

# Gelation kinetics of PAM/PEI system

## DSC investigation

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**Abstract** Excess water production in oil and gas wells causes serious productivity and environmental problems in the oilfield. A mixture composed of a polymer, cross-linker, and water is usually injected into the reservoir to block unwanted water by forming a three-dimensional structure. This transition process from solution to gel is a function of temperature, time, salinity of mixing water, and concentration of the various components. The gelling solution was prepared by mixing polyacrylamide (PAM) with distilled water, and then polyethylenimine (PEI) was added as a cross-linker. The injection process was simulated and investigated by differential scanning calorimeter (DSC) over the temperature range of 80–120 °C. The DSC dynamic scan showed two consecutive peaks. An endothermic peak was observed at low temperature due to PAM alkaline hydrolysis which ends at around 60 °C. Another exotherm was observed at ~70 °C which corresponds to the onset of cross-linking of PAM and PEI. It was found that high temperatures lead to high release of heat due to gelation. The effect of salts on the cross-linking was also examined. More delay in cross-linking was observed in the case of NH<sub>4</sub>Cl compared to NaCl. The gelation kinetics was modeled using a rate process model that relates fractional gelation with time. Further,

Avrami model, usually used to study crystallization kinetics, was also used to model the gelation process. Kinetic parameters were obtained from the two different models, and the results showed good agreement with experimental data. The presence of salts in seawater leads to a drop of 60–80 % in the rate constant without influencing the order of the gelation reaction.

**Keywords** Gelation · Kinetics · DSC · Polymeric gel · Water shutoff

## Introduction

Excess water produced from matured oil and/or gas wells is a serious issue in hydrocarbon production. This can impose additional operational costs [1] as well as environmental impacts. This water needs special plants to deal with, which increases the production costs. In addition, this type of water may contain elements such as mercury and arsenic [2] which affect the environment with toxicity concerns if disposed without further treatment. One of the common remediate methods is the use of cross-linked polymer gels. Polymer gels have been used in different ways in oilfield industry. They were used to totally block water production zones [3, 4], reduce permeability to water [5, 6], and increase reservoir sweep efficiency in injection wells [7, 8]. Beside other factors such as identification of the water source, the understanding of gelation kinetics is an important factor for successful application to avoid injectivity problems.

Two types of polymer gels were developed and used worldwide: inorganic gel systems, in which trivalent cations such as Cr<sup>+3</sup> were used to cross-link the carboxylate groups on partially hydrolyzed polyacrylamide (PHPA) [9, 10]; this cross-linking is believed to be through

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coordination covalent bonds. The second type was based on organic cross-linkers with PAM-based polymers [11, 12]. Organically cross-linked gels are preferable at high temperatures due to their higher thermal stability compared to inorganic gels. An example is polyacrylamide (PAM)/polyethylenimine (PEI) gel system.

Polymer gels are based on a mixture of a polymer, cross-linker, and water. This mixture is referred to as gelant. When injected in the target zone, the gelant forms a three-dimensional (3D) structure which works as a physical barrier to water flow. The transition process from gelant (solution) to polymeric gel is a function of temperature, time, salinity of mixing water, and the concentration of various components. The gelation time is a key factor for gelant placement. Thus, longer gelation times are required for high-temperature reservoirs. Salts like NaCl and  $\text{NH}_4\text{Cl}$  were used to retard the gelation and delay the cross-linking process. Most of the previous gelation kinetics studies have focused on rheological techniques [13–16] and Nuclear Magnetic Resonance (NMR) spectroscopy [17, 18].

In this research, we would like to explore the use of differential scanning calorimeter (DSC) in studying the gelation kinetics of PAM/PEI system which is quite uncommon. DSC was widely used before in studying crystallization kinetics [19–21]. The main reason for extending the use of DSC to study the gelation kinetics is the similarity of the two processes. If we look into the crystallization and gelation phenomena, one can realize that in both cases heat is released as a result of cooling and heating, respectively. In crystallization, heat is released due to the formation of solid crystals when a liquid is cooled. In gelation, heat is released due to cross-linking reactions, and 3D gels are formed when solutions are heated. Therefore, due to the similarity of the physics of the gelation and crystallization processes, we proposed to study the gelation kinetics using the same earlier techniques used in studying crystallization kinetics. The DSC could be an effective tool in studying the gelation kinetics which would help in understanding the gelation mechanism as well as investigating the influence of different parameters and conditions. Hence, the objective of this work is to study the gelation process and its kinetics using DSC. Moreover, the influence of different parameters such as gelation temperature, water salinity, and impact of some salts on the gelation time was studied. Further, two different approaches were used to model the gelation kinetics, and kinetic parameters were extracted and related to gel composition and gelation conditions.

## Gelation kinetics

Classical reaction rate equations were used previously to analyze the isothermal regime of PAM hydrogels [22]. All

samples were kept at the specified temperature for a time after which no heat change was observed in the DSC curves. The total heat released in the isothermal part was used as a basis to calculate the fractional gelation at time  $t$ . The fractional conversion,  $x$ , was defined as the ratio of the heat released up to time  $t$  to the total heat released during the whole gelation process. Hence, isothermal scans can be analyzed with a reaction rate equation in the form:

$$\frac{dx}{dt} = k(T)(1-x)^n, \quad (1)$$

where  $\frac{dx}{dt}$  is the rate of conversion,  $x$  is the fractional conversion,  $k(T)$  is the specific rate constant at absolute temperature  $T$  (K), and  $n$  is the reaction order. The rate constant can be related to temperature through Arrhenius equation as follows:

$$k(T) = k_0 e^{-E/RT}, \quad (2)$$

where  $E$  is the Activation energy ( $\text{J mol}^{-1}$ ),  $k_0$  is the Arrhenius frequency factor ( $\text{min}^{-1}$ ), and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). By substituting Eq. 2 in 1 and taking the logarithms of both sides yields the following rate model:

$$\ln\left(\frac{dx}{dt}\right) = \ln k_0 - \frac{E}{RT} + n \ln(1-x). \quad (3)$$

To study the gelation kinetics in the isothermal regime, the conversion  $x$  at different times was calculated. The fractional gelation was obtained as the ratio of the area under the curve up to time  $t$  to the total area. Each isothermal gelation kinetics test was performed at a constant temperature and the test was repeated at different temperatures. Equation (3) was fitted by the linear least squares method using Mathematica software to obtain the values of  $n$ ,  $k_0$ , and  $E$ .

On the other hand, we proposed to use the well-known models used in studying crystallization kinetics due to the similarity of both processes as stated earlier. One of the common methods for studying the crystallization kinetics is the Avrami equation which is given elsewhere [21]. This equation can be used in the linear form as follows [23]:

$$\ln[-\ln[1-x_t]] = \ln k_t + m \ln t, \quad (4)$$

where  $x_t$  is the fractional gelation,  $m$  is an exponent related to the order,  $t$  is the time during gelation, and  $k_t$  is the rate constant. A plot of  $\ln[-\ln[1-x_t]]$  versus  $\ln t$  gives a straight line with a slope of  $m$  and intercept of  $\ln k_t$ . Hence, the cross-linking rate constant  $k_t$ , and the exponent  $m$  can be determined. In the non-isothermal part, the total heat released was found by integrating the area under the whole gelation curve and used for calculating the fractional gelation  $x_t$ . The fraction gelation  $x_t$  was obtained as the ratio of heat released up to time  $t$  to total heat.

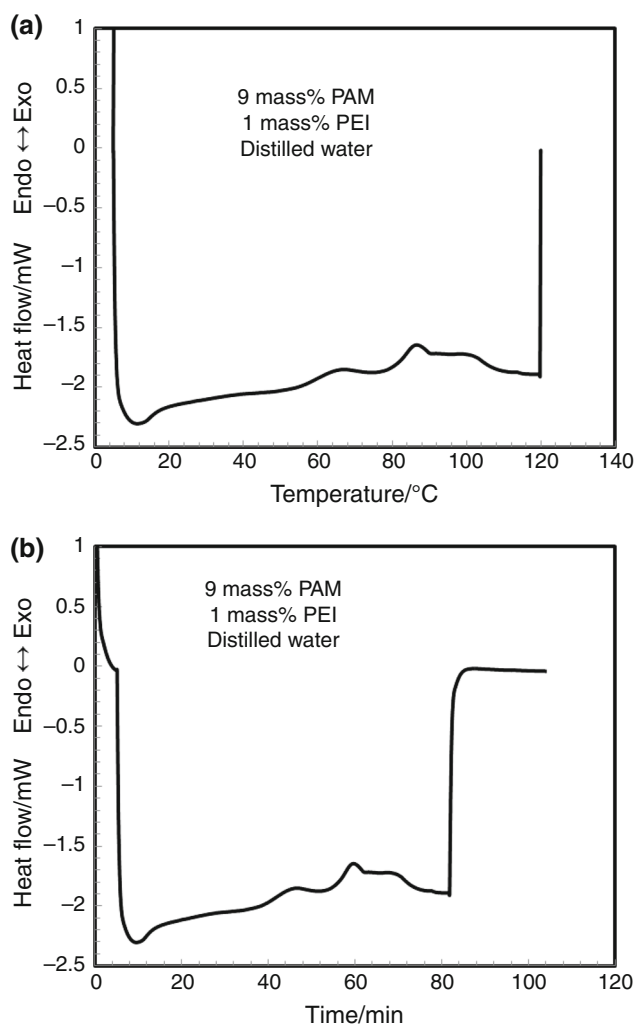
Earlier, rheology was widely used in studying gelation kinetics [24, 25]. In another publication, DSC was coupled with different techniques to characterize PAM hydrogels [26]. The authors are aware of only one study that used DSC to study gelation using the above rate model (Eq. 3) to analyze the gelation process [22]. Here, we used the same rate model and we proposed, for the first time, another model (Eq. 4) to study the gelation kinetics.

### Materials and sample preparation

Two polymer solutions were used in this study. PAM was used as an aqueous solution obtained from SNF Floerger. It has 20 mass% activity, about 250,000–500,000 g mol<sup>-1</sup> molecular mass, and pH ~4.0. PEI is also provided as a solution with pH 11.7, molecular mass of 70,000 g mol<sup>-1</sup>, and activity of 30 mass%. These polymer solutions were used without further treatments. The samples were prepared by adding a predetermined amount of PAM to water (either distilled or sea water) while stirring for about 2 min. Then the required amount of cross-linker (PEI) was added in drops while continuous stirring was performed for an extra 10 min to obtain a homogenous polymer solution. This mixture is referred to as gelant.

### Differential scanning calorimetry (DSC)

All measurements were carried out in a TA Q1000 instrument. This machine is equipped with a refrigerating cooling system (RCS) in which nitrogen is used to purge the instrument at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. The gelant was poured in aluminum hermetic pan and sealed with a lid in a compression tool. An empty aluminum hermetic pan was used as a reference. All samples were equilibrated at 30 °C for 5 min, and then ramped at 1.5 °C min<sup>-1</sup> to a specific final temperature of 80, 100, and 120 °C. For PAM hydrolysis, the sample was equilibrated at 5 °C and then ramped at 1.5 °C min<sup>-1</sup> to 120 °C. One of the gelation experiments was started at lower temperature (5 °C); however, no change was observed compared to samples started from 30 °C. The sealed pan was weighed after the experiment and in all cases the same original mass was obtained. This confirms that the pan is well sealed and no water has escaped. As reported by the manufacturer, these pans can operate up to 140 °C without any leak. After that, the final temperature was kept constant for about 2 h to complete the gelation process. It should be mentioned that the DSC machine was calibrated before the experiments using indium. Moreover, the baseline was checked by running the same thermal program using empty pans. The heating rate was chosen to mimic the field application. It



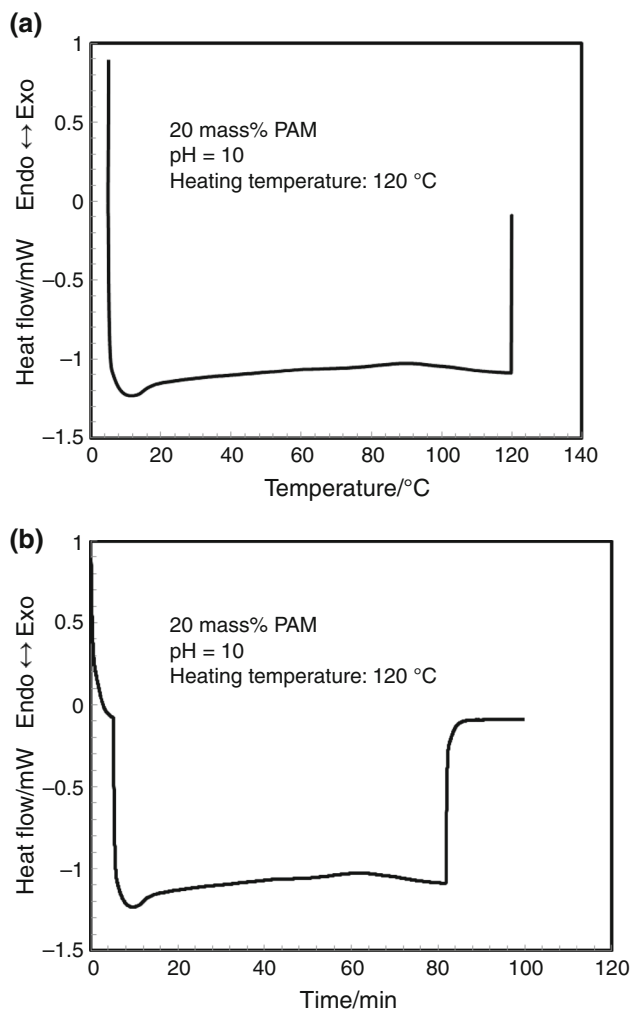
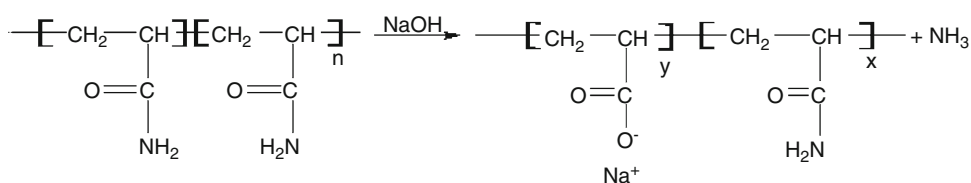
**Fig. 1** Dynamic DSC scan of PAM/PEI system (9/1) mass ratio and final heating temperature of 120 °C. **a** Heat flow versus temperature, **b** heat flow versus time

was reported that typical gelant placement needs 55 min to reach the target zone [27]. In the field, the temperature increases from 40 °C at the surface to about 120 °C at the wellbore, and the injection time was about 55 min in a typical injection. Therefore, to simulate this injection process and achieve the same injection time assuming linear increase in temperature the gelant was heated at ~1.5 °C min<sup>-1</sup> (80 °C/55 min). The DSC was calibrated at the same heating rate. Another advantage of using this low heating rate is the low thermal lag.

### Results and discussion

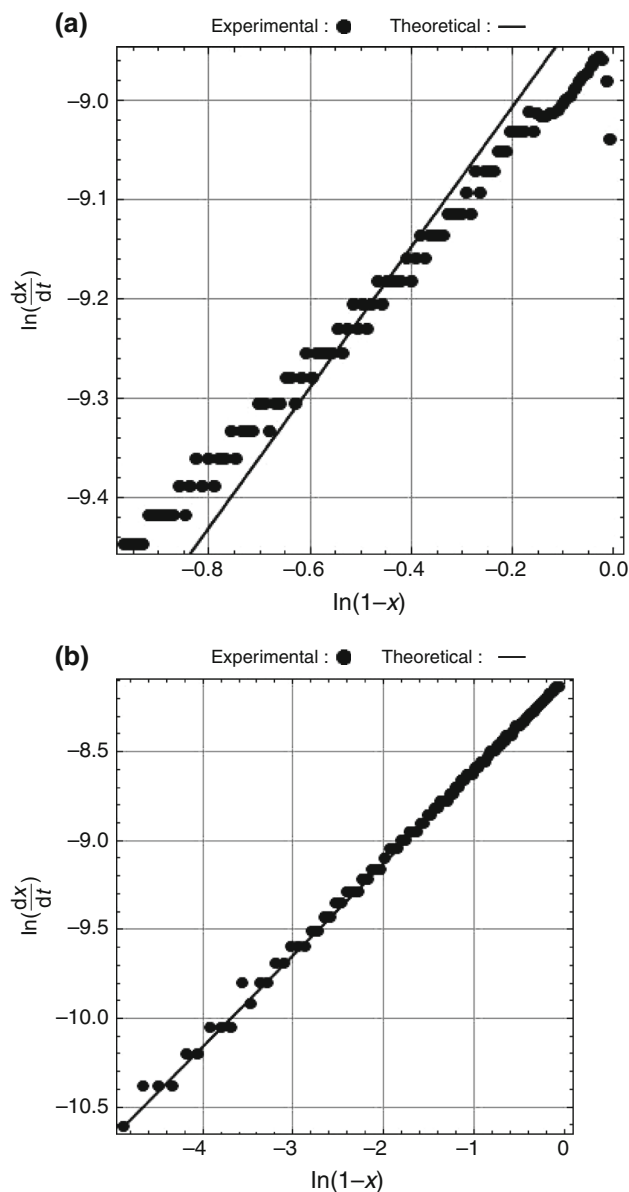
The gelation kinetics of PAM/PEI system was studied by heating the samples from 40 °C at a rate of 1.5 °C min<sup>-1</sup> to a final temperature of 80, 100, or 120 °C. A DSC scan of a gelant containing PAM/PEI at a mass ratio of 9/1 is

**Fig. 2** Alkaline hydrolysis of PAM groups [24, 25]



**Fig. 3** Dynamic DSC scan of PAM up to 120 °C (20 mass% activity). **a** Heat flow versus temperature, **b** heat flow versus time

shown in Fig. 1. The gelant was heated to 120 °C, and then kept at this temperature until no thermal change was noticed to ensure complete gelation. Initially, the DSC curve in Fig. 1a, b shows a strong endotherm which ends at a temperature of ~60 °C followed by an exotherm. This suggests that multiple reactions are taking place during the heating of PAM/PEI system including both endothermic and exothermic processes. The pH of PEI is ~11.7 which makes the gelant alkaline solution. The endothermic reaction is a result of the well-known hydrolysis of PAM under alkaline conditions. In the



**Fig. 4** Experimental data versus predicted data (Rate model) for PAM/PEI (9/1) mass ratio and heating temperature up to 120 °C in a distilled water and b seawater

hydrolysis of PAM, PAM amide groups are converted to carboxylates [28, 29] (Fig. 2).

In order to confirm this endothermic peak, the pH of PAM only was adjusted to 10 by adding few drops of NaOH (1 M). The sample was equilibrated at -5 °C, and then the temperature was ramped at a rate of

1.5 °C min<sup>-1</sup>–120 °C. The curve in Fig. 3a and b shows only endothermic peak which starts immediately with the sample ramping and it ends at around 79 °C. Starting the hydrolysis from lower temperature (5 °C) or room temperature did not show big difference in the amount of heat (~12 %).

The program of studying the kinetics of cross-linking of PAM with PEI was composed of non-isothermal and isothermal parts to mimic the actual injection process when the system is applied in oilfields for water control. Therefore, each regime was analyzed separately. A sample containing 9 mass% of PAM and 1 mass% PEI was

$$x_t = \frac{\text{Total heat released up to time } t}{\text{Total heat released for the isothermal and non-isothermal regime}} \quad (5)$$

prepared in distilled as well as in seawater and subjected to the above thermal program up to 80, 100, and 120 °C. The experimental data showed a good fit to the above model (Eq. 3) as shown in Fig. 4. The total heat released in the isothermal part was used as a basis for analysis (Eq. 3).

For the rate model, the values of  $n$ ,  $k_0$ , and  $E$  were found to be 0.5,  $0.062 \cdot 10^{-4} \text{ min}^{-1}$ , and  $3.1 \text{ kJ mol}^{-1}$ . The value of the rate constant  $k$  was  $0.023 \cdot 10^{-4} \text{ min}^{-1}$ . This indicates that the gelation process is slow. The sample prepared in seawater gives almost the same value of  $n$ . However,  $E$  and  $k_0$  increased to  $4.7 \text{ kJ mol}^{-1}$  and  $0.065 \cdot 10^{-4} \text{ min}^{-1}$ , respectively. The rate constant,  $k$ , decreased from  $0.023 \cdot 10^{-4} \text{ min}^{-1}$  in distilled water to  $0.067 \cdot 10^{-4} \text{ min}^{-1}$  in seawater which represents about 60 % drop. The increase in  $E$  is likely due to the high salinity of seawater ( $57 \text{ g L}^{-1}$ ) where the reaction is retarded by the presence of salts. Hence, more energy is needed to achieve the same conversion. The same data for distilled water were analyzed by Avrami method presented in Eq. 4.

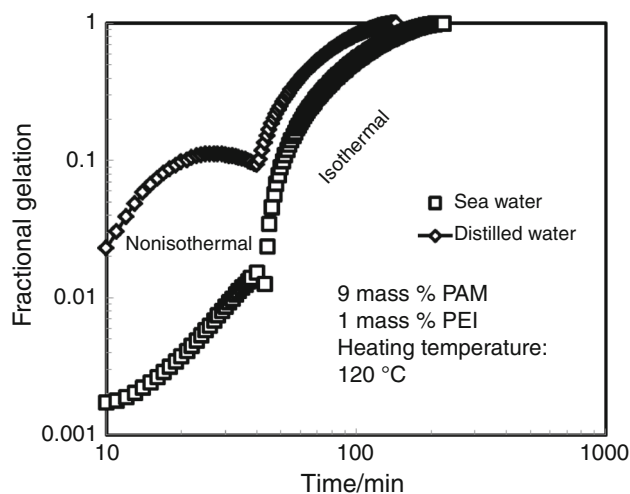
For Avrami model, the values of  $m$  and  $k_t$  were calculated for distilled water as 1.2 and  $0.0183 \cdot 10^{-4} \text{ min}^{-1}$ , respectively. The analysis of PAM/PEI in seawater resulted in a value of  $0.003 \cdot 10^{-4} \text{ min}^{-1}$  for  $k$ , whereas the value of  $m$  was 1.4. It should be noted that in the rate model, the value of  $n$  is related to the order of the reaction while  $m$  in Avrami model is related to the nucleation (here gelation) mechanism and growth dimensions. However, the values of  $k$  and  $k_t$  in the two models relate to the rate of the gelation process. Therefore, we do not expect exact match in the two values of  $n$  and  $m$  and  $k$  and  $k_t$  obtained from the two different models. Irrespective of the model used, the two models agree that the values of  $n$  obtained from the rate model or  $m$  from Avrami model are almost

the same in distilled and sea water. However, the rate parameters ( $k$  and  $k_t$ ) dropped by 60–80 % as a result of the presence of salts. Therefore, both models agree that salts retard the gelation process. These results show how this well-known fact in the field can be revealed by a simple DSC test.

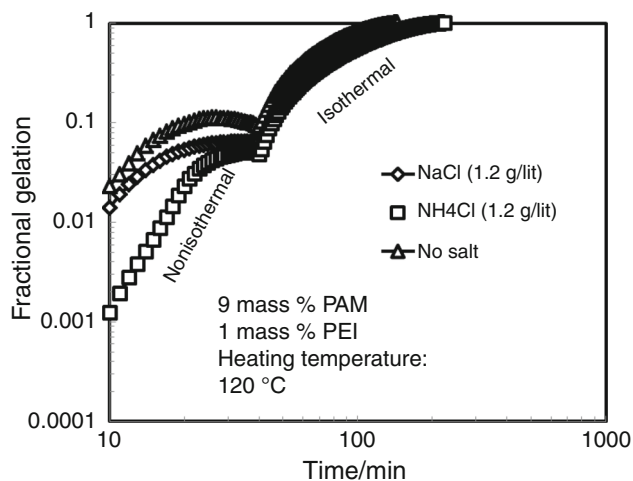
Furthermore, the retardation of gelation in seawater was analyzed once more by considering the whole gelation process using Eq. 5. This was achieved by integrating the area under the curve that corresponds to the gelation in both isothermal and non-isothermal regimes. The fractional gelation was calculated by the following equation:

The results in Fig. 5 show that  $x_t$  is higher when distilled water is used instead of seawater. This is another confirmation for the retardation effect of seawater. For example, 10 % of gelation was achieved after ~20 min in distilled water. In the case of seawater, this time increased to ~50 min. At higher conversions, this observation is still valid. The time needed to complete 90 % of the gelation was ~114 and 167 min for distilled and sea water, respectively.

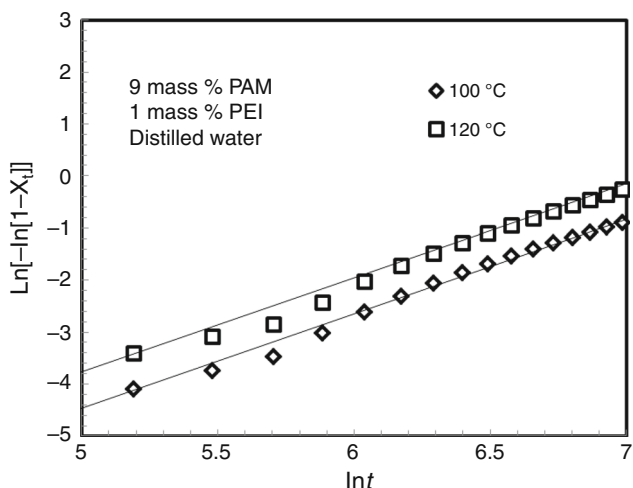
The effect of salts on the isothermal gelation kinetics was examined by adding NaCl and NH<sub>4</sub>Cl. These salts are used in the oilfield industry to retard the gelation. Two samples of gelants with a formulation of PAM/PEI of (9/1) mass ratio were prepared in distilled water by adding  $1.2 \text{ g L}^{-1}$  of the two salts, and the previous thermal



**Fig. 5** Fractional conversion as a function of time for the gelation of PAM/PEI (9/1 mass ratio) at different salinities



**Fig. 6** Effect of salts ( $1.2 \text{ g L}^{-1}$ ) on fractional gelation of PAM/PEI (9/1 mass ratio) for a final temperature of  $120 \text{ }^\circ\text{C}$



**Fig. 7** Avrami plots for PAM/PEI at different temperatures for the non-isothermal regime

program was applied up to  $120 \text{ }^\circ\text{C}$ . Equation 1 was used to analyze the isothermal gelation data. The value of  $n$  was observed to be almost the same in NaCl (0.51) and in  $\text{NH}_4\text{Cl}$  (0.50). The rate constant,  $k$ , decreased from  $0.0195 \times 10^{-4}$  in the case of NaCl to  $0.002 \times 10^{-4} \text{ min}^{-1}$  in  $\text{NH}_4\text{Cl}$  ( $\sim 90 \%$  drop). Therefore,  $\text{NH}_4\text{Cl}$  is a very efficient retarder for the gelation of PAM/PEI in comparison with NaCl. These findings are in agreement with previous results obtained from rheological measurements [24]. The retardation of gelation due to the presence of salts was also examined by considering both the isothermal and non-isothermal data.  $1.2 \text{ g L}^{-1}$  ( $0.021 \text{ mol}$ ) of NaCl and  $1.2 \text{ g L}^{-1}$  ( $0.022 \text{ mol}$ ) of  $\text{NH}_4\text{Cl}$  were used. Figure 6 shows the influence of NaCl and  $\text{NH}_4\text{Cl}$  on the gelation process.

Salt-free water showed higher values of fractional gelation at any time which is retarded by the presence of NaCl and  $\text{NH}_4\text{Cl}$ . At all times,  $\text{NH}_4\text{Cl}$  showed stronger retardation effect in comparison with NaCl. Therefore, the different models and methods of data analysis confirm the retardation of gelation due to the presence of salts.

To investigate the effect of temperature on the gelation kinetics, two samples of PAM/PEI (9/1 mass ratio) were prepared in distilled water and subjected to the same thermal program. Two different final temperatures of  $100$  and  $120 \text{ }^\circ\text{C}$  were used. The results of Avrami analysis for the non-isothermal regime are shown in Fig. 7. The gelation rate constants were found to be  $0.015 \times 10^{-6}$  and  $0.001 \times 10^{-6} \text{ min}^{-1}$  at  $120$  and  $100 \text{ }^\circ\text{C}$ , respectively. This illustrates that the rate of gelation in distilled water at  $120 \text{ }^\circ\text{C}$  is almost 15 times faster than the rate at  $100 \text{ }^\circ\text{C}$ .

## Conclusions

The gelation kinetics of PAM with PEI was studied by the use of DSC. The gelation kinetics was analyzed using well-known crystallization kinetic models due to the similarity of the physics of the two processes. The summary of this study is:

- (1) The DSC is an effective tool for studying the cross-linking (gelation) kinetics of PAM with PEI gel system used for water shutoff in petroleum reservoirs.
- (2) The DSC curves revealed that the cross-linking of PAM/PEI gel system is associated with endothermic as well as exothermic processes. The endotherm was characterized to be due to the hydrolysis of PAM since it is endothermic in nature, whereas the exotherm is a result of the gelation reaction which occurred with heat liberation.
- (3) The rate of PAM/PEI gelation in distilled water at  $120 \text{ }^\circ\text{C}$  is almost 15 times faster than the rate at  $100 \text{ }^\circ\text{C}$ . These results are likely due to the increase in cross-linking density at higher temperatures.
- (4) Irrespective of the model used, the two models agree that the value of  $n$  is almost the same in distilled and sea water. This parameter is related to the order of the cross-linking reaction which is not affected by the presence of salts which acts as a retarder.
- (5) Seawater and salts were found to elongate the gelation time by shifting the onset of cross-linking. This observation suggests that salts delay the gelation by lowering the rate of gelation.
- (6)  $\text{NH}_4\text{Cl}$  is stronger than NaCl in the retardation of the gelation process. This is due to the fact that  $\text{NH}_4\text{Cl}$  is more effective than NaCl in shielding the negative

charges on the carboxylate groups. Consequently, it reduces the available sites on the polymer to cross-link with PEI.

- (7) The presence of salts in seawater leads to a drop of 60–80 % in the rate constant without influencing the order of the gelation reaction which can be interpreted in the same way like the effect by  $\text{NH}_4\text{Cl}$ .
- (8) The DSC proved to be a promising technique for studying the gelation reactions.

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