

# DSC investigation of the gelation kinetics of emulsified PAM/PEI system

## Influence of surfactants and retarders

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**Abstract** Water production in the oilfields has a negative impact on the production and economy. It is highly desired to shut off water paths without affecting the hydrocarbon zones. Polymer gels are frequently used for water control in oil and gas wells. However, a risk will be taken, which is blocking the oil-producing zones alongside the water zones. Hence, a selective system is proposed, which is based on emulsified polymer gel that contains a water phase which will form a gel, and an oil phase remains mobile to secure the flow of oil. The gels formed in situ by breaking up of an emulsified gel made of an oil phase and an aqueous water-soluble polymers (gelant). Breaking of the emulsion and the subsequent gelation is a function of temperature, time, salinity of mixing water, and concentration of the various components, including surfactants and salts. The gelant was prepared by mixing polyacrylamide (PAM) with a mixing brine and then adding polyethylenimine (PEI) as a cross-linker. Diesel and a surfactant were used to form the emulsified gel. In this

study, differential scanning calorimetry (DSC) is utilized to study the emulsified gel reaction kinetics for the first time. The rate of increase in temperature and the final temperature used in DSC were chosen to approximate (mimic) the field injection conditions. The impact of parameters such as temperature, water salinity, surfactant, and retarder type on gelation is investigated to compare the kinetics of the polymeric gels and their emulsified forms. At a given emulsifier concentration, emulsified PAM/PEI has a lower rate of cross-linking (gelation) when compared to that of PAM/PEI. This is most likely due to less heat conducted to the gelant. As a result, the cross-linking density will be less. Ammonium chloride is found to be more efficient than sodium chloride in retarding the gelation process. The type of surfactant is an additional parameter which can be used to control gelation in emulsified gel systems.

**Keywords** Gelation kinetics · DSC · Emulsified gel · Polymeric gel · Water shutoff

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## Introduction

Oil and gas wells in mature fields suffer from high water production during hydrocarbon recovery. Large amounts of water result in a rapid corrosion of well equipment and a rapid decline in hydrocarbon production, ultimately leading to a premature abandonment of the well. Such wells require more complex water–oil separation techniques, incurring additional operational costs [1]. Moreover, the water may contain a high concentration of mercury and arsenic [2], rendering the disposal of the water without further treatment a serious threat to the environment.

Polymer and polymer gels are well suited to totally block the water production zones [3, 4]. The use of

polymeric gels reduces the relative permeability of water [5, 6] during oil and gas production and improves the sweep efficiency of injection wells [7, 8]. Inorganic cross-linked gels [9, 10] and organically cross-linked gels [11, 12] are the most common systems used in oilfields. However, there is a risk that they also reduce the oil flow appreciably, together with water. The risk is smaller when water production is decreased using disproportionate permeability reduction.

Using emulsified gels is a newly proposed smart method for controlling excessive water production in oil and gas fields [13]. The injection of emulsified gels into the near wellbore formation has the advantage of selectively reducing the relative permeability of water more significantly than the hydrocarbon phase. Usually, mechanical means are employed to isolate the treated zone. In this approach, the bullhead placement technique is used without the need of a zone isolating routine, which leads to restricting the water flow and improving the hydrocarbon recovery. Thus, this method can be applied to oil wells without risking their productivity, unlike when a rigid gel is used where the risk of blocking the oil-producing zones is high. This method of water shutoff treatment is referred to as relative permeability modification, and the mechanism by which the water is controlled is known as the disproportionate permeability reduction mechanism.

However, as the injection of polymeric solutions is associated with injectivity problems, the understanding of the gelation kinetics is a critical issue for the successful implementation of this method. A solution containing a mixture of polymers (gelant) is generally emulsified in the oil phase using an appropriate surfactant (emulsifier). This system is designed in such a manner that the emulsion breaks up into a water phase and oil phase in the porous media at the reservoir conditions. In the pore space, the water phase, which contains the gelant, forms a gel, while the oil phase remains mobile. The de-emulsification of the emulsified system and the subsequent gelation are a function of temperature, time, the salinity of makeup (mixing) water, and concentration of the components present.

The time required for the de-emulsification and the formation of the gel is a decisive factor for the placement of the treatment. Appropriate de-emulsification and a longer gelation time are necessary for high-temperature reservoirs. Normally, salts (retarders) are used to delay the gelation and slow down the cross-linking process. Almost all of the previous gelation kinetics studies have used rheological measurements [14–17] and nuclear magnetic resonance (NMR) spectroscopy techniques [18, 19].

Differential scanning calorimetry (DSC) has been commonly employed in studying crystallization kinetics [20, 21]. The mechanisms of the gelation and crystallization processes are similar, with heat released in both cases

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 the cross-linking reactions forming 3-dimensional (3-D) gels when solutions are heated. Recently, DSC has been suggested as a tool which can be used to study the gelation kinetics of polymeric gels systems [22].

In this study, DSC is used to study the gelation kinetics of emulsified gel systems. DSC is a valuable tool to study kinetics of emulsified systems, providing an insight into the separation and gelation physics in addition to exploring the effects of various factors and circumstances. The influence of different emulsifiers, water salinity, and retarders on the gelation time was also studied. Furthermore, a kinetic comparison between the polymeric gels and its emulsified form was performed. Finally, new propositions were used to analyze the gelation kinetics and kinetic parameters were extracted and related to the gel composition and gelation conditions.

## Gelation kinetics

In the past, gelation kinetics was commonly studied using rheological measurements [25, 26]. In a recent study, DSC was used together with several other techniques to characterize PAM hydrogels [27]. The authors are aware of only one study in which DSC has been used to study the gelation process employing classical reaction rate equations to analyze the isothermal regime of polyacrylamide hydrogels [23].

On the other hand, as stated earlier the use of well-known crystallization kinetic models to study gelation kinetics was proposed due to the similarity of both processes [22]. One of the common methods for studying crystallization kinetics is using the Avrami equation, details of which are given elsewhere [23]. This equation can be used in the linear form as follows [24]:

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

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 an intercept of  $\ln k_t$ . Hence, the cross-linking rate constant  $k_t$  and the exponent  $m$  can be determined. The total heat released is found by integrating the area under the entire gelation curve, which is used to calculate the fractional gelation  $x_t$  (the ratio of heat released up to time ( $t$ ) to the total heat).

All samples were heated at a specific heating rate up to the final temperature and held at the final temperature until a heat change was not observed in the DSC curves. The total heat released was used as the basis to calculate the fractional gelation at time ( $t$ ).

## Experimental

### Materials

The following surfactants were used in this study: Ethomeen T/12 (ethoxylated amides) and ANSC (CRV) RD (Amine Acetates). Seawater and field mixing water (FMW) were used as the water phase, and the concentration of dissolved ions is shown in Table 1. Diesel ( $814.6 \text{ kg m}^{-3}$ ), which is representative of that used in the oilfield for preparing emulsified acids, was procured from the local gas stations.

Polyacrylamide (PAM) and polyethylenimine (PEI) polymer solutions were used in this study. The aqueous PAM solution, which is 20 mass % active and has a molecular mass in the range 250 to  $500 \text{ kg mol}^{-1}$  with a pH of  $\sim 4.0$  (according to the supplier), was obtained from SNF Floriger and used without further treatment. The PEI solution with an activity of 30 mass % and a molecular mass of  $70 \text{ kg mol}^{-1}$  was used as a cross-linker. Sodium chloride (NaCl) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) used in this study are of ACS reagent grade.

### Sample preparation

Polymer gels and emulsified polymer gel systems were prepared in a systematic manner to ensure reproducibility. The polymer gels were prepared at room temperature by adding a specific amount of PAM (9 mass%) to water (either seawater or FMW) over a period of 2 min while stirring. Then, 1 mass% of the cross-linker (PEI) was added drop-wise, and the mixture was continuously stirred for an additional 10 min to obtain a homogenous solution. This mixture is identified as the gelant. It should be noted that fresh samples are prepared at room temperature just before running the experiments to avoid or minimize any

hydrolysis. Our previous work [22] showed that detectable hydrolysis was observed above  $80 \text{ }^\circ\text{C}$ .

In this study, the emulsified systems were prepared with two surfactants. Each emulsifier at a specific concentration (0.35 vol%) was added to diesel, giving it sufficient time to mix with diesel thoroughly. Then, the desired volume (70 vol%) of the water phase (gelant) was slowly added to 30 vol% of the hydrocarbon phase (diesel containing the emulsifier), while continuously agitating for about 5 min until a homogenous emulsion is obtained. Appropriate amounts ( $43.2 \text{ g L}^{-1}$ ) of NaCl and/or  $\text{NH}_4\text{Cl}$  were added to seawater or FMW before the addition of the polymer and the cross-linker to determine the effect of retarders.

### Differential scanning calorimetry (DSC)

All experiments were performed on a TA Q1000 instrument in which nitrogen is used for purging in a refrigerated cooling system (RCS) at a flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ . The gels (polymer gels or emulsified polymer gels) were placed in a hermetic aluminum pan and sealed with a lid using a compression tool. An empty aluminum hermetic pan was used as a reference to establish the baseline. Initially, samples were equilibrated at  $30 \text{ }^\circ\text{C}$  for 5 min, and the temperature was increased at a rate of  $2 \text{ }^\circ\text{C min}^{-1}$  to reach a final temperature of  $130 \text{ }^\circ\text{C}$ . The sealed pan was weighed after the experiment to ensure that material is not lost and in all cases the same original mass was obtained, indicating that water was not lost from the samples due to evaporation. After ensuring that the pan is sealed well, it was heated isothermally (at  $130 \text{ }^\circ\text{C}$ ) for about 4 h to complete the gelation process. The heating rate used in experiments approximates that encountered in field applications. It has been found that it requires  $\sim 55$  min to place a gelant in the target zone [27]. It has also been reported that the temperature increases from  $\sim 30 \text{ }^\circ\text{C}$  at the surface to about  $130 \text{ }^\circ\text{C}$  at the wellbore. Therefore, to subject the reaction mixture to the same heating rate encountered in the field (and thus to the same injection time, assuming a linear increase in temperature), the gelant was heated at approximately  $2 \text{ }^\circ\text{C min}^{-1}$  ( $100 \text{ }^\circ\text{C}/55 \text{ min}$ ). Then, the sample was held at that temperature, simulating the conditions encountered in reservoirs. The DSC was calibrated at the same heating rate.

### Results and discussion

The gelation kinetics of several polymer systems were studied by heating the samples from  $30 \text{ }^\circ\text{C}$  at approximately  $2 \text{ }^\circ\text{C min}^{-1}$  to a final temperature of  $130 \text{ }^\circ\text{C}$  and then holding at this temperature until further thermal

**Table 1** Concentration of dissolved ions of the mixing waters used in the experiments

Ion	Water type	
	FMW/ppm	Seawater/ppm
Na	175	17,085
Mg	46	2200
Ca	112	1040
Cl	377	31,267
$\text{SO}_4$	266	4308
$\text{HCO}_3$	146	140
Total dissolved solids/TDS*	1122	56,040

\* Sum of the concentration of the ions

changes were not observed to ensure complete gelation. The DSC signal was corrected by a factor based on the mass percent, which is the effective mass of PAM/PEI in the specific system. At the beginning, several responses are observed during heating of the reaction mixtures (PAM/PEI and emulsified PAM/PEI), including signals due to

process using Eq. (2). This was realized by integrating the area under the curve for the gelation in the non-isothermal and isothermal regimes. It should be mentioned that the peak was integrated linearly. The fractional gelation ( $x_t$ ) was calculated using the following equation:

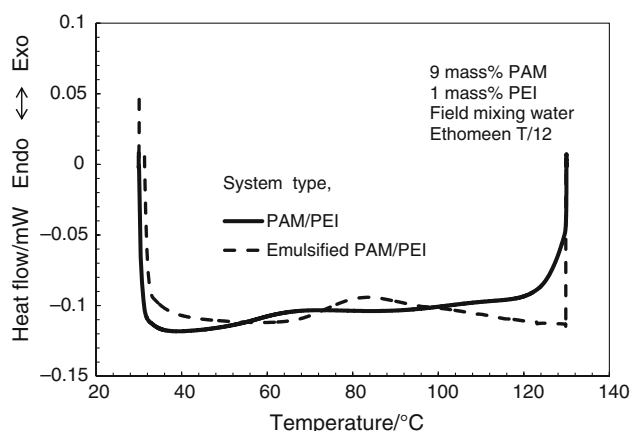
$$x_t = \frac{\text{Total heat released up to time } t}{\text{Total heat released for the isothermal and nonisothermal regimes}} \quad (2)$$

both endothermic and exothermic processes. As shown in Fig. 1, an endothermic process which ends at a specific temperature is followed by an exothermic process. The DSC dynamic scans show that the amount of heat released after 100 min in period from 35 to 130 °C ( $\sim 33 \text{ J g}^{-1}$ —exothermic) is larger for un-emulsified PAM/PEI. The heat released decreases to  $\sim 9.894 \text{ J g}^{-1}$  when PAM/PEI is emulsified. Both systems (PAM/PEI and emulsified PAM/PEI) contain PEI (The pH of PEI is  $\sim 11.7$ ) which renders the PAM/PEI mixture alkaline. The endothermic response is due to the hydrolysis of PAM under the alkaline environment, which converts the amide groups of PAM into carboxylates [28, 29]. Literature reports revealed that the cross-linking reaction is believed to be due to a nucleophilic substitution resulting from the attack of the imine nitrogen in PEI to the amide groups in PAM [30].

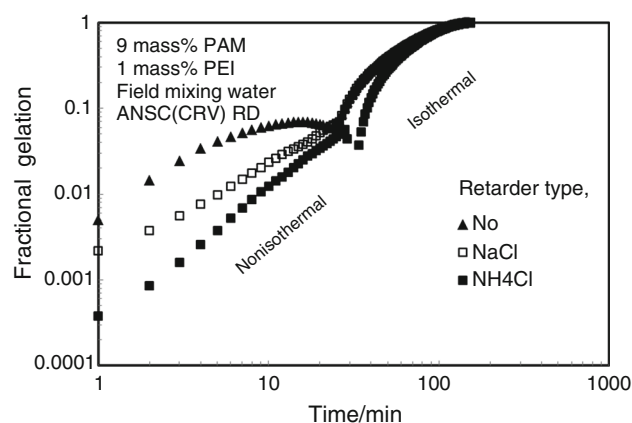
The program for studying the kinetics of the cross-linking process of PAM/PEI and emulsified PAM/PEI was designed to simulate the conditions encountered during the actual injection when the emulsified gel system is applied in the oilfield for water shutoff. The delay of gelation was analyzed by taking into account the complete gelation

The results in Fig. 2 show that  $x_t$  is higher when FMW is used without added salt, when compared to the case where  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$  are used. For example, a  $\sim 7\%$  gelation was achieved after  $\sim 15$  min in FMW without salt. However, when salt is added, the time increases to  $\sim 26$  min and  $\sim 36$  min for  $\text{NaCl}$  and  $\text{NH}_4\text{Cl}$ , respectively. The same trend prevails even at higher values of  $x_t$  in the isothermal region (130 °C).

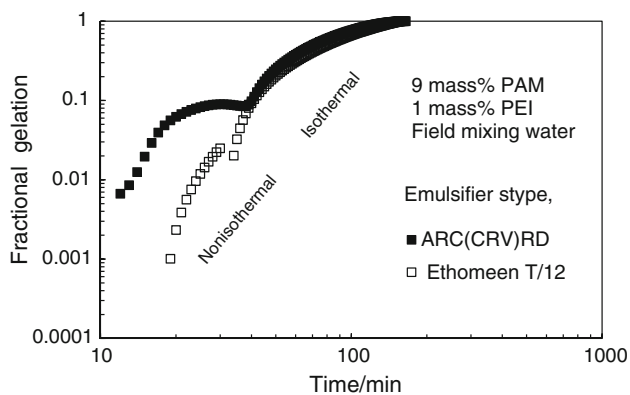
Two emulsifiers were utilized to investigate the influence of emulsifier type. The total heat released for an emulsified gel prepared with ANSC (CRV) RD is  $257.3 \text{ J g}^{-1}$ , whereas  $329.44 \text{ J g}^{-1}$  is released when Ethomeen T/12 was used. Figure 3 shows that  $x_t$  is higher when the ANSC (CRV) RD emulsifier is used to form emulsified PAM/PEI instead of Ethomeen T/12. For example,  $\sim 5\%$  of gelation was attained after  $\sim 35$  min ( $14.67 \text{ J g}^{-1}$ ) with Ethomeen T/12, whereas it takes only 18 min ( $12.5 \text{ J g}^{-1}$ ) when ANSC (CRV) RD is used. Furthermore, this is true above 10 % gelation ( $x_t = 10\%$ ). For instance, 50 % of gelation was achieved after  $\sim 80$  min ( $165.36 \text{ J g}^{-1}$ ) with Ethomeen T/12 and in  $\sim 70$  min ( $126.65 \text{ J g}^{-1}$ ) with ANSC



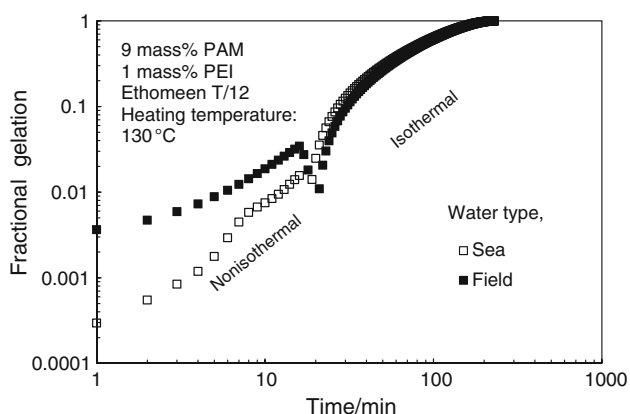
**Fig. 1** DSC scan of PAM/PEI and emulsified PAM/PEI systems with a 9:1 mass ratio and a final heating temperature of 130 °C



**Fig. 2** Effect of salts ( $43.2 \text{ g L}^{-1}$ ) on fractional gelation of emulsified PAM/PEI (9:1 mass ratio)



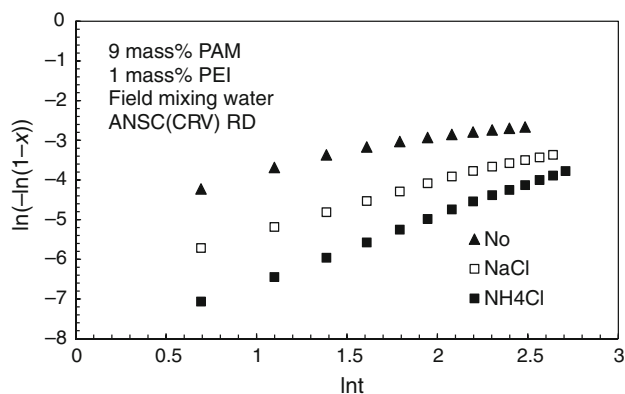
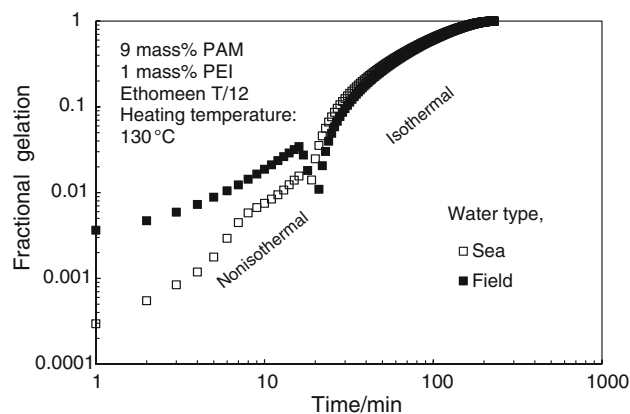
**Fig. 3** Effect of the emulsifier type on the fractional gelation of emulsified PAM/PEI (9:1 mass ratio) at a final temperature of 130 °C



**Fig. 4** Effect of salinity of makeup water on the fractional gelation of emulsified PAM/PEI (9:1 mass ratio) at a final temperature of 130 °C

(CRV) RD. As a postulate, this is most likely due to the presence of some groups that delay the gelation process in Ethomeen T/12. More experimental work is required to reach a definite conclusion.

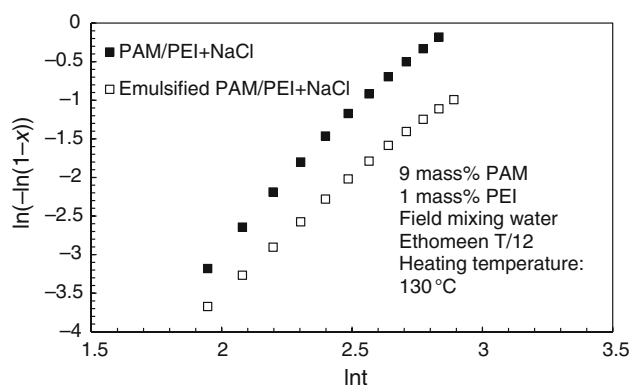
A slightly higher fractional gelation is observed in the isothermal (130 °C) region for a gelant prepared with sea water when compared to that for a gelant prepared with FMW. As shown in Fig. 4, this behavior is not observed in the non-isothermal (35–130 °C) region. In the non-isothermal region, fractional gelation for a gelant prepared with FMW is higher than that for a gelant prepared with sea water. A similar trend has been observed in a rheological study in which the impact of seawater and FMW on the gel strength and gelation time was investigated [27]. In Figs. 2–4, some gelation reaction rate decreases with increasing temperature during non-isothermal step, and this is obviously contradict to the common reaction kinetics which shows reaction rate increases exponentially with temperature. This decrease is probably due to small endothermic peak (hydrolysis), which follows the first exothermic peak.



**Fig. 5** Avrami plots for NaCl and NH<sub>4</sub>Cl (retarders) in the non-isothermal regime

Furthermore, the Avrami model has been proposed to study the gelation process for emulsified polymer gel systems. This model has been used to analyze the gelation process of the polymer gels of (PAM/PEI) [22]. Figure 5 illustrates the effect of salts on the emulsified polymer gel system. The values of  $m$  and  $k_t$  were calculated for the emulsified PAM/PEI without salt addition using the Avrami model, as 0.834 and  $9.842 \times 10^{-3} \text{ min}^{-1}$ , respectively. The values of  $m$  and  $k_t$  for the emulsified system in the presence of NaCl are 1.22 and  $1.49 \times 10^{-3} \text{ min}^{-1}$ , respectively. In the case of NH<sub>4</sub>Cl, the values of  $m$  and  $k_t$  are 1.66 and  $2.67 \times 10^{-4}$ , respectively. These results indicate that the rate of gelation is almost 6 times slower in the presence of NH<sub>4</sub>Cl than in the presence of NaCl. This is due to the efficiency of NH<sub>4</sub>Cl in shielding the negative charges on the carboxylate groups when compared to NaCl. As a result, fewer sites will be available on PAM for cross-linking with PEI. This is in agreement with results reported in the literature [27].

Figure 6 shows a comparison between the polymer gel and the emulsified polymer gel. The values of  $k_t$  for PAM/PEI and the emulsified PAM/PEI are  $1.23 \times 10^{-4} \text{ min}^{-1}$  and  $4.44 \times 10^{-5} \text{ min}^{-1}$ , respectively. This suggests that more cross-linking reactions are taking place in the case of



**Fig. 6** Avrami plots for the two systems in the non-isothermal regime

PAM/PEI and indicates that the rate of gelation in emulsified PAM/PEI is almost 3 times slower than in PAM/PEI. It has been postulated that lower cross-linking rate in the emulsified form is likely due to the partial dissolution of the cross-linker in the oil phase [13]. Authors postulate that a better explanation is that the presence of the gelant emulsified in the oil phase leads to less heat conducted to the gelant, resulting in a slower reaction rate.

## Conclusions

The gelation kinetics of emulsified form of PAM/PEI was studied by means of DSC. Avrami model, which has been applied to crystallization kinetics, was applied to gelation kinetics due to the similarity of the crystallization and gelation processes. The results of this work can be summarized as follows:

1. DSC is an efficient means for studying the gelation kinetics of emulsified PAM/PEI gel systems applied for water control in oilfields.
2. The suitability of salts to extend the gelation time by shifting the onset of cross-linking reaction rather than slowing down the gelation by lowering the rate of gelation was established.
3.  $\text{NH}_4\text{Cl}$  is found to be more efficient than  $\text{NaCl}$  in the retardation of the gelation process. This is due to the efficiency of  $\text{NH}_4\text{Cl}$  in shielding the negative charges on the carboxylate groups when compared to  $\text{NaCl}$ , leading to a decrease in the sites available on the polymer for cross-linking with PEI.
4. Emulsified PAM/PEI was found to have a lower rate of cross-linking (gelation) when compared to PAM/PEI due to the partial dissolution of the cross-linker in the oil phase. These observations suggest that the emulsified form slows down the gelation by lowering the rate of reaction (cross-linking) at a given surfactant

concentration. Hence, higher concentrations of PEI should be used to account for the partial dissolution of the cross-linker in the oil phase.

5. DSC can be used to study gelation kinetics and obtain an insight into the factors that influence gelation.
6. The nature of the surfactant affects the rate of gelation. This means that the type of surfactant is an additional parameter that can be used to control the gelation process of emulsified gel systems.

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