A rheological investigation of a high temperature organic gel used for water shut-off treatments

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Abstract

Polyacrylamide-based gels are used in many water shut-off treatments. In this study, a copolymer of polyacrylamide/tert-butyl acrylate is cross-linked with polyethyleneimine. The kinetics parameters of the gelation reactions were determined using steady shear viscometry at temperatures of 80 to 130 °C.

The addition of salts to the mixing water was found to increase the gelation time. On the other hand, higher polymer and cross-linker concentrations reduced the gelation time. The activation energy was found to be 118 kJ/mol in distilled water and decreased to 93 kJ/mol in seawater. The reaction orders were found to be first order with respect to both PA and PEI. The effects of initial pH and contamination with iron(III) on the gelation time were also examined in detail. Recommendations for field application of this gelling system are given.

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Keywords: Polyacrylamide-based gels; Organic cross-linkers; Gelation kinetics

1. Introduction

As oil and gas reservoirs mature, water production increases. The cost of lifting, separating, treating and disposing produced water is high. Moreover, problems such as scale, corrosion, emulsion, bacteria, and sand production can arise as a result of excessive water production. It is estimated that for each barrel of oil produced worldwide, an average of three barrels of water are produced. Disposing of the produced water costs $40 billion every year (Bailey et al., 2000) and, therefore, it is essential to minimize water production.

Several techniques are available for water shut-off including mechanical and chemical means. The choice of a specific method to reduce water production depends on the candidate well. Chemical means, including gelling polymers are cost effective as they do not necessarily require a workover rig and they control water production for a longer period of time. In addition, the gelling solution can be placed deep into the reservoir by controlling the gelation time (Hutchins et al., 1996).

Water-soluble polymers such as polyacrylamides and polysaccharides have been used as means for improved oil recovery since the 1950s (Prud’homme et al., 1983). These polymers are cross-linked to form three-dimensional structures. For polyacrylamide-based gels, the
cross-linker can be either metallic or organic. In metallic cross-linking, the carboxylate groups of the polymer chain react with multivalent cations forming ionic bonds. Chromium is the most commonly used metallic cross-linker. The chromium cross-linkers, especially those based on Cr⁶⁺ (Lockhart, 1991), are toxic and do not meet the current environmental regulations. Moreover, the ionic bonds are unstable at temperatures greater than 70 °C (Moradi-Araghi, 2000). Another concern with inorganic cross-linkers is their short gelation times at temperatures greater than 60 °C (Albonico et al., 1994; Lockhart, 1994). At temperatures greater than 100 °C, polyacrylamide-based polymers exhibit hydrolysis and oxidative degradation of the polymer chains (Moradi-Araghi and Doe, 1987). Also, at temperatures greater than 75 °C, and in the presence of multivalent cations, overcross-linking occurs, which results in expulsion of water out of the gel structure, known as syneresis (Moradi-Araghi and Doe, 1984).

Organically cross-linked gels (OCP) are known to have good stability at elevated temperatures. This is attributed to the covalent bonds between the polymer and the organic cross-linker (Moradi-Araghi, 2000). There are several organically cross-linked gels reported in the literature such as phenol and formaldehyde (Moradi-Araghi, 1994). These gels were reported to be stable at temperatures up to 150 °C (Moradi-Araghi et al., 1993). However, phenol and formaldehyde are not environmentally friendly (Moradi-Araghi, 1994). One way to overcome this problem is to use precursors of phenol and formaldehyde such as phenyl acetate and hexamethylenetetramine (HMTA) that thermally hydrolyze in situ forming phenol and formaldehyde, respectively.

A copolymer of acrylamide and tert-butyl acrylate (PAtBA) cross-linked with polyethyleneimine (PEI) was reported to be stable at high temperatures (Hardy et al., 1998, 1999). Due to the high temperatures encountered in some local oil and gas reservoirs, the PAtBA/PEI system was investigated in this study. The PEI cross-linker has a low toxicity and was approved for food contact in the USA (Reddy et al., 2003).

Several researchers examined the propagation and ability of this gel system to reduce permeability of reservoir cores (Hardy et al., 1998; Hoek et al., 2001; Alqam et al., 2001; Okasha et al., 2001; Zitha et al., 2002; Vasquez et al., 2003). The gel strength of this system in bulk was also reported (Al-Muntasher et al., 2007a). Hardy et al. (1999) and Polo et al. (2004) reported field applications of this gelling system in the North Sea and south of Mexico, respectively.

A successful water shut-off treatment requires careful examination of key factors that affect the gelation time and a thorough examination of compatibility between the gelling solution and reservoir fluids. Temperature is a key parameter that determines the gelation time. The gelation time at reservoir temperature is needed to find out how deep the gel can be placed in the formation and how long the shut-in time should be. At room temperature, the viscosity of the gelling solution increased over a period of several days, but no strong gel was noted. It is clear from this result that the gelling solution should be pumped within a few hours following mixing on the surface. It will be difficult to pump a gelling solution that has been sitting in the mixing tank for several days. In addition to temperature, it is important to examine the effect of polymer and cross-linker concentrations on the gelation time.

Therefore, the objectives of this study were to: (1) determine the effects of the following parameters on the gelation time: type of mixing water, type and concentration of simple inorganic salts, initial pH, temperature, polymer concentration, cross-linker concentration, and contamination with ferric iron, (2) explain variations in the gelation time in terms of published gelation mechanisms, (3) examine compatibility of gelling solution with reservoir fluids, and (4) give recommendations for field application.

2. Experimental studies

2.1. Materials

The gelling system consisted of the PAtBA copolymer cross-linked with an organic cross-linker, PEI. Both chemicals were received in liquid form and were used without further purification. The active contents of the polymer and the cross-linker were determined by thermogravimetric analysis (TGA) and were found to be 20 and 30 wt.%, respectively. The activity of PAtBA was further confirmed by precipitation in pure ACS grade isopropanol following the procedure described by Taylor and Nasr-El-Din (1994). The activities of PAtBA and PEI agree with those reported by Zitha et al. (2002).

All gel compositions are reported in terms of the concentration of the active chemical present in the sample received. Most of the gelation tests were conducted with a polymer concentration of 7 wt.% and a cross-linker concentration of 0.3 wt.%. The pH value of gelling solution at these concentrations was found to be 8.3. No attempts were made to adjust the pH of the gelling solution, unless otherwise indicated.

The polymer has an initial degree of hydrolysis less than 0.1 mol%. The weight average molecular weight of the polymer is 250,000–500,000 g/mol (Hardy et al., 2000).
147 1999; Reddy et al., 2003). The ester groups of the 148 copolymer represent 5 mol% (Reddy et al., 2003). The 149 degree of hydrolysis and ester content of the polymer 150 were experimentally confirmed by running $^{13}$C Nuclear 151 Magnetic Resonance ($^{13}$C NMR) on the polymer using 152 equipment and procedures given elsewhere (Al-Mun- 153 tasheri et al., 2006). The pH of neat polymer solution is 154 4.2. The molecular weight of PEI is nearly 70,000 g/mol 155 and has a pH of 11.6.

156 Mixing waters with three salinity levels were used to 157 prepare the gelling solutions. These were distilled water, 158 seawater and field mixing waters. Seawater and field 159 mixing waters were filtered to 0.45 μm to remove sus- 160 pended solids. Chemical analyses of the field mixing 161 water (typical mixing water used in Southern fields pres- 162 ent in Saudi Arabia) and seawater from the Arabian Gulf 163 are given in Table 1.

164 The effect of various inorganic salts on the gelation 165 time was examined in detail. Salts examined included: 166 NaCl, KCl, CaCl$_2$·2H$_2$O and FeCl$_3$·6H$_2$O. All salts 167 were ACS grade.

168 3. Gelation mechanism

169 A detailed investigation on the gelation mechanisms 170 of this system is reported by Al-Muntasheri et al. (2006). 171 Hence, a brief summary will be presented in this section. 172 The ester groups (–COO–R') on the PAtBA polymer 173 provide masked cross-linking sites. These groups either 174 hydrolyze or thermolyze according to pH and tempera- 175 ture. At low pH values and temperature, PAtBA hy- 176 drolyzes and forms partially hydrolyzed polyacrylamide 177 (PHPA) and tert-butyl alcohol as confirmed through $^{13}$C NMR by Al-Muntasheri et al. (2006). On the other hand, 178 PAtBA thermolyses at high temperatures and pH 179 values. PAtBA hydrolyze or thermolyze according to pH and temper- 180 ature. At low pH values and temperature, PAtBA hy- 181 drolyzes and forms partially hydrolyzed polyacrylamide 182 (PHPA) and tert-butyl alcohol as confirmed through $^{13}$C NMR by Al-Muntasheri et al. (2006).

183 Table 1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Field water</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>126</td>
<td>592</td>
</tr>
<tr>
<td>Mg</td>
<td>53</td>
<td>2304</td>
</tr>
<tr>
<td>Na</td>
<td>228</td>
<td>19,325</td>
</tr>
<tr>
<td>K</td>
<td>14</td>
<td>730</td>
</tr>
<tr>
<td>Cl</td>
<td>361</td>
<td>31,106</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>233</td>
<td>4108</td>
</tr>
<tr>
<td>HCO$_3$</td>
<td>171</td>
<td>183</td>
</tr>
<tr>
<td>TDS$^a$</td>
<td>1186</td>
<td>58,348</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>7.9</td>
</tr>
</tbody>
</table>

185 All concentrations are in mg/l.

186 $^a$ Total dissolved solids (TDS) were determined by addition.

189 reported the chemical reactions of this system. After the 190 breakage of the ester groups, carboxylate groups are 191 formed. Hardy et al. (1999) reported the cross-linking 192 mechanism of this system as a nucleophilic substitution 193 by an imine nitrogen from the PEI on the carbonyl 194 carbon attached to the ester groups. This should result in 195 a covalent bond between the PEI nitrogen and the ester 196 carbonyl carbon. A second mechanism for the gelation 197 process was reported by several authors (Reddy et al., 198 199; Vasquez et al., 2005) where the PEI nitrogen 200 forms a covalent bond with the acrylamide carbonyl 201 carbon on the PAtBA. In fact, both mechanisms are 202 nucleophilic substitution where the leaving group is 203 substituted by an imine nitrogen (nucleophile) of the 204 PEI. The leaving groups are either the tertiary butyl ester 205 (–CO–O(CH$_3$)$_3$) as in the first mechanism or the 206 amide (–CO–NH) as in the second mechanism.

199 4. Measurement of the gelation time

200 A thorough literature review revealed that the gela- 201 tion time is measured using various techniques and is 202 defined in several ways. The gelation time is defined as 203 the time needed to reach a certain viscosity (Terry et al., 204 1981; Jordan et al., 1982).

205 A second definition for the gelation time is the time 206 needed to reach a specific gel strength (Sydansk, 1993; te 207 Nijenhuis et al., 2003). An oscillatory viscometer is used 208 to measure gel strength evolution as a function of time, 209 hence determine the gelation time. The point that cor- 210 responds to the maximum slope in the elastic modulus– 211 time curve has been defined as the gelation point (Prud- 212 homme and Uhl, 1984).

213 A third definition of the gelation time is the time 214 needed for the elastic and viscous moduli to intersect 215 (Mortimer et al., 2001). A more precise definition is the 216 time at which the moduli ratio becomes independent of 217 frequency (Ponton et al., 2002).

218 In the present study, the gelation time is defined as 219 the time needed to reach the inflection point on the 220 viscosity–time curve (Fig. 1). The inflection point cor- 221 responds to the onset of the gel formation (Hardy et al., 222 1998) and has been used by several authors to determine 223 the gelation time (Jurinak et al., 1991; Broseta et al., 224 2000; Reddy et al., 2003; Vasquez et al., 2005).

225 Steady shear measurements were performed using a 226 Brookfield viscometer (Model PVS) with Couette geom- 227 etry. The outer and inner radii of the cup and bob were 228 3.8 and 3.4 cm, respectively. Sample volume was 30 ml. 229 Viscosity measurements during gelation were made at 230 various temperatures up to 150 °C. The shear rate was 231 kept constant at 8.52 s$^{-1}$. In order to prevent sample 232
evaporation, nitrogen gas was used to pressurize the system up to 2.07 MPa (300 psi). The elastic modulus was measured using an ARES rheometer at room temperature with a cone and plate geometry. The angle of the cone was 1° and the plate diameter was 25 mm.

Samples of the gelling solutions were prepared at room temperature and loaded immediately into the viscometer, which was set at the desired test temperature. It should be noted that zero time was taken as the time the gelling solution was placed in the viscometer. Table 2 lists the parameters investigated in the present work and their ranges.

5. Results and discussion

5.1. Effect of mixing water on the gelation time

Gels can be prepared in the field using fresh water, aquifer water or seawater. These waters contain various ions that can impact the gelation process. Therefore, it is of interest to measure the gelation time for gels prepared in various waters (Table 1). Fig. 2 shows the viscosity evolution for two gelling solutions that contained 0.3 wt.% PAIBA/PEI. The first solution was prepared in distilled water (initial pH of 8.3); whereas the second solution was prepared in seawater (initial pH of 8.7). Viscosity measurements were conducted at 120 °C. The gelation time for the gel prepared in distilled water was 1.5 h. However, the gelation time was doubled for the gel that was prepared using seawater.

It is clear from the data shown in Fig. 2 that increasing the salt content of the mixing water increased the gelation time. These results can be explained as follows. The initial degree of hydrolysis of the polymer is less than 0.1 mol% and its ester content is nearly 5 mol%. At high temperatures, the ester groups will thermolyze/hydrolyze into carboxylate groups, which carry negative charges. Carboxylate groups can also form upon the hydrolysis of the amide groups of the polymer in alkaline conditions (Kurenkov et al., 2001). The repulsive forces between the negative charges will increase the hydrodynamic volume of the polymer chains. As a result, the cross-linking sites become more accessible to the cross-linker molecules. This explains the short gelation time that was noted when distilled water was used to prepare the gel.

On the other hand, the concentrations of mono- and divalent cations in seawater are high (Table 1). These cations shield the negative charges available on the carboxylate groups and, as a result, the polymer chains collapse (Ward and Martin, 1981; Nasr-El-Din et al., 1991). Consequently, potential cross-linking sites on the polymer chain are not as accessible to the cross-linker molecules. The gelation induction period will be longer in this case and hence the gel will take a longer period of time to form. The effect of simple inorganic salts on the gelation time was noted with other polyacrylamide-based gelling systems (Kakadjian et al., 1999; Broseta et al., 2000; Romero-Zeron et al., 2004).

The most important aspect of the results shown in Fig. 2 is that the gelation time is strongly dependent on the salt content (ionic strength) of the mixing water. The viscosity deeps and humps noted in Fig. 2 will be discussed in the gelation kinetics section. Therefore, the
gelation time should be measured for gels that are prepared using either the field water or a mixing water representative of that used in the field. Using a different type of water can cause large differences between the measured and the actual gelation time in the field. This can lead to inadequate shut-in time or premature gelling during pumping the solution, which can cause operational problems.

5.2. Effect of monovalent cations on the gelation time

The effect of the salt content (ionic strength) of the mixing water on the gelation time was significant. It was decided to examine the effects of mono- and divalent cations on the gelation time separately. Gelling solutions were prepared and various amounts of sodium chloride were added such that the final polymer and cross-linker concentrations were 7 and 0.3 wt.%, respectively. The gelation time was measured at a temperature of 120 °C. Fig. 3 shows the effect of sodium ion concentration on the gelation time. The gelation time increased when 5000 mg/l of sodium ions was added to the gelling solution. The gelation time further increased with increasing sodium ion concentration and reached 14 h at 50,000 mg/l of sodium ions. Fig. 3 also shows that the effect of potassium ion on the gelation time was similar to that of the sodium ions. However, sodium ions delayed gelation more than potassium ions. This is mainly because of the higher charge density (ionic charge/size) of sodium ions compared to that of the potassium ions (Uddin et al., 2002).

5.3. Effect of divalent cations on the gelation time

The effect of divalent cations on the gelation time was also examined. Fig. 4 shows that Ca$^{2+}$ delayed the cross-linking reaction more than K$^+$. Calcium ions are divalent, whereas potassium ions are monovalent. The charge/size ratio for calcium ions is twice that of potassium ions. This result suggests that the gelation time is a function of the charge/size ratio of the cation that is present in the mixing water.

From the previous discussion, it is clear that mono- and divalent cations increase the gelation time. If only saline water is available on site, then the gelation time can be reduced by either increasing the concentration of the polymer or the cross-linker.

Shorter gelation times at higher salinity levels can be obtained by adding more polymer, Fig. 5, or cross-linker, Fig. 6. However, adding too much cross-linker may cause over-cross-linking and loss of gel volume with time, which is known as gel syneresis (Eggert et al., 1992). It should be noted that syneresis is not desirable, especially when the gel is placed in naturally fractured reservoirs. This is because the reduction in gel volume will generate new flow paths, which will reduce the effectiveness of the gel treatment (Bryant et al., 1996).

It was visually observed that gels prepared in saline water were physically weaker than those prepared in distilled water. To further investigate the effect of salts on gel strength, the elastic modulus, \(G'\), for various gels was measured in the linear viscoelastic region at a frequency of 0.3 rad/s. The procedure described by Al-Muntasheri et al. (2007a) was followed. Table 3 summarizes \(G'\) values for gel samples prepared in different salinity brines. The elastic modulus or gel strength was highest for gels prepared in distilled water. The elastic modulus decreased by nearly 45% when the gel was prepared in the field mixing water. The elastic modulus decreased as the concentration of sodium ion was increased. Potassium ions at 5000 mg/l also decreased the elastic modulus of the gel.

5.4. Effect of the initial pH value on the gelation time

To examine the effect of the initial pH value on the gelation time, the initial pH value of the gelling solution was adjusted by adding a few drops of either 1 N NaOH or 15 wt.% HCl. The viscosity was measured as a
function of time at a constant shear rate and a temperature of 120 °C (Fig. 7).

A rapid increase in the viscosity of the gelling solution was noted at initial acidic pH conditions. The apparent viscosity reached the maximum viscosity that can be measured with the viscometer (35.6 Pa s); however, it gradually decreased to 7000 mPa s after a few hours (Fig. 7). The gel formed under acidic conditions did not last for a long period of time. According to Hardy et al. (1999) and Meszaros et al. (2004) the free-pair of electrons on the imine nitrogen of PEI becomes more protonated at low pH value. As a result, PEI nucleophilicity decreases making it less effective in cross-linking the PAtBA. This may lead to gel breakage that was noted in the results shown in Fig. 7.

At pH = 8.3, Fig. 8, the gelation time was nearly 1.6 h. The viscosity started to increase after 1.5 h and monotonically increased with time. A similar trend was noted at pH = 11.9, however, the gelation time increased to nearly 2.7 h. This delay in the cross-linking reaction is most likely due to sodium ions that were introduced to the gelling solution with the addition of sodium hydroxide.

The most important conclusion that can be inferred from these results is that the gelation time depends on the initial pH value of the solution. Low pH values can adversely affect the gelation process. A pH value of at least 8 is needed to produce a stable gel under the conditions given in Fig. 8.

5.5. Gelation kinetics

5.5.1. Effect of temperature on the gelation time

Fig. 9 shows the viscosity evolution obtained at various temperatures (80 to 135 °C), and a pressure of 2.07 MPa (300 psi). Measurements were conducted on gelling solutions that contained 7 wt.% PAtBA and 0.3 wt.% PEI prepared in distilled water. At 80 °C, the initial apparent viscosity was nearly 10 mPa s and sharply increased after 17 h, indicating the onset of gel formation. At 100 °C, the gelation time decreased to 4.3 h. The gelation time further decreased to 1.9 h at a temperature of 110 °C. Viscosity evolution was similar at all temperatures examined, but the gelation time decreased with increasing temperature. This reflects the endothermic nature of the gelation reactions.

At temperatures of 110 and 120 °C, a gel break point can be seen in Fig. 9 as the apparent viscosity dropped and then resumed its build-up. This trend was noted in the results reported by Vasquez et al. (2005) who examined this system at higher PEI concentrations. It was noted also in the data reported by Broseta et al. (2000) for polyacrylamide cross-linked with chromium acetate. It should be mentioned that this break in viscosity evolution was not considered in the determination of the gelation time, and most probably occurred due to the shear applied while measuring the gelation time.

The gelation time of this system was very short at high temperatures (less than 1 h at 135 °C). Therefore, in high temperature reservoirs, a suitable preflush should...
be used to cool-down the formation and extend the gelation time as needed.

The effect of temperature on the gelation time can be predicted using Arrhenius-type relationship (Hurd and Letteron, 1932; Jordan et al., 1982):
\[
GT = M \exp \left( \frac{E_a}{RT} \right)
\]
(1)

where \( E_a \) is the activation energy in kJ/mol, \( GT \) is the gelation time in hours, \( R \) is the universal gas constant in kJ/mol K, \( T \) is the absolute temperature in K and \( M \) is the frequency factor in hours.

From Eq. (1), a plot of the natural log of \( GT \) vs. \( 1/T \) should give a straight line with a slope of \( E_a / R \) and an intercept of \( \ln M \).

Eq. (1) was used to fit the gelation time for gels prepared in the three mixing waters as shown in Fig. 10. It should be mentioned that these data were obtained at temperatures greater than 100 °C. It is clear that gel prepared in seawater had the longest gelation times at all temperatures examined.

The activation energy, calculated using Eq. (1), decreased with increasing water salinity as shown in Table 4. The variation of \( E_a \) with salt content is similar to that noted with polyacrylamide-based gels (Jordan et al., 1982).

Table 5 gives the literature values reported for the activation energy of various acrylamide-based polymers cross-linked with various organic cross-linkers, including the results obtained in the present study. The data obtained for the gelling system examined are within the same order of magnitude as those reported in the literature. It is important to note that the activation energy extracted from the data reported by Hardy et al. (1999) is slightly lower than those reported in the present study. This is mainly due to preparing the gel using water with different salinities and measuring the gelation time at a different temperature range. Hardy et al. (1999) measured the gelation time at temperatures less than 100 °C; whereas we measured the gelation time at temperatures greater than 100 °C. They also prepared their gel in 2 wt.% KCl brine.

5.5.2. Effect of polymer concentration on the gelation time

The effect of polymer concentration was examined by measuring the viscosity of gelling solutions that
contained 0.3 wt.% PEI and various polymer concentrations from 4.33 to 7 wt.%. In order to simulate field conditions, field mixing water was used to prepare these solutions and viscosity measurements were conducted at a temperature of 120 °C. It can be seen in Fig. 11 that as the polymer concentration was increased, the gelation time decreased. As the polymer concentration or the number of cross-linking sites increases, the rate of gelation increases and hence, the gelation time decreases. The effect of polymer concentration on the gelation time at 0.3 wt.% of PEI and 120 °C can be presented using Eq. (2):

$$ GT = 9.8C_p^{-n} $$

where $C_p$ is the polymer concentration in wt.% and $n$ is the reaction order with respect to the polymer. The reaction order was found to be 1.0, which is in good agreement with the data obtained by Hardy et al. (1999) for this system at polymer concentrations of 3 to 10 wt.% and a cross-linker concentration of 2 wt.% of PEI. Their data were collected at 96 °C using 2 wt.% KCl brine.

5.5.3. Effect of cross-linker concentration on the gelation time

Fig. 12 shows the apparent viscosity of gelling solutions that contained 7 wt.% PAtBA and various cross-linker concentrations as a function of time. Increasing the cross-linker concentration reduced the gelation time. Similar to the effect of polymer concentration, the gelation time was found to vary exponentially with the initial cross-linker concentration according to Eq. (3):

$$ GT = 0.39C_x^{-m} $$

where $C_x$ is the cross-linker concentration in wt.% and $m$ is the reaction order with respect to the cross-linker. The reaction order with respect to PEI is calculated as 1.0 which is in agreement with literature values for this system (Hardy et al., 1999) reported at 96 °C with 8 to 10 wt.% of PAtBA and PEI concentration from 0.5 to 2 wt.%.

5.6. Effect of iron contamination on the gelation time

In a typical field application, the polymer and cross-linker are mixed with water in large tanks that may contain corrosion products. There is a possibility of contamination with Fe(III), especially if the tank contains residual acid (tank bottoms). Similar to Cr(III), Fe(III) is a trivalent cation and can interact with the polymer molecules and affect the gelation time. In order to investigate the effect of
Fe(III) on the gelation time, FeCl₃·6H₂O was added to gelling solutions that contained 7 wt.% PATBA and 0.3 wt.% PEI in distilled water such that the final solutions contained 100 and 1000 mg/l of Fe(III). Then, the apparent viscosity of each solution was measured as a function of time at 120 °C.

**Fig. 13** shows a fast build-up in the apparent viscosity of the gelling solution that contained 100 mg/l Fe(III). A gel was formed that did not break by shear for 10 h. Increasing the concentration of Fe(III) to 1000 mg/l reduced the time needed to build-up the viscosity. The high viscosity did not last more than 25 min, and significantly decreased to 3200 mPa s.

The results shown in **Fig. 13** indicate that Fe(III) did reduce the gelation time at 120 °C. This result indicates that some of the iron(III) ions did cross-link the polymer (via the carboxylate groups). The gel formed at 1000 mg/l iron did not last, indicating the iron contamination can adversely affect the quality of the gel.

**5.7. Implication on field application**

The viscosity of the gelling solution increased with time at ambient conditions. It will be very difficult to pump the gelling solution if it is left for several days after mixing. Therefore, it is recommended to add the cross-linker just before pumping.

The results obtained in the present study highlighted the importance of the salinity of mixing water. It is strongly recommended to prepare the gelling solution using the field mixing water.

It is also important to use clean tanks for mixing the gel in the field. Residual acids can adversely affect the gelation time.

Iron(III) can react with the polymer and accelerate the gelation process and produce a gel that breaks in a short period of time. Therefore, every effort should be made to use clean tanks or better internally coated tanks.

It is advisable not to apply this gel right after acid treatments, especially in sandstone reservoirs. In this case, the concentration of iron in the wellbore area is high. This iron can cause premature setting of the gel. If there is a need to apply gel treatment following an acid treatment, then the well should be allowed to flow back until iron concentration is reasonably low. This procedure will also ensure that there is no residual acid downhole.

The pH of this gel system is greater than 8. The formation brine contains a high concentration of divalent cations (ranges from 10,000 to 15,000 mg/l). There is a potential of divalent cations precipitation once the gelling solution enters the formation. This can cause injectivity problems during gel placement. This problem can be addressed by injection of a low-salinity preflush. The main objective of this preflush is to reduce the concentrations of divalent cations around the critical wellbore area. A second objective is to cool-down the formation. This will give adequate time for gel placement, which is needed in high temperature wells.

There is also a good chance that the gelling solution will be mixed with the native crude oil. The gelling solution has a high pH value and some crude oils contain acidic components (Nasr-El-Din, 1996). Mixing of the two fluids can result in the generation of in-situ surface active species, which can cause emulsion formation. To address this issue, compatibility tests should be conducted using reservoir fluids (oil and produced water).

The gelling system exhibited syneresis at a cross-linker concentration of 1.2 wt.% for gels prepared in the field mixing water or seawater. Therefore, it is very important to use the right cross-linker concentration.

**6. Conclusions**

The gelation time of the PATBA/PEI system was measured as a function of various key parameters. The following conclusions were obtained:

1. Salts of mono- and divalent cations were found to increase the gelation time and this effect was found to be a function of the charge/size ratio of the cation present.
2. The gelation time decreased with temperatures following Arrhenius-type of relationship.
3. The activation energy of PATBA/PEI gelling system was found to be 118 kJ/mol in distilled water and 93 kJ/mol in seawater.

4. The reaction orders with respect to both PAtBA and PEI agree with those reported in literature at temperatures less than 100 °C.

5. Initial pH value showed a strong influence on the viscosity of the gel. Higher viscosities were obtained at high initial pH values. At acidic conditions, the gelation time was short and the gel did not last for a long period of time.

6. The presence of high iron concentration (1000 mg/1 Fe(III)) resulted in short gelation times and the gel did not last for more than a few hours.

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