



**Figure 12.**  $\tan \delta$  as a function of the degree of hydrophobe at 1 rad/s and 1% strain for 0.086M NaCl and 1.72M mixed solution with polymer concentration of 5000 ppm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

hydrophobicity in the polymer to get onset of sufficient associative behavior to significantly influence shear viscosity.

Below 75% relative hydrophobicity, the shapes of the shear viscosity versus polymer concentration plots are similar to those of non-associating polyelectrolytes for all investigated brine compositions. The same is true for the polymer with 75% hydrophobicity (A75) at 0.086M NaCl brine. However, with an increase of salinity to 0.86M NaCl, there is a distinct change in the shape of the shear viscosity against concentration plots for A75. Thus, increasing salinity promotes hydrophobic associations when the relative hydrophobicity is high enough for the onset of sufficient associative behavior.

The storage modulus also increases with an increase in ionic strength. However, the elasticity seems to be more affected by the divalent salts than the ionic strength. The effect of divalent ions is not this evident in the shear viscosity.

In both, 1.71M NaCl and 1.72M mixed solution at 1000 ppm, has A100 one order of magnitude higher viscosity than A0, which implies a much more suited polymer for high salinity reservoirs.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge SNF for supplying polymer samples.

#### REFERENCES

1. Lake, L. W. *Enhanced Oil Recovery*; Prentice Hall: California, **1989**; p 550.
2. Sorbie, K. S. *Polymer-Improved Oil Recovery*; Blackie: Glasgow, **1991**; p 359.
3. Levitt, D.; Pope, G. A. *Selection and Screening of Polymers for Enhanced-Oil Recovery*; Society of Petroleum Engineers.
4. Dupuis, G.; Rigolini, J.; Clisson, G.; Rousseau, D.; Tabary, R.; Grassl, B. *Anal. Chem.* **2009**, *81*, 8993.
5. Pancharoen, M. *Physical Properties of Associative Polymer Solutions*; Stanford University: Stanford, CA, **2009**.
6. Feng, Y.; Billon, L.; Grassl, B.; Bastiat, G.; Borisov, O.; François, J. *Polymer* **2005**, *46*, 9283.
7. Petit-Agnely, F. I. I. *Langmuir* **2000**, *16*, 9921.
8. Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. *Prog. Polym. Sci.* **2011**, *36*, 1558.
9. Kujawa, P.; Audibert-Hayet, A.; Selb, J.; Candau, F. *Macromolecules* **2006**, *39*, 348.
10. Roland Reichenbach-Klinke, B. L.; Benjamin, W.; Christian, S.; Gregor, B. *Soc. Petrol. Eng.* **2011**, doi:10.2118/141107-MS.
11. Feng, Y.; Grassl, B.; Billon, L.; Khoukh, A.; François, J. *Polym. Int.* **2002**, *51*, 939.
12. Thormann, E. *RSC Adv.* **2012**, *2*, 8297.
13. Taylor, K. C.; Nasr-El-Din, H. A. *Hydrophobically Associating Polymers for Oil Field Applications*; In Canadian International Petroleum Conference, Petroleum Society of Canada: Calgary, Alberta, **2007**.
14. Volpert, E.; Selb, J.; Candau, F. *Macromolecules* **1996**, *29*, 1452.
15. Regalado, E. J.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580.
16. Chassenieux, C. N.; Benyahia, T. L. *Colloid Interface Sci.* **2011**, *16*, 18.
17. Gupta, P.; Elkins, C.; Long, T. E.; Wilkes, G. L. *Polymer* **2005**, *46*, 4799.
18. Perttamo, E. K. *Characterization of Associating Polymer (AP) Solutions*; University of Bergen: Bergen, **2013**.
19. Argillier, J. F.; Audibert, A.; Lecourtier, J.; Moan, M.; Rousseau, L. *Colloids Surf. A* **1996**, *113*, 247.
20. Taylor, K. C.; Nasr-El-Din, H. A. *J. Petrol. Sci. Eng.* **1997**, *19*, 265.
21. Penott-Chang, E. K.; Gouveia, L.; Fernández, I. J.; Müller, A. J.; Díaz-Barríos, A.; Sáez, A. E. *Colloids Surf. A* **2007**, *295*, 99.
22. Vermolen, E. C. M.; van Haasterecht, M. J. T.; Masalmeh, S. K. *A Systematic Study of the Polymer Visco-Elastic Effect on Residual Oil Saturation by Core Flooding*; Society of Petroleum Engineers, doi:10.2118/169681-MS.
23. Metzger, T. G. *The Rheology Handbook*, 3rd ed.; Vincentz Network: Hannover, **2011**; p 434.
24. Kujawa, P.; Audibert-Hayet, A.; Selb, J.; Candau, F. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 1640.
25. Gaillard, N.; Favero, C. U.S. Pat. 7,700,702 (**2010**).
26. Martínez-Ruvalcaba, A.; Chornet, E.; Rodrigue, D. *Carbohydr. Polym.* **2007**, *67*, 586.
27. Caputo, M. R.; Selb, J.; Candau, F. *Polymer* **2004**, *45*, 231.
28. Flory, P. J.; Osterheld, J. E. *J. Phys. Chem.* **1954**, *58*, 653.