

Impact of Salts on Polyacrylamide Hydrolysis and Gelation: New Insights

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ABSTRACT: Polyacrylamide (PAM) and its derivatives are the most commonly used polymers in the preparation of polymeric gels for water control in petroleum reservoirs. This study involved the use of polyethylenimine (PEI) as a crosslinker for PAM. In this study, we investigated PAM alkaline hydrolysis at high temperatures. The effects of salts [sodium chloride (NaCl) and ammonium chloride (NH₄Cl)] on the degree of hydrolysis (DH) of PAM were investigated. These salts were used as retarders to elongate the gelation time of the PAM/PEI system. The data obtained from ¹³C-NMR was used to understand the retardation mechanisms by salts. We found that NH₄Cl accelerated the extent of hydrolysis more in comparison with NaCl. Moreover, the apparent viscosity of the hydrolyzed samples was measured. PAM hydrolysis in the presence of NH₄Cl resulted in a lower solution viscosity than that in the presence of NaCl. Therefore, NH₄Cl was more effective in shielding negative charges on the carboxylate groups of the partially hydrolyzed polyacrylamide (PHPA) chain. NaCl and NH₄Cl were compatible with the PHPA/PEI system, but sodium carbonate showed a white precipitate. In addition, high-temperature/high-pressure elastic modulus data were reported for the first time for this system. Differential scanning calorimetry was coupled with rheology to explain the PAM/PEI crosslinking in the presence of salts. Models were developed to assess the impact of the salts on the PAM DH and the induction period before gelation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 41185.

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INTRODUCTION

Polyacrylamide (PAM) is one of the most commonly used water-soluble polymers in oilfield processes. These processes comprise drilling, polymer flooding and other enhanced oil recovery methods, such as alkaline and alkaline-surfactant-polymer (ASP) flooding. In improved oil recovery, PAM is used in water control,¹ friction reduction,² and more recently as a fracturing fluid.³ PAM can be crosslinked with different types of crosslinkers to produce polymeric gels for water control in conformance improvement treatments. These include inorganic crosslinkers such as chromium⁴⁻⁸ and organic crosslinkers such as phenol and formaldehyde⁹ or polyethylenimine (PEI).^{10,11} Chitosan, which is a natural crosslinker, has also been used to form polymeric gels.¹² Organically crosslinked gels are more preferable than inorganic crosslinked gels. This is due to their stability at high temperatures.

In organically crosslinked gels, the gelation time (t_{gel}) was found to be shorter at high temperatures. When PAM was crosslinked

with PEI at a concentration ratio of 7/0.3 wt % PAM/PEI at 120°C (248°F), t_{gel} (defined as the inflection point in the viscosity vs time plot) was less than 1 h.¹³ This t_{gel} is too short for the successful placement of the gel in reservoirs at high temperatures. The gel may form inside the tubings before it reaches the desired zone, and this may lead to severe plugging problems. A practical t_{gel} should be more than 55 min. This is based on studies in local fields.¹⁴ Thus, there is a need to increase t_{gel} to an optimum value. Different options have been implemented to overcome this issue. These options have included cooling the near wellbore area with a preflush, crosslinker modification, and the addition of some retarders (salts). The injection of large amounts of water is not an acceptable option in oilfields. In addition, it was reported that the permeability to oil could be altered by the injection of a small amount of water. Different literature reports discussed the modification of the crosslinker. Specifically, PEI was modified to derivatized PEI^{15,16} and poly(amino acid).¹⁶ Different retarders (salts) were reported to

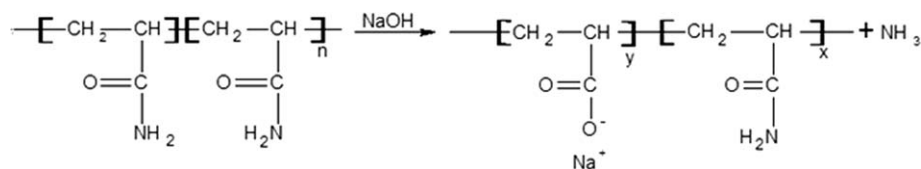


Figure 1. Hydrolysis of amide groups under alkaline conditions.^{18–20}

elongate t_{gel} for polyacrylamide *tert*-butyl acrylate (PATBA)/PEI. These retarders include sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and ammonium chloride (NH_4Cl). Although Na_2CO_3 was found to have a good retardation effect for the PATBA/PEI system,¹⁷ but it showed some compatibility problems with high-salinity brines.¹⁴ NaCl and NH_4Cl were chosen as alternatives for Na_2CO_3 to increase t_{gel} of the PATBA/PEI system in high-temperature applications. NaCl did not give an acceptable increase in t_{gel} ,¹⁴ whereas NH_4Cl extended t_{gel} to 1.5 h at 150°C (302°F).

The mechanism by which salts elongate the crosslinking reaction of PAM-based polymers with PEI has been a subject of discussion over the past several years. It was hypothesized that salts affect the hydrolysis of PAM, where they reduce the extent of hydrolysis. Moreover, it was thought that salts do affect the hydrodynamic volume of the polymer and thus reduce the number of accessible sites on the polymer. PAM undergoes alkaline hydrolysis under high temperatures to produce partially hydrolyzed polyacrylamide (PHPA; containing carboxylate groups) and ammonia.^{18–20} This chemical reaction is shown in Figure 1.

The formation of PHPA through the hydrolysis reaction turns the polymer into a polyelectrolyte carrying negative charges on the carboxylate groups. This may lead to strong interactions with the cations depending on the degree of hydrolysis (DH). DH is an important factor, which plays a major role in polymer instability and in determining the charge density of the polymer backbone. The use of salts can also be negative if the compatibility with the field-mixing brines is not examined.

The first study of the PAM/PEI polymeric gel system was reported by Allison and Purkale.²¹ The authors observed the formation of aqueous gels at room temperature. The PAM/PEI gel system was found to be rigid and stable in distilled water for 8 weeks at 130°C with polymer and crosslinker concentrations of 7 and 1 wt %, respectively.²² The use of representative field water in laboratory studies is a key factor for the success of the system in field applications. Also, the DH plays an important role in crosslinking reactions. There is a need to understand how salts affect the polymer DH and its subsequent effect on the elongation of t_{gel} of the PAM/PEI gel system. Recently, our group conducted a critical literature review on the development of polymer systems used in water shutoff applications.²³ In addition, differential scanning calorimetry (DSC) was used to investigate the effect of salts on a PAM/PEI crosslinked system.²⁴

Hence, the objectives of this study were to investigate the effect of salts on the DH through ^{13}C -NMR; the use of various analytical techniques, such as DSC and oscillatory rheological

measurements, to contribute to the understanding of the salt-retardation mechanisms of PAM/PEI gels.

EXPERIMENTAL

Materials

The PAM used in this study was supplied by SNF Floerger as an aqueous solution with a 20 wt % active content, and it was used as provided. The molecular weight as disclosed by the supplier ranged from 250 to 500 kg/g mol. The pH of PAM was around 4.0. The crosslinker was PEI and had a pH of about 11.7. The molecular weight and active content of PEI were 70 kg/g mol and 30%, respectively (as disclosed by the supplier). NaCl, NH_4Cl , and Na_2CO_3 were used. All of these salts were American Chemical Society grade. The pH of the solutions was adjusted to 10 through the addition of NaOH (1M). An HQ40D pH meter was used to measure the pH of the polymer solution. All of the samples were purged with nitrogen before they were heated to remove oxygen. This was because at high temperatures, oxygen could lead to a negative impact on the polymer thermal stability.²⁵ Field water was collected from a close field, whereas sea water was obtained from the Arabian Gulf. The pH values of the field and sea water were 8.02 and 7.75, respectively. The chemical analysis of these waters is given in Table I.

Methods

To determine the DH values, various techniques have been reported in the literature. These techniques have included conductometric titration, nitrogen content, potentiometric titration, IR and UV spectroscopy, thermogravimetric analysis, ^{13}C -NMR, and calorimetry.²⁶ Because of its accuracy and availability, ^{13}C -NMR spectroscopy was used in this study for the measurement of the DHs of polymers and has been used by other researchers.^{27,28} To prepare a sample for ^{13}C -NMR, a predetermined amount of salt (NaCl or NH_4Cl) was added to PAM with

Table I. Chemical Analysis of the Mixing Waters Used in the Experiments

Ion (ppm)	Water type	
	Field	Sea
Na	175	17,085
Mg	46	2,200
Ca	112	1,040
Cl	377	31,267
SO_4	266	4,308
HCO_3	146	140
TDS ^a	1,122	56,040

^a Determined by addition.

stirring. All of the hydrolysis of PAM in this study was carried out under alkaline conditions. This was due to the fact that PAM/PEI crosslinking reactions took place under alkaline conditions (pH 9.9–10.5) because of the high pH of PEI (11.7). Use has been made of NaOH (1M) to adjust the pH of the solution to 10. After that, the polymer solutions were transferred to a Screw-Thread GL 18 Schott-type high-thermal-resistance glass tubes. The tubes were sealed during heating. All of the samples were placed in a Haake N3 oil bath maintained at 120°C (248°F). This oil bath was equipped with a digital temperature display having an accuracy of $\pm 0.1^\circ\text{C}$. The samples were maintained at these conditions for 1 week, and each day, a sample was taken for NMR testing.

A JEOL 500 MHR NMR spectrophotometer equipped with multinuclear probes was used for the ^{13}C -NMR characterization. The NMR spectroscopy was run at 125.65 MHz, and the spectra were collected at room temperature (25°C or 77°F). *P*-Dioxane was used as a reference at 67.4 ppm. A few drops of D_2O were added to the polymer solution to lock the signal. Other experimental parameters comprised the use of a 6-s delay time, a pulse width of 4.3 μs , 8246 scans, and an acquisition time of 0.96 s. Inverse-gated decoupling was used to overcome nuclear overhauser enhancement. All spectra were collected for at least 10 h to improve the noise-to-signal ratio. The resulting spectra were integrated, and their DH was calculated.

In the compatibility tests, samples of 7/1 wt % PAM/PEI were prepared in a preflush (field water in 2 wt % KCl) with a total of 250 lb/1000 gal (30,000 ppm) of three retarders: NaCl, Na_2CO_3 , and NH_4Cl . Other samples of 1 wt % PEI were prepared in field water without PAM with the three retarders with the same previously mentioned concentration of salts. A volume of 10 mL of the solution was mixed with 10 mL of preflush. Then, the samples were heated in an oven that was maintained at 150°C (302°F). The samples were aged for 1 day with Screw-Thread GL 18 Schott-type, high-thermal-resistance glass tubes.

The gelling solutions for the gelation tests were prepared at room temperature. PAM was added to water first and stirred for about 1 min; then, PEI was added, and the mixture was stirred for 10 more min. Then, the sample was transferred to the pressure cell mounted on the rheometer. All rheology measurements were conducted a rheometer that was equipped with a high-pressure cell. For steady-shear measurements, a concentric cylinder geometry with bob and cup diameters of 28 and 30.43 mm, respectively, was used. The gelation tests were performed in the high-pressure cell setup with bob and cup diameters of 26 and 28 mm, respectively. The rheometer had a torque limit of 100 μNm to 0.2 Nm, a pressure of 500 psi, and a maximum temperature of 150°C (302°F).

DSC measurements were performed with a Q1000 DSC instrument provided by TA Instruments. This machine was equipped with a refrigerating cooling system that used nitrogen and an autosampler. The instrument was purged by nitrogen at a flow rate of 50 mL/min. The samples were put in aluminum hermetic pans and then sealed with a pressing tool. An empty pan was used as a reference. All of the samples were equilibrated at

30°C (86°F) for 5 min, ramped at 1.5°C/min to 120°C (248°F), and then kept at this temperature until no change in the heat flow was observed.

RESULTS AND DISCUSSION

Analysis of the NMR Spectra

Samples of PAM were aged at 120°C (248°F) for different times after their pH was adjusted to 10. Then, the DH was determined through ^{13}C -NMR with the following equation:

$$\tau = \frac{(I_{\text{C=O}})_{\text{OH}}}{(I_{\text{C=O}})_{\text{OH}} + (I_{\text{C=O}})_{\text{NH}_2}} \times 100 \quad (1)$$

where $(I_{\text{C=O}})_{\text{OH}}$ and $(I_{\text{C=O}})_{\text{NH}_2}$ represent the areas under the resonance peaks of the carbonyl carbons attached to the carboxylate and amide groups, respectively. These peaks were located at 181–184 and 177–180 ppm, respectively. The DH of neat PAM was found to be 0% as disclosed by the supplier. This was confirmed through ^{13}C -NMR testing for the neat PAM, and the spectrum did not show any peak for the carboxylate group in the chemical shift range 180–184 ppm [Figure 2(a)].

Hydrolysis of PAM

The DH plays a major role in the thermal instability of polymeric gels. At the same time, the addition of retarders (salts) is very important to the extension of t_{gel} to allow for successful and safe gel placement in the target zones. Hence, it is important to investigate the effect of these salts on DH and its extent at high temperatures.

The DH was plotted versus time, as illustrated in Figure 2(b); this shows the hydrolysis of neat PAM at 120°C (248°F). These results were characterized by two different steps. In the first step, the DH increased at a high rate until it reached about 42 mol %. Then, the rate of increase of the DH decreased. The initial high rate was explained by the influence of the neighboring amides in the catalysis of the reaction and the high concentration of OH^- .²⁰ The high increase could also be explained by the effect of the carboxylate groups formed during the hydrolysis. It was reported that the carboxylate groups increased the hydrolysis of the amide groups attached nearby.²⁰ Note that at high DH, greater than 45%, another mechanism took place. The repulsion between the negative carboxylate and hydroxide ions caused a reduction in the hydrolysis rate.

The experimental data in Figure 2(b) showed a strong dependency of the DH on time. The hydrolysis of PAM has been reported as a first-order reaction with respect to the amide concentration ($[A]$);^{29–35} this could be represented as follows:

$$-\frac{d[A]}{dt} = k_A[A] \quad (2a)$$

where k_A is the first-order hydrolysis reaction rate constant. The solution of eq. (2a) yields

$$[A] = 100 \exp(-k_A t) \quad (2b)$$

where t is the time in seconds and $[A]$ is 100% at $t = 0$.

The degree of hydrolysis (τ) was calculated from eq. (2b) as follows:

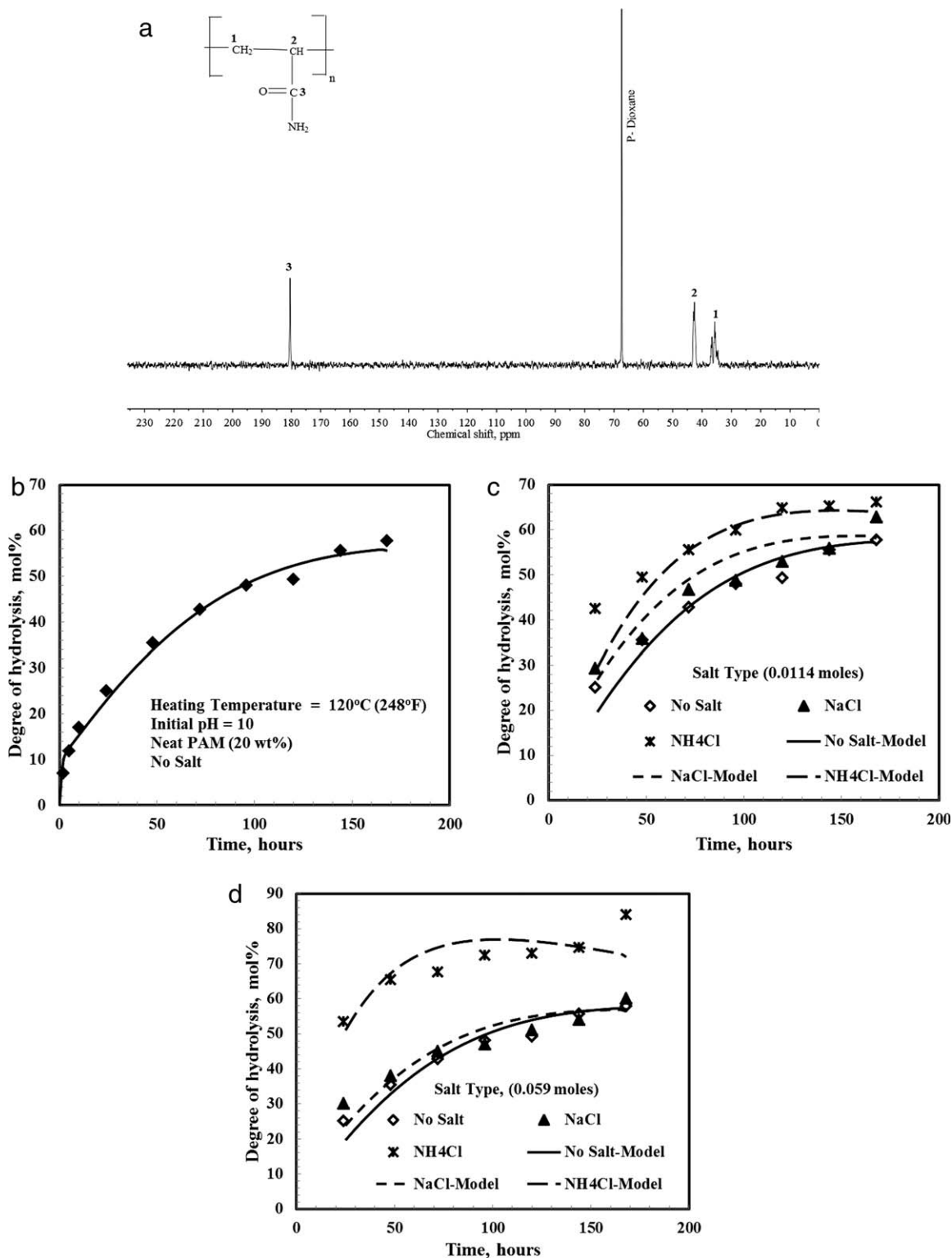


Figure 2. (a) ^{13}C -NMR spectrum of the neat sample of PAM. (b) Hydrolysis of the neat PA at 120°C (248°F) and pH 10. Experimental versus model data of amide hydrolysis at 120°C (248°F) with an initial pH of 10 at (c) low and (d) salt concentration. PA = polyacrylamide.

$$\tau = 100 - [A] \quad (3)$$

The negative charges on PHPA and OH^- created repulsive forces, which led to a reduction in the hydrolysis reaction rate, which could be represented with the model of a charged coil:³¹

$$k_i = k_i^{(0)} \exp[-W_i(\{\psi_i\})/kT] \quad (4)$$

where $i = 0, 1$, and 2 indicate the sequences of the carboxylate groups in the polymer chain and k_i and $k_i^{(0)}$ represent the hydrolysis reaction rates estimated at $\tau(t + \Delta t)$ and $\tau(t)$ where

Table II. PAM Hydrolysis Rate Constants at 120°C (248°F) at Different Salt Concentrations

Salt type	$k_A \times 10^3$ (h ⁻¹)	ϕ_1	$\phi_2 \times 10^{-4}$	τ_s
No salt	8	0.035	-3.07	1.52
NaCl (0.0114 mol)	8.3	0.041	-3.17	8.08
NaCl (0.0228 mol)	8.5	0.041	-3.17	10.72
NaCl (30,000 ppm)	7.8	0.082	-7.46	6.1
NH ₄ Cl (0.0114 mol)	11.6	0.03	-3.85	4.35
NH ₄ Cl (30,000 ppm)	16.4	0.036	-1.28	17.39

Δt represents the difference between two consecutive periods for measuring DH, respectively. The term $\exp[-W_i(\{\psi_i\})/kT]$ denotes the retardation to hydrolysis, where $W_i(\{\psi_i\})$ is a work term, k is the Boltzmann constant (J/K), and T is the absolute temperature (K). The term $W_i(\{\psi_i\})$ is further defined as follows:³¹

$$W(\{\psi_i\}) = W_c(\tau) - W_n(\{\psi_i\}) \quad (5)$$

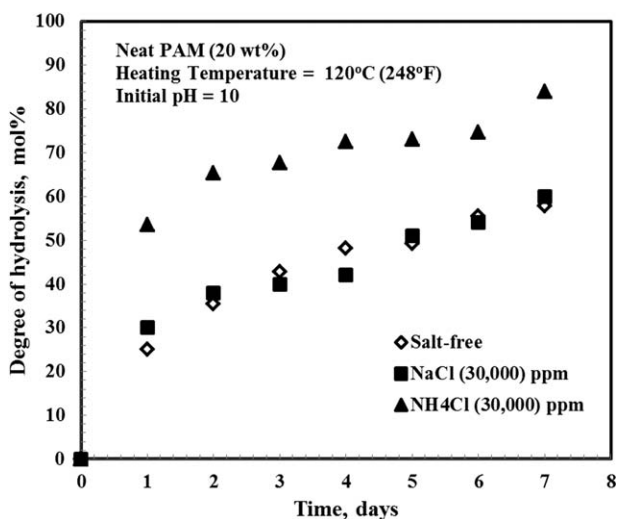
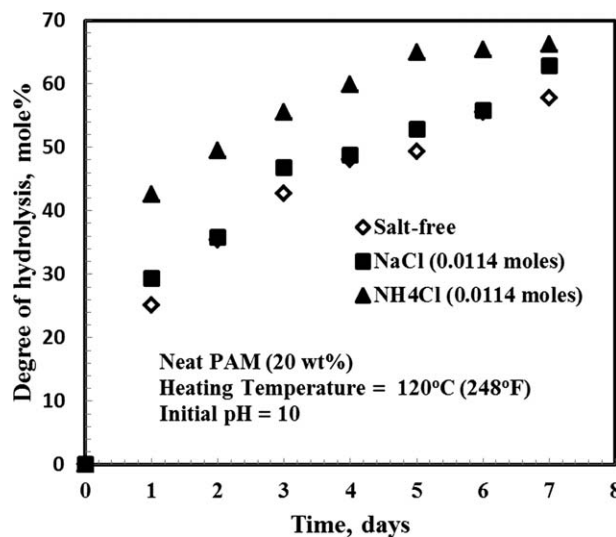
where $W_c(\tau)$ and $W_n(\{\psi_i\})$ are the works countered to the repulsion of the polymer chains and against the carboxylate groups, respectively. A relationship reported in ref. 36 could be used to determine $W_c(\tau)$ in eq. (5) as follows:

$$W_c(\tau)/kT = 2.3(\phi_1\tau^2 + \phi_2\tau) \quad (6)$$

where ϕ_1 and ϕ_2 are two factors that depend on the molecular weight of the polymer and the salt concentration.^{31,36} The term $W_n(\{\psi_i\})$ is chain-composition-dependent and was studied elsewhere.³⁷ In fact, this term is significant only at pH > 11.5.³⁸ Hence, eq. (3) was used to explain the data presented in Figure 2(b) with the value of k_A evaluated from eq. (7):

$$k_A = k^{(0)} \exp[-2.3(\phi_1\tau^2 + \phi_2\tau)] \quad (7)$$

The value of k_A reported in Table II was found by the fitting of the experimental data with eq. (3). The values of ϕ_1 and ϕ_2 for salt-free PHPA and PHPA with different salt concentrations are

**Figure 3.** Effect of a high salt concentration (30,000 ppm) on D_H of PAM at 120°C (248°F).**Figure 4.** Effect of the salt concentration (0.0114 mol) on D_H of PAM at 120°C (248°F).

presented in Table II. These results were obtained by the solution of eqs. (3) and (7) with Mathematica software. The hydrolysis was influenced by the presence of salts, and the predictions of eq. (3) were lower than the experimental data. Therefore, we proposed the modification of eq. (3) to account for the impact of salts on hydrolysis through the introduction of the parameter τ_s , which represents the plateau (steady state) value of DH. Consequently, eq. (3) was modified to the following form:

$$\tau = [1 - \exp(-k_A t)] \times 100 + \tau_s \quad (8)$$

Figure 2(c,d) shows the fitting of the model by eq. (8) to the experimental data at low (0.0114 mol) and high (0.059 mol) salt concentrations. The values of τ_s are given in Table II.

To investigate the effect of salts on the hydrolysis behavior of the polymer, additional tests were conducted with inorganic salts, which were used as retarders in water-control treatments. The salts were introduced to PAM, and the pH of the solution was adjusted to 10. Then, the samples were heated, and the DH was obtained from ¹³C-NMR, as discussed earlier. The results of DH are shown in Figure 3 for 30,000-ppm salt. The data showed that there was a difference between the various salts and the base salt-free case. For example, after 1 day, the DH values were found to be 53, 30, and 25% for PAM solutions with NH₄Cl, NaCl, and PAM, respectively. It was evident that the influence of NH₄Cl on the extent of PAM hydrolysis was very strong, whereas that of NaCl was less.

Because the effect of the salts was significant, further tests were conducted to examine the effect of the salt concentration on the extent of PAM hydrolysis. PAM solutions containing NaCl and NH₄Cl with the same number of moles (0.0114 mol) were used. The results are shown in Figure 4. The same trend of increasing DH was observed. A high DH was obtained in the case of NH₄Cl in comparison with NaCl and neat PAM. The results for NaCl and neat PAM were almost identical; this suggested the weak influence of NaCl on PAM hydrolysis. Although NaCl was doubled in another run (Figure 5), we found that this increase

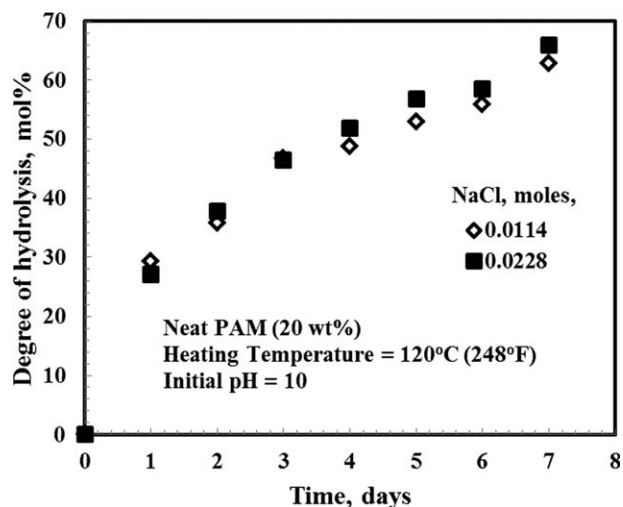


Figure 5. Effect of the number of moles of NaCl on D_H of PAM at 120°C (248°F) and 20 wt % PAM.

in the number of moles did not increase the DH of PAM. The hydrolysis data were fitted by an exponential relationship, and the values of k_A are reported in Table II.

Effect of Salts on PHPA Crosslinking with PEI

The crosslinking of PHPA/PEI was investigated previously for applications in low-temperature reservoirs.³⁹ The PHPA/PEI gel system exhibited a good performance at 40°C (104°F). t_{gel} was optimized from 15 h to 9 days at 40°C (104°F), and a rigid gel system was obtained. Moreover, a high PHPA loading and high PHPA molecular weight resulted in a stable and high-strength gel. An optimum concentration of PEI had to be added because low and high concentrations of PEI could lead to either no gelation or more syneresis, respectively. The effect of the total dissolved solids (TDS) on t_{gel} of PHPA/PEI was observed to be similar to the effect on other systems such as PATBA/PEI,⁴⁰ in which a longer t_{gel} was noted. However, TDS led to a weaker gel

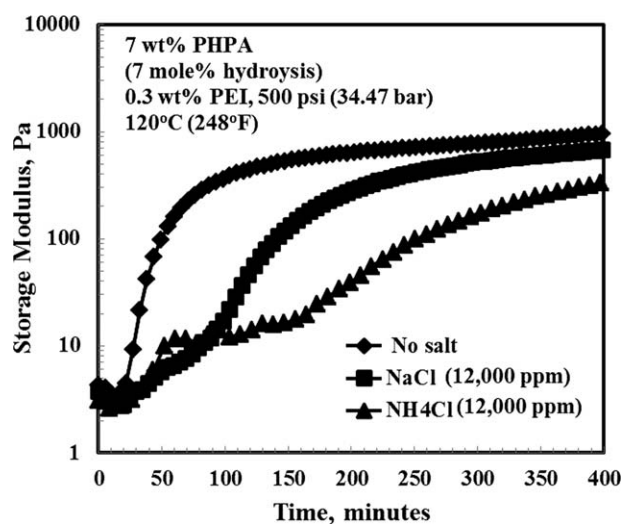


Figure 6. Effect of salts on the crosslinking of PHPA (7 mol % hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar).

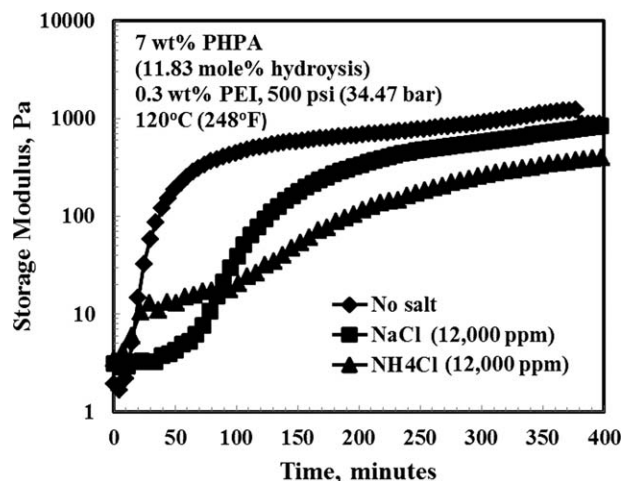


Figure 7. Effect of salts on the crosslinking of PHPA (11.83 mol % hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar).

and was also like the effect of PATBA/PEI.⁴¹ Although the mechanism of PHPA/PEI gelation was reported as a nucleophilic substitution in which the imine nitrogen on PEI attacked the carbonyl carbon attached to the amide group on PHPA,³⁹ different suggestions have been made for the mechanism of t_{gel} delay done by salts.⁴² These suggestions have included charge-shielding effects, PEI molecular weight effects, and the low contribution of polymer molecules in the presence of salts. The application of PHPA/PEI needed to be studied at a higher temperature (>100°C) because some reservoirs exhibited temperatures greater than 40°C (104°F). Also, more insights were required to understand the delay in gelation due to the presence of salts.

The crosslinking of PAM with PEI needs to be delayed in high-temperature applications to give oilfield operators adequate time to place the gelling solution safely. Different salts were tested and applied; these included NaCl and NH₄Cl. These salts increased t_{gel} when neat polymers were used with a crosslinker. Hence, the effects of the salts on PHPA with different DHs were

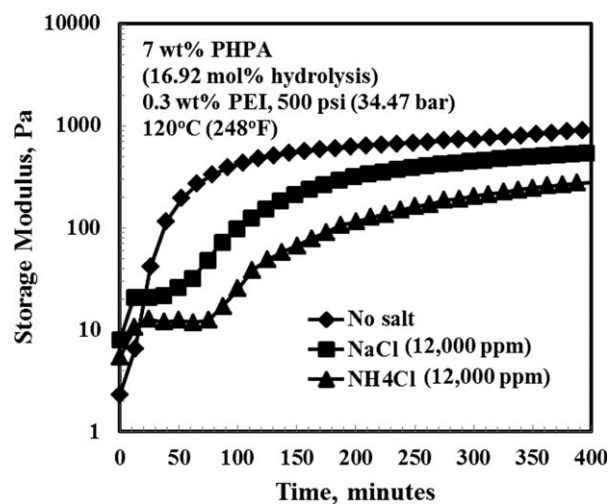


Figure 8. Effect of salts on the crosslinking of PHPA (16.92 mol % hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar).

Table III. Effect of the Salts (12,000 ppm) on the PHPA/PEI System at 120°C (248°F)

Heating time (min)	Initial DH (mol %)	t_{gel} (min)			Equilibrium G' (Pa)		
		Salt-free	NaCl	NH ₄ Cl	Salt-free	NaCl	NH ₄ Cl
120	7	47	123	194	900	636	286
300	11.83	41	104	154	1139	773	360
600	16.92	46	52	145	1042	630	368
10,080	57.8	27	34	31	1183	598	962

introduced in the next tests. Also, the strength of the polymer system, which is an important factor for the gel lifetime in field applications, were investigated.

To investigate the effect of the salts on the PHPA/PEI cross-linked gel, samples of PAM were hydrolyzed for different times. The pH was adjusted to 10, and then, the samples were heated to 2, 5, 10, and 168 h at 120°C in an oil bath. The DHs of these samples were measured by ¹³C-NMR and were found to be 7, 11.83, 16.92, and 57.8 mol %. These polymer samples were crosslinked with PEI in the presence and absence of salt. The concentration of each salt (NaCl and NH₄Cl) used in these experiments was 100 lb/1000 gal (12,000 ppm).

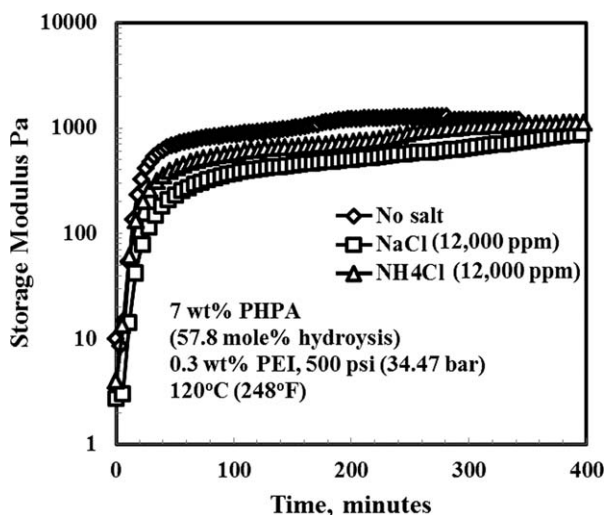
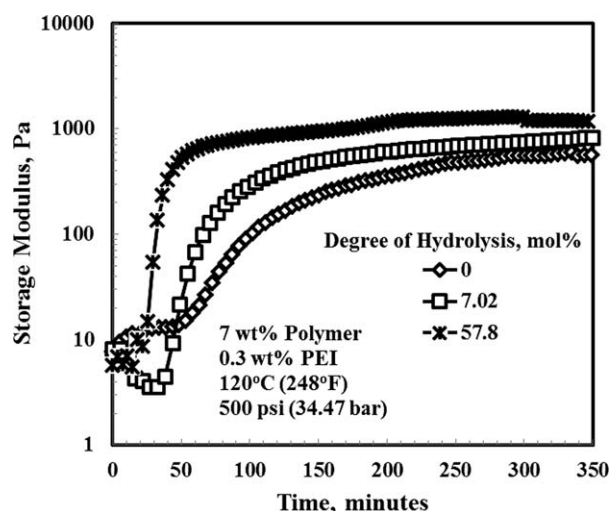
Salts were reported to increase t_{gel} of the PAM/PEI gel system and other systems, such as PAtBA crosslinked with PEI. The data from Figures 6, 7, and 8 showed that the addition of salts increased t_{gel} , even when a partially hydrolyzed polymer was used instead of the neat polymer. However, the addition of salts was found to have a negative impact on the gel strength at a given time with little influence on the ultimate gel strength. NH₄Cl increased t_{gel} more compared to NaCl. However, NH₄Cl weakened the produced gel more compared to NaCl. The higher effect on t_{gel} caused by NH₄Cl could be explained through the progress of hydrolysis.

The data in Table III were extracted from the crosslinking tests done via dynamic rheology measurements. Here, the t_{gel} and gel

strength [storage modulus (G') vs time] were measured. The measurement of G' represented a quantitative approach in comparison with the qualitative Sydansk's codes.³⁹ Our results for the different retarders show that t_{gel} decreased with increasing DH; this was in agreement with previous reports on salt-free PHPA.²²

We observed that when DH increased to about 57.8 mol % (obtained by the aging of PAM for 7 days), there was no effect on t_{gel} (the same t_{gel} in all cases), and there was no trend in G' either (NH₄Cl gave a higher G' compared to NaCl; Figure 9). This may have been due to the high DH of the polymer, where the charges could not be shielded efficiently by the cations. It could have also indicated a different gelation mechanism; this is discussed in the next section.

In Figure 10, a plot of G' versus time is given at different DHs to examine whether PHPA could be used instead of PAM to produce a gel with a high strength. The plateau values of G' at 0, 7.02, and 57.8 mol % DHs were found to be 680, 900, and 1183 Pa, respectively. It was clear that a higher DH produced a higher G' but at the expense of increasing t_{gel} . To relate t_{gel} to the DH, t_{gel} was obtained by the extrapolation of the linear portions of the gelation curves around the gelation onset point for the different DHs. Then, t_{gel} in the salt-free system and in the presence of salts (NaCl and NH₄Cl) was fitted to τ by an exponential relationship ($t_{\text{gel}} = k_{\text{gel}}e^{-A\tau}$) as shown in Figure 11. The values of k_{gel} and A are reported in Table IV. The factor k_{gel} is a

**Figure 9.** Effect of salts on the crosslinking of PHPA (57.8 mol % hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar).**Figure 10.** Effect of DH on the gel strength at 120°C (248°F).

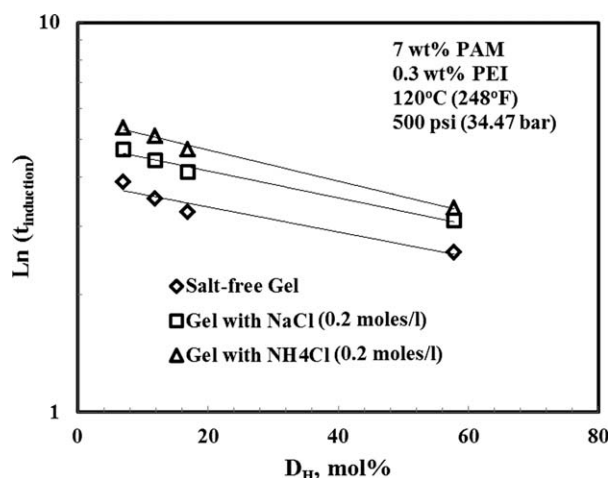


Figure 11. Effect of DH on the induction time ($t_{\text{induction}}$) of the crosslinking of PHPA with PEI.

rate parameter for the delay of the gelation, whereas A is a constant related to the activation energy of the gelation process. k_{gel} was more sensitive to the type of salt used than A because the temperature was constant. k_{gel} increased by 25% when NaCl was used, whereas A increased by only 14%. For NH_4Cl , k_{gel} increased by 45%; this was almost double the increase in k_{gel} in the case of NaCl (25%). This confirmed the previous findings in which NH_4Cl was stronger than NaCl in retarding the gelation of the PAM/PEI system.

Generally, the salt-free samples of PHPA/PEI exhibited the highest G' followed by that which contained NaCl. The addition of NH_4Cl resulted in lower values of G' in comparison with NaCl and the salt-free gel systems. The reasons behind these observations were explained by the following DSC measurements.

Insights into the Retardation Mechanisms of the PAM/PEI Crosslinking Reactions

In this section, light will be shed on the conclusions that were drawn from the NMR and dynamic rheological measurements. The retardation of the PAM/PEI crosslinking reaction by the addition of simple inorganic salts was evident. Although NH_4Cl was more effective in retarding t_{gel} of the PAM/PEI gels, its presence accelerated the hydrolysis of PAM significantly. On the other hand, NaCl, which was found to be less effective in retarding gelation, showed a lesser extent of hydrolysis. This indicated that the retarding mechanism by which these salts functioned was not the delay of the hydrolysis reaction of the polymer. However, the presence of carboxylate groups on polymers is known to cause a screening effect by which the viscosity of these solutions drops. To explore this further and to see how

Table IV. Parameters of the Induction Period During the Gelation of PHPA with PEI

Salt type	k_{gel}	$A \times 10^{-3}$	Regression coefficient
Salt-free	3.89	7	0.940
NaCl	4.87	8	0.984
NH_4Cl	5.66	9	0.993

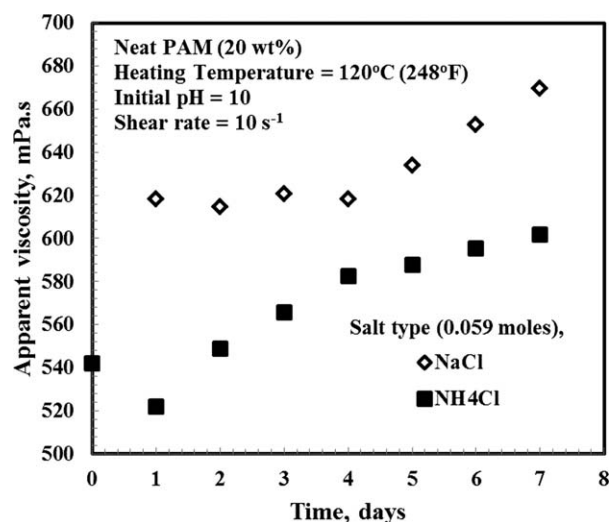


Figure 12. Effect of the salt type on the PAM viscosity at 10 s^{-1} after aging at 120°C (248°F) for 7 days at a salt concentration of 7500 ppm.

effective these salts were in screening the negative charges on PHPA, additional tests were conducted with steady-shear viscometry.

The samples of PAM solutions were prepared by the addition of NaCl and NH_4Cl at concentrations of 7500 and 30,000 ppm (corresponding to 0.0114 and 0.059 mol/L, respectively); these were the same concentrations used in the hydrolysis analysis of Figures 3 and 4. Then, the pH was adjusted to 10, and all of the samples were aged for 7 days in an oil bath at 120°C (248°F) with the same procedure used for preparing ^{13}C -NMR samples. Then, the viscosity of these samples was measured every day for 7 days. The viscosity was found to be Newtonian in the shear rate range of $1\text{--}200 \text{ s}^{-1}$.

As shown in Figure 12, samples containing NH_4Cl had lower viscosities than those containing NaCl. This was true, even though the number of moles (0.059 mol) was kept the same. Hence, the low viscosity caused by NH_4Cl was due to the

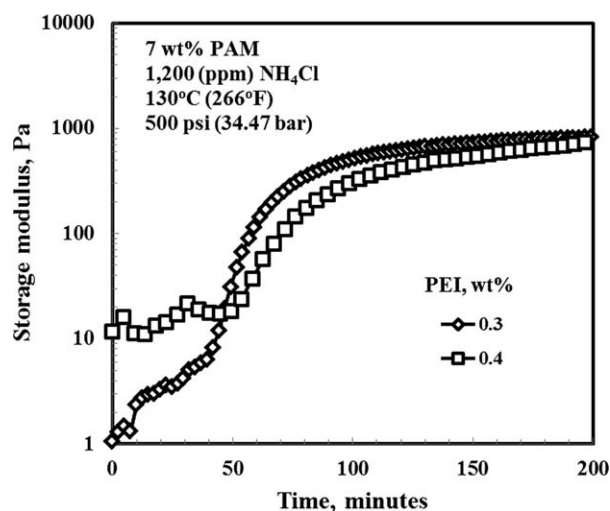


Figure 13. PAM crosslinked with different PEI concentrations and 1200-ppm NH_4Cl .

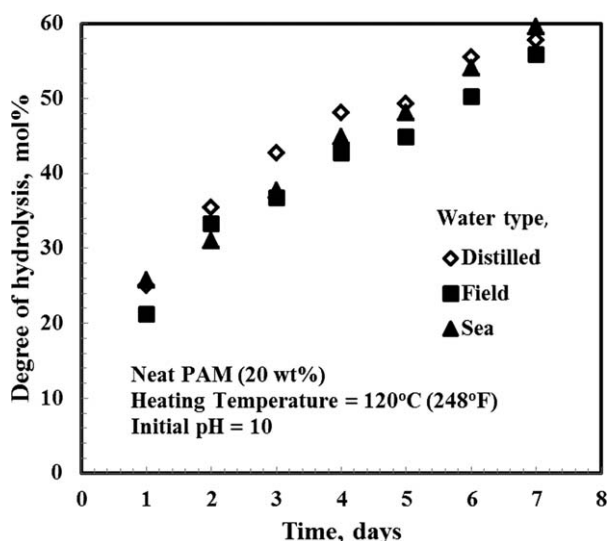


Figure 14. Effects of distilled, field, and sea water on the D_H values of PAM at 120°C (248°F) and 20 wt % PAM.

polymer structure (shrinkage). Different literature reports have discussed the interaction of salts with carboxylate groups. In an article by Kherb et al.,⁴³ it was shown that ammonium ions had a stronger binding to carboxylate groups compared with sodium ions at a low salt concentration. Moreover, it was reported that an interaction constant for NH_4^+ was higher than that for Na^+ at a salt concentration of 1.5N.⁴⁴ From the NMR results, the addition of NH_4Cl showed a higher DH; this was supposed to give lower t_{gel} in crosslinking with PEI, but t_{gel} was observed to be elongated in this case. Also, in the case of increasing PEI concentration in the presence of the same NH_4Cl concentration, t_{gel} also increased (Figure 13). This confirmed that PEI was not a limiting reactant in this case. As a tentative explanation, although there were more carboxylate groups in the solution as a result of the addition of NH_4Cl , but these groups were not accessible to PEI because of the shrinkage of the polymer chain. This finding was further confirmed with a mixture of waters from the field and from the sea. The hydrolysis of the polymer

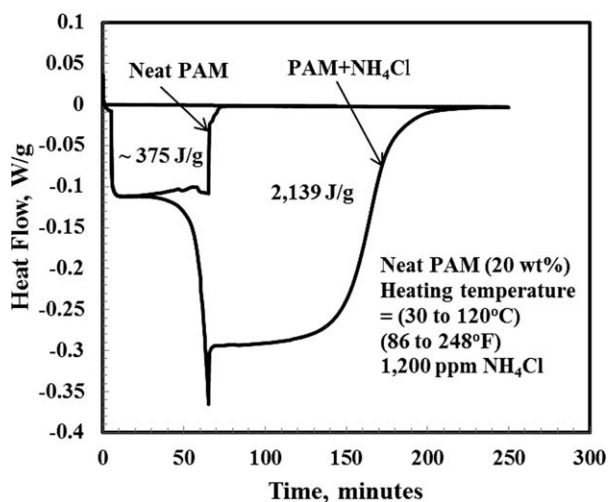


Figure 15. Effect of NH_4Cl on the PAM hydrolysis (DSC scan).

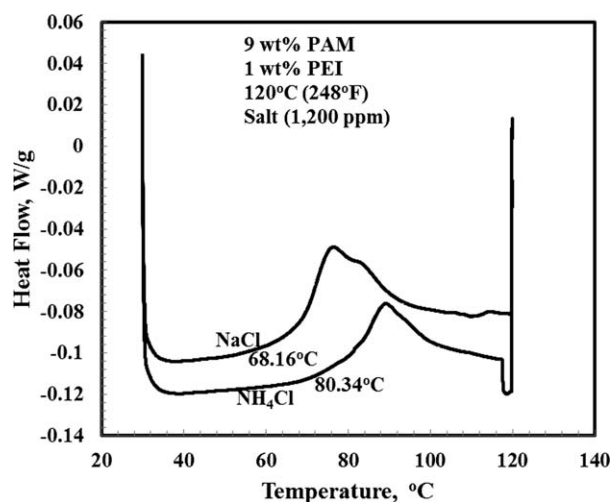


Figure 16. Effect of the salts on the onset gelation temperature of 9:1 PAM/PEI (wt %).

with these waters is reported in Figure 14. As shown in this figure, there was no appreciable difference in the DHs with these waters. In view of the effect of these salts on t_{gel} , it was clear that the salts did not elongate the gelation by retarding hydrolysis. This also indicated that the gel was partly based on the ionic interaction between PEI and the negatively charged carboxylate as an additional crosslinking mechanism.

DSC was used as an additional method to further explain these trends. Two samples of gelling solutions (9/1 PAM/PEI wt %) with NaCl and NH_4Cl (1200 ppm) were heated to 120°C (248°F) - at a rate of 1.5°C/min. The DSC dynamic scans showed that more heat was absorbed with the sample having NH_4Cl . The heat absorbed was found to be about 375 J/g for PAM. This amount of heat increased to 2139 J/g when NH_4Cl was added to PAM. As shown in Figure 15, the heat absorbed (endothermic) by the addition of NH_4Cl was higher than that of NaCl . The alkaline hydrolysis of PAM was endothermic in nature. The onset of the crosslinking temperature shifted to

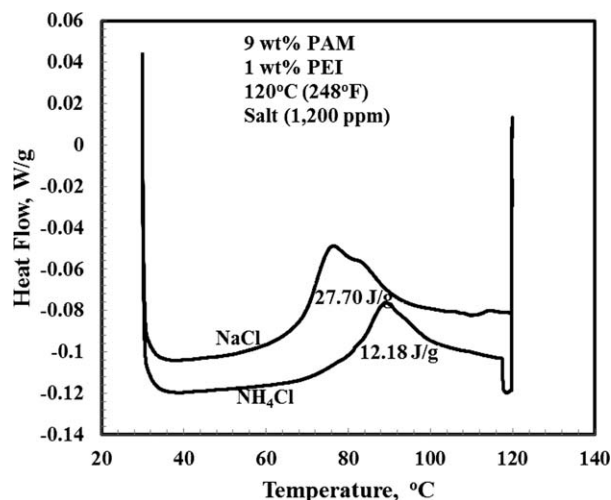


Figure 17. Effect of the salts on the heat of gelation of 9:1 PAM/PEI (wt %).

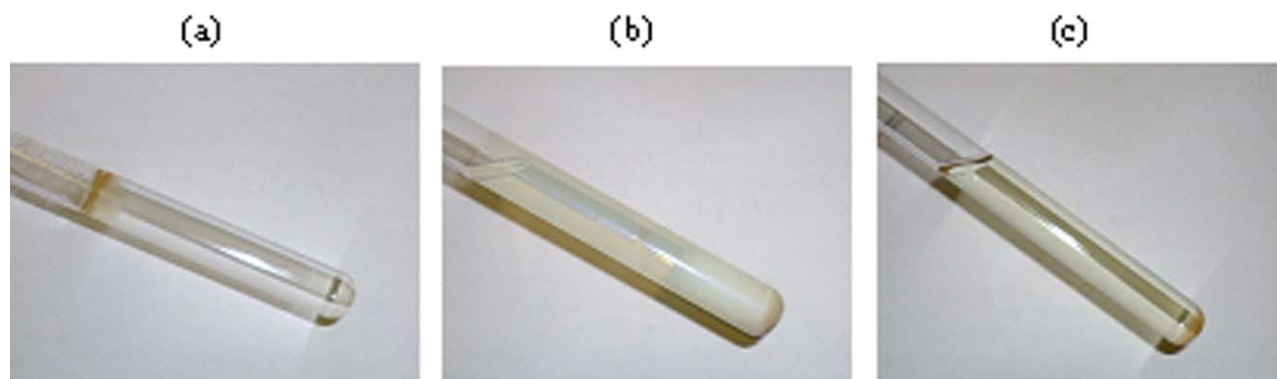


Figure 18. Sample of 7:1 PAM/PEI (wt %) with 30,000 rpm retarders: (a) NaCl, (b) Na₂CO₃, and (c) NH₄Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 80°C by the addition of NH₄Cl, whereas it was 68.18°C in the case of NaCl (Figure 16). The heat released (exothermic) was higher in the case of NaCl (27.7 J/g) compared to that of NH₄Cl (12.18 J/g; Figure 17). This suggested that more cross-linking reactions took place in the case of NaCl; this resulted in a higher gel strength and explained the earlier measurements. For NH₄Cl, the observed low strength could be explained by these DSC results. Therefore, the addition of NH₄Cl to the PHPA solution led to more hydrolysis but shifted the onset of gelation to higher temperatures. This shift explained the observed weakness in the gel strength.

Compatibility of Salts with the PAM/PEI Gel System

Preflush fluids (2 wt % KCl in field water) are usually injected into the wellbore to displace divalent cations such as Ca²⁺ and Mg²⁺ and to cool down the near wellbore area. The preflush must be compatible with the gelant and the formation brine. This was to prevent any precipitation in the formation face, which may have resulted in difficulties for gelant placement and high injection pressures. Thus, it was highly important to examine the compatibility of the gelant with the preflush fluids. The samples of 7/1 wt % PAM/PEI were prepared in a preflush with different kinds of salts, such that the concentration of these salts was 250 lb/1000 gal (30,000 ppm). This level of concentration was selected because of the high t_{gel} (ca. 4.4 h) obtained in a previous study²² with NaCl. All salts were added at the same concentration. With the addition of NaCl and NH₄Cl, the solutions were transparent, and no precipitation was observed. So, NaCl and NH₄Cl were found to be compatible with the polymeric gel system 7/1 wt % PAM/PEI. In the case of Na₂CO₃, the gel solution was observed to be milky, and a white precipitate was observed after heating to 150°C (302°F). Figure 18 shows samples of 7/1 wt % PAM/PEI with the three retarders. Other samples were prepared in field water without PAM to examine the compatibility of the salts with PEI. NaCl and NH₄Cl samples mixed with a preflush (50/50 vol %) and then heated at 150°C (302°F) showed transparent solutions. However, white solids precipitate was observed in the case of Na₂CO₃. These solids precipitate were filtered from the solution, and X-ray diffraction was used to analyze the nature of these solids. X-ray diffraction revealed that the solid precipitate was composed of calcium carbonate (Ca₂CO₃;

31%) and calcium silicate chloride (Ca₂SiO₃Cl₂; 69%). The formation of this precipitate was due to the presence of Ca⁺² in field water.

CONCLUSIONS

In this study, PAM hydrolysis was examined in the presence of salts (NaCl and NH₄Cl) at 120°C (248°F). The compatibility of the salts with the PAM/PEI gel system was also checked. ¹³C-NMR was used to study the effect of the salts on PAM hydrolysis. Moreover, steady-shear measurements were conducted to correlate the viscosity to the DH. The crosslinking of PHPA with PEI along with salt addition was performed through dynamic oscillatory testing.

The conclusions from this study are summarized in the following points:

1. The hydrolysis of 20 wt % PAM at 120°C (248°F) was correlated to a first-order reaction kinetics with a rate constant of about $5 \times 10^{-3} \text{ h}^{-1}$. This value increased to $8 \times 10^{-3} \text{ h}^{-1}$ when NH₄Cl was added at a concentration of 30,000 ppm, whereas NaCl had a rate constant of $5 \times 10^{-3} \text{ h}^{-1}$ at this concentration.
2. NH₄Cl increased the hydrolysis more than NaCl.
3. The viscosity of the hydrolyzed polymer dropped in the first day of aging upon the addition of salts; this was followed by an increase in the subsequent 6 days. The increase in the viscosity correlated well with the DH.
4. NaCl and NH₄Cl were found to be compatible with the PAM/PEI gel system, whereas, Na₂CO₃ was observed to produce a white precipitate with the gelling solution.
5. Increasing the DH was found to increase the strength of the produced gel, but t_{gel} decreased at the same time.
6. The addition of salts to the PHPA/PEI led to an increase in t_{gel} .
7. NH₄Cl increased t_{gel} of PHPA/PEI more than NaCl because of a shifting in the onset gelation temperature. The point at which the heat started to be released was assumed to be the onset of crosslinking.
8. With the combination of all techniques reported in the article, the t_{gel} delay by salts at high temperatures was believed to be through a charge-shielding effect.

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