REGULAR ARTICLE

Influence of salinity on the properties of the different HPAM/Al³⁺ systems

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Abstract. In order to achieve oil increment and water cut reduction in the heterogeneous oil reservoirs, a conformance control technology by using HPAM/Al³⁺ systems has been widely used due to the low price and environmental friendliness. However, the complex structure and state of high-valent metal ions in brine water can directly affect the properties of the different HPAM/Al³⁺ systems, which may lead to unreasonable applications. Therefore, in order to better utilize the HPAM/Al³⁺ systems, the characteristics of gelation of HPAM and the three types of aluminum citrate under different salinities are systematically studied. Experimental results show that an important reason for the cross-linking reaction of HPAM/Al³⁺ being affected by salinity is that the morphology and structure of the aluminum citrate complex is different under the different salinities. Although the change of characteristics of the reaction time and the cross-linking degree of the three HPAM/Al³⁺ systems are different, the process of the cross-linking reactions of the three HPAM/Al³⁺ systems are the same. Besides, the thermal stability of the HPAM/Al³⁺ gels is weakened with the increasing of salinity regardless of the ratio of citrate ligands to Al³⁺. According to the matching relationship between salinity and HPAM/Al³⁺ systems, the reaction time can be controlled to achieve the requirements of on-site construction operation for the conformance control of a given heterogeneous oil reservoir.

Nomenclature

HPAM	Hydrolyzed Polyacrylamide
T	Delay time, s
T_1	The ith component of spin-lattice relaxation time, s
I(t)	Total magnetic moment at time, t
I_{0i}	Initial magnetic moment of the ith component
N	Number of components with different relaxation environments
The three	The three different HPAM/Al³⁺ systems
LPS	Linked Polymer Solution
CDG	Colloidal Dispersion Gel

1 Introduction

With the development of mature oilfields by water flooding in China, excess water production problems have gradually arisen from the heterogeneity of continental sedimentation oil reservoirs [1–5]. For example, the comprehensive water cut of Daqing oilfield has exceeded 95% now. Treatment of the produced water leads to an unnecessary operating expense, such as water lifting, wastewater treating, descaling, and aczoiling, etc. [6]. Presently, although there are two means (One is chemical and the other is mechanical) to decrease the excess water production, only the chemical methods can play a treatment role in the depths of the stratum, so that the chemical methods are widely used to increase oil production and decrease water cut in heterogeneous reservoirs around the world [7–9]. Among the many chemical methods, a polymer gel for conformance control and water shutoff is the most widely used due to a good adaptability and a low price [10]. The polymer gel is based on a solution of water, a polymer and a cross-linker, which is prepared at the surface. And then the gelant with a low viscosity is injected to the target zone through the wellbore. After gelation under the reservoir environment, the formed gel can plug the large water flow channel to divert the followed fluids.

As a type of polymers, partially Hydrolyzed Polyacrylamide (HPAM) has been widely used as the main agent

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of the polymer gel because of its reasonable cost and high efficiency, which is a polyelectrolyte macromolecule with a flexible chain [11–15]. As a type of cross-linkers, the aspiration to use high valence metal ion (Al^{3+} or Cr^{3+}), provided in the form of polynuclear olation complex ion (AlCit or Ac_3Cr), is remarkable due to its economic cost and good adaptability. The cross-linking reaction of HPAM and Al^{3+} or Cr^{3+} occurs between negatively charged carboxylate groups of HPAM and hydrated Al^{3+} or Cr^{3+} [16–21]. However, due to the different reactivity between Al^{3+} and Cr^{3+}, and their different ligands, the cross-linking mechanism and influence factors of HPAM/Al^{3+} and HPAM/Cr^{3+} are different. The HPAM/Al^{3+} system is suitable for applied to medium temperature reservoirs, while the HPAM/Cr^{3+} system is suitable for applied to low temperature reservoirs. More importantly, the aspiration to use Al^{3+} is remarkable due to its favorable environmental status. Due to the successful application of HPAM/Al^{3+} system for conformance control of medium temperature reservoirs, many scholars have conducted extensive research and obtained many great breakthroughs in the research of cross-linking reaction mechanisms [22].

In 2001, Zhang *et al.* [23] studied the morphological structure and properties of HPAM/Al^{3+} gels and found that the formed gels had three typical states with the variation of HPAM concentration (a dispersed gel, a gel containing both dispersed and continuous network phase, and a gel with continuous network structure are successively formed over the increase of HPAM concentration). In 2009, Wang and Lu [24] found that the higher the salinity of solvent, the higher the concentration of Al^{3+}, and the higher the temperature, the easier the intramolecular cross-linked polymer there had been formed. In addition, for the influence on the cross-linked polymer, that of Ca^{2+} is the biggest, then Mg^{2+}, the least being Na^+. In 2014, Kedir *et al.* [25] investigated that phase transition of aluminum cross-linked HPAM under a low salinity condition and revealed that the phase transition is a stepwise process. The first step is the transition from a random polymer coil to structured coils, the second step is that the networked weak gel is formed by coil aggregates above the threshold concentration. In 2016, Kedir *et al.* [26] found that Linked Polymer Solution (LPS) solution at a high salinity solvent underwent a phase transition by chain re-expansion, called reentrant transition, of which the rate is affected by the concentrations of Al^{3+}. The above literature can provide a basis for us to better understand the reaction mechanism of HPAM/Al^{3+}.

From the above analysis, both of the parameters of HPAM and Al^{3+} have an effect on the cross-linking reaction. For HPAM, its structure and performance are now very clear [27–30]. For Al^{3+}, it has been recognized that Al^{3+} in aqueous solution is a complex in the presence of ligands, such as organic acids, and the specific form of existence of the complex of Al^{3+} has been mainly effected by the mole ratio of the ligands to Al^{3+}, which should have been attracted a great deal of attention due to its importance in effect on cross-linking reaction of HPAM/Al^{3+} [31]. However, the reported complex of Al^{3+} as a cross-linker used for conformance control in the heterogeneous
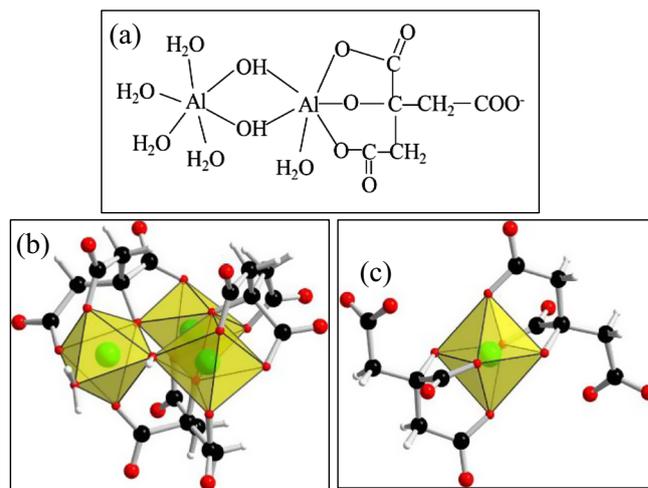
Fig. 1. Structure of the aluminum citrate complex. (a) Mole ratio of 2:1 of Al^{3+} to citrate; (b) Mole ratio of 1:1 of Al^{3+} to citrate; (c) Mole ratio of 1:2 of Al^{3+} to citrate.

reservoirs is simplex or not clearly stated. Only a few of literature presented the aluminum citrate complex with a 2:1 of molar ratio of Al^{3+} to citrate, but many of literature had not given the composition or formation process of aluminum citrate [32–35].

Actually, the aluminum citrate complex can be formed in various ratios of Al^{3+} to citrate ligand, which has attracted a great deal of attention due to its importance in many processes related to environment, biology, and materials [36]. In 1988, Mumallah [37] studied the structure of the formed complex with a mole ratio of 2:1 of Al^{3+} to citrate, which was shown in Figure 1. The two aluminum atoms were bridged by two hydroxyl groups. For one of the Al, three of the coordination sites were occupied by citrate and the last was occupied by water. For the other Al, four sites were occupied by water. In 1990, Feng et al. [38] studied the structure of the formed complex with a mole ratio of 1:1 of Al^{3+} to citrate and found that the mole ratio of Al^{3+} to citrate was 3:3 in a unit structure, which was shown in Figure 1b. Each of the three citrates provided a hydroxyl group and three carboxyl groups for an aluminum atom. In 2006, Happel and Seubert [39] studied the structure of the formed complex with a mole ratio of 1:2 of Al^{3+} to citrate, which was shown in Figure 1c. The aluminum atom was bridged by two hydroxyl groups and four carboxyl groups, which were provided by the two citrates.

Due to the different mole ratios of Al^{3+} to citrate ligand, the different types of aluminum citrate have different reactivity, which can lead to the different characteristics of cross-linking reaction with HPAM. Therefore, it is very important and necessary to study the characteristics of the gelation between the different types of aluminum citrate and HPAM to expand the scope of application of HPAM/Al^{3+} for conformance control. Presently, as is well-known, there have many influencing factors on the crosslinking reaction under an oil reservoir environment, such as reservoir temperature, the parameters of polymer and

cross-linking agent, the properties and salinity of the formation water, etc. However, in this paper, we focus on investigating the influence of salinity on the gelation of aluminum citrate and HPAM. This is because the quality of injection water is easy to be changed and controlled during water flooding. The aim of this paper is to study the influence of salinity on the gelation of the different aluminum citrates and HPAM, which can provide an important theoretical basis for determining a matching relationship between the different HPAM/Al^{3+} systems and the formation water.

2 Experiment

2.1 Reagents and equipment

HPAM is from *Beijing Hengju Chemical Group Corporation* in China. Its molecular weight is 12 million g/mol and its hydrolysis degree is 25%. NaCl, NaOH, AlCl$_3$·6H$_2$O, and sodium citrate are all analytically pure and obtained from *Beijing Chemical Reagents Company*. The main instruments include a UV2550 ultraviolet-visible spectrophotometer from *Shimadzu Corporation*, a DV-III Brookfield viscometer from *Brookfield Company*, a Bruker DMX-300 nuclear magnetic resonance spectrometer from *Bruker Company*, and a DSC823 differential scanning calorimeter from *Mettler Toledo Company* in Switzerland. The shear rate of measuring viscosity is 7.34 s^{-1}. If there are no other instructions, the experimental temperature is 60 °C, in accordance with the formation temperature of most of maturing oilfields in China. Simulated formation water is prepared with the different concentration of NaCl and deionized water, which is used for preparing the HPAM solutions and the HPAM/Al^{3+} systems in the experiment.

2.2 Testing the spin-lattice relaxation time of ^{27}Al in the three aluminum citrates under different salinities

In 2014, Kedir *et al.* [25, 32] summarized that a multitude of species coexist in solution and one species dominate over the other due to the highly complex of the chemistry of aluminum citrate. However, they thought it is difficult to establish a complete characterization because of the dynamic equilibrium between complexes and versatility of the polynuclear complexes in aqueous environment. Therefore, the present work is motivated to study the existent forms of Al^{3+} in the three aluminum citrate solutions under different salinities, which is used to revealed the effect of salinity on the cross-linking of HPAM/Al^{3+}.

The spin–lattice relaxation time of the nucleus is mainly caused by the dipole–dipole interaction between the nucleuses, of which the value is directly related to the interaction between the atoms. When the molecular movement slows down, the spin–lattice relaxation time can be increased. Under different salinities, the ionic strength is different, which can result in the different existent forms of Al^{3+} and the molecular motion, so that the spin–lattice relaxation time is different.

Liquid state ^{27}Al NMR measurements are performed on a Bruker DMX-300 nuclear magnetic resonance spectrometer. A 5 mm liquid phase wide frequency probe with cold pre-amplification is used for the DMX 300. The concentrations of Al^{3+} in the three aluminum citrates used for NMR measurements are also 100 mg/L. Other experimental operating parameters are resonance frequency of 78.2 MHz, spectrum width of 46 728.97 Hz, and the accumulative frequency of 1196 at the temperature of 25 °C. The spin–lattice relaxation time is measured by the inversion recovery method. During reversal recovery experiment, the mathematical expression for the attenuation of intensity of spectral lines with time is as following:

$$I(t) = \sum_{i=1}^{n} I_{0i}\left(1 - 2\exp\left(-\frac{t}{T_{1i}}\right)\right).$$

After the relaxation curve is obtained, the spin–lattice relaxation time of different states of molecular motion in the system can be calculated by performing nonlinear fitting.

2.3 Preparation of the three HPAM/Al^{3+} systems

The cross-linking agent is an aluminum citrate solution consisting of AlCl$_3$·6H$_2$O and sodium citrate in a certain proportion (mole ratio), which can be used when the pH value is fixed at seven by adding NaOH solution. According to the different compositions, three types of the aluminum citrate systems are prepared. Aluminum citrate 1 is a system with the mole ratio of citrate to Al^{3+} of 1:2. Aluminum citrate 2 is a system with the mole ratio of citrate to Al^{3+} of 1:1. Aluminum citrate 3 is a system with the mole ratio of citrate to Al^{3+} of 2:1. The concentrations of Al^{3+} in the three stock solutions of aluminum citrate are all 5000 mg/L.

The three different aluminum citrate solutions correspond to the three types of HPAM/Al^{3+} systems. The HPAM/Al^{3+} system 1 consists of HPAM and aluminum citrate 1, the HPAM/Al^{3+} system 2 consists of HPAM and aluminum citrate 2, and the HPAM/Al^{3+} system 3 consists of HPAM and aluminum citrate 3. The details parameters of the three HPAM/Al^{3+} systems are shown in Table 1 [40–42]. All solutions are prepared by using the simulated formation water samples.

2.4 The basic principle of experiments

In general, it is convenient and cheap to judge whether the cross-linking reaction has occurred by the change of viscosity of the HPAM/Al^{3+} system, but this method cannot understand the nature of the chemical reaction caused by the change of concentration of each reactant involved in the cross-linking reaction. As is known to us, the chemical reaction between HPAM and aluminum citrate is caused by Al^{3+} cross-linking the carboxyl groups of HPAM. In addition, Mack and Smith [43] thought the cross-linking reaction between HPAM and high metal ions is mainly controlled by the concentration of high metal ions. So that it is reasonable to study the cross-linking reaction of HPAM/Al^{3+} by measuring the concentration of Al^{3+}.

Table. 1. Compositions of the different HPAM/Al^{3+} systems.

Type of conformance control and oil displacement agent	Type of Al^{3+}	Al^{3+} (mg/L)	HPAM (mg/L)
HPAM/Al^{3+} system 1	Aluminum citrate 1	100	2000
HPAM/Al^{3+} system 2	Aluminum citrate 2	100	2000
HPAM/Al^{3+} system 3	Aluminum citrate 3	100	2000

Although there are many ways to solve the problem (such as nuclear magnetic resonance, computerized tomography, core flooding, etc.), UV–VIS spectrophotometry is the most accurate and rapid method. In Sikora and McBride's article [44, 45], they found that ultraviolet spectrophotometry can provide valuable information on the composition and stability constant of a metal-ligand complex, and then they studied the ultraviolet spectrogram of aluminum complex, which had the maximum absorption peak in a certain band. In Kedir *et al.*'s article [25, 26, 32] UV−visible spectroscopy was used for investigating the phase transition of LPS. On the basis of the principles, the absorption curves of the three aluminum citrates, which are prepared with deionized water and measured by UV–VIS spectrophotometer, are shown in Figure 2. From Figure 2, it can be observed that the maximum peaks of aluminum citrate 1, aluminum citrate 2, and aluminum citrate 3 are observed at 208 nm, 203 nm, and 198 nm, respectively. Therefore, fixing the wavelength at 208 nm, 203 nm, and 198 nm can make the results of the cross-linking reaction of the HPAM/Al^{3+} system 1, 2, and 3 more comparable in the experiment, respectively. The process of the reaction is researched by analyzing how the absorbance value varies with time under the different salinities. In addition, the absorbance difference before and after the cross-linking reaction, rather than absorbance alone, is used to characterize the cross-linking degree in the following sections to eliminate the effects of the composition changes of reactant or resultant salinity on absorbance. Therefore, the absorbance difference can represent the cross-linking degree, which is related to the change of concentration of aluminum citrate.

2.4.1 Testing the absorbance and viscosity of the HPAM/Al^{3+} systems during gelation under different salinities.

First, prepare the simulated formation water samples with different salinities within the range of 0–80 000 mg/L by adding the different mass concentrations of NaCl into the deionized water. Second, prepare the HPAM/Al^{3+} systems with the different simulated formation water samples in accordance with the following steps: ① Add HPAM into the different simulated formation water samples and fully stir to form a series of homogeneous HPAM aqueous solutions, respectively; ② Add aluminum citrate 1, aluminum citrate 2, or aluminum citrate 3 to the HPAM solutions and stir well under a low and constant stirring rate, respectively; ③ Measure the viscosity and absorbance of the three HPAM/Al^{3+} systems (the three) during gelation
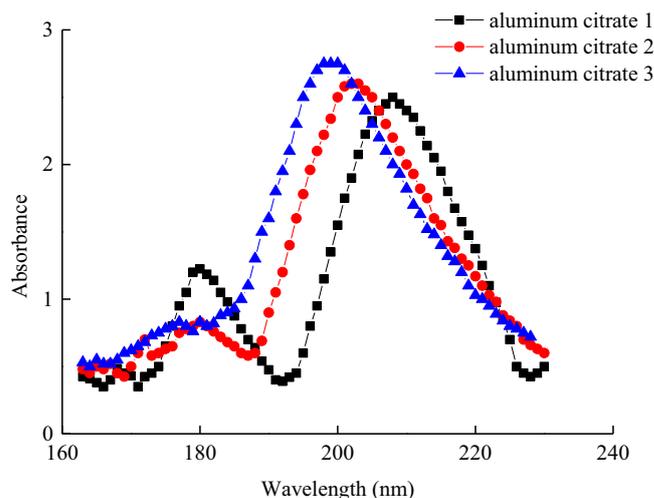
Fig. 2. Absorption curves of the three aluminum citrates measured by UV–VIS spectrophotometer.

by viscometer and UV–VIS spectrophotometer, respectively. For us, we can judge by that the gelation of an HPAM/Al^{3+} system stops when the value of viscosity and absorbance of an HPAM/Al^{3+} system no longer change with reaction time. Finally, record the final values to establish the relationship between viscosity, absorbance difference and salinities.

2.4.2 Differential Scanning Calorimetry (DSC) measurement of HPAM/Al^{3+} gel

Thermal stability is an important indicator of long-lasting and effective physical blockage for HPAM/Al^{3+} gel in the stratum. This indicator can be used for optimizing a suitable gel system for a given reservoir. DSC measurement is an effective method to characterize the thermal properties of a material. Thus, DSC measurements are conducted to study the effect of salinity on the thermal stability of HPAM/Al^{3+} gels. The three are prepared with the simulation formation water samples on condition that the salinity is in their respective appropriate range based on the results in Section 2.4.1. After gelation at 60 °C, the formed gels are used for DSC measurement. During each measurement, about 10 mg of gel sample is placed in a hermetic pan with a nitrogen purge rate of 50 cm^3/min. And an empty hermetic pan is set as a reference sample. All samples are equilibrated at 25 °C for 5 min to remove the former
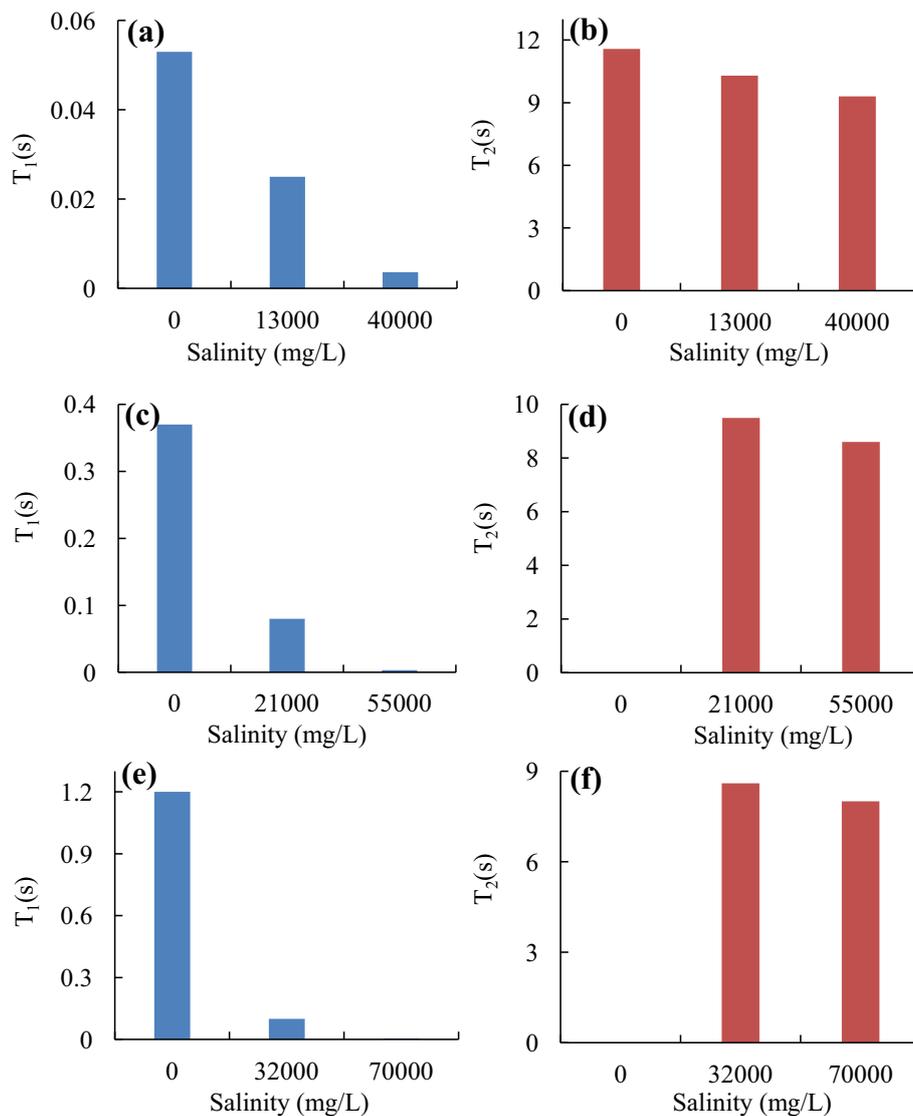
Fig. 3. Relaxation time of the three aluminum citrates under the different salinities. (a) Longitudinal relaxation time $T_1(s)$ of aluminum citrate 1; (b) Horizontal relaxation time $T_2(s)$ of aluminum citrate 1; (c) Longitudinal relaxation time $T_1(s)$ of aluminum citrate 2; (d) Horizontal relaxation time $T_2(s)$ of aluminum citrate 2; (e) Longitudinal relaxation time $T_1(s)$ of aluminum citrate 3; (f) Horizontal relaxation time $T_2(s)$ of aluminum citrate 3.

thermal history. The heating rates are 3 °C/min for all measurements.

3. Results and discussion

3.1 Structure of aluminum citrate under the different salinities

The nature of the effect of salinity on the cross-linking reaction is that the salinity can affect the structure and morphology of aluminum citrate. Therefore, it is of great significance to study the morphology of aluminum citrate under different salinities for understanding and controlling the cross-linking reaction. As is known to all, the different states of aluminum ions have different relaxation times

due to different interaction forces between the different atoms. The detection results of the relaxation time of the three aluminum citrates under different salinities are shown in Figure 3. For aluminum citrate 1, there are two relaxation times under the given salinities, indicating that there are two states of aluminum. And the two relaxation times are both shortened with the increase of the salinity, which indicates that the interaction between atoms is increased and the molecular motion is accelerated, which leads to an increase in the rate of cross-linking reaction. For aluminum citrate 2 and aluminum citrate 3, there is only one relaxation time when the salinity is 0, which means that only a state of aluminum exists in the solution under this condition. It could be because the aluminum has been surrounded by citrate ligands and cannot participate in the cross-linking reaction. Therefore, it can be explained
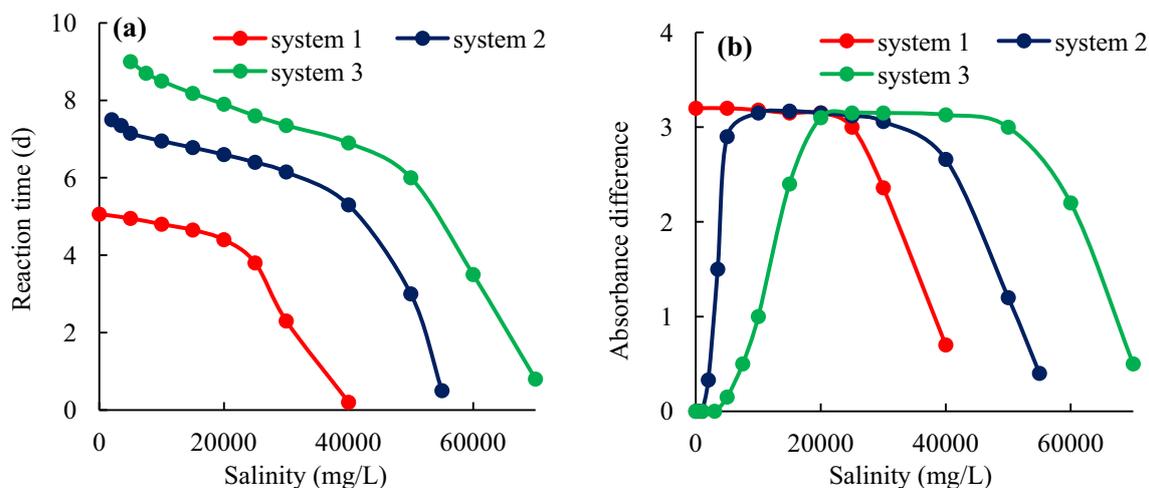
Fig. 4. Changes in the reaction time and absorbance difference of the HPAM/Al^{3+} systems with salinity. (a) Reaction time *versus* salinity; (b) Absorbance difference *versus* salinity.

that T_1 represents the relaxation time of the aluminum complex, and T_2 represents the relaxation time of the aluminum hydrate. With the increase of salinity, two states of aluminum both appear in aluminum citrate 2 and aluminum citrate 3, and the cross-linking reaction begins to occur. Similar to aluminum citrate 1, the two relaxation times of aluminum citrate 2 and aluminum citrate 3 are both shortened and the rate of the cross-linking reaction is increased with the increase of salinity. Due to the different ratios of composition of the three aluminum citrates, the magnitude of the variation of the relaxation time with the salinity is different. Therefore, each aluminum citrate corresponds to a suitable range of salinity.

3.2 Characteristic of cross-linking reaction of the HPAM/Al^{3+} systems under the different salinities

3.2.1 Changes in the reaction time and absorbance difference

The effect of salinity on the reaction time and the cross-linking degree of the HPAM/Al^{3+} systems are shown in Figure 4. For HPAM/Al^{3+} system 1, the reaction time is gradually shortened with the increase of salinity at the range of salinity of 0–25 000 mg/L. After this, the reaction time is greatly shortened with the further increase of salinity. In addition, within the range of salinity of 0–25 000 mg/L, the absorbance difference remains basically unchanged with the increase of salinity, which is indicating that the cross-linking degree is not affected by salinity at this range. However, when the salinity exceeds this range, the cross-linking degree is began to decrease significantly with the increase of salinity.

For the structure of aluminum citrate 1, a part of the coordinate bonds is formed due to the interaction of Al^{3+} and the hydroxyl groups. However, due to a lower polarity of the hydroxyl group than that of the carboxyl group, the hydroxyl group can be replaced by the carboxyl group of

HPAM when the aluminum citrate 1 is mixed with HPAM. With the increase of salinity, the ionic action in the solution is enhanced, which can accelerate the movement of molecules. In addition, due to Hofmeister salt effect, NaCl solution has a strong salt solubility effect, which can change the surface energy of HPAM and citrate. Therefore, the chance of collision between anionic polyelectrolyte HPAM and cationic Al^{3+} complex is increased, while the chance of collision between anionic citrate and Na$^+$ is increased. Thus, Al^{3+} surrounded by the citrate ligands can be relatively quickly released under the stronger action of the ions and the concentration of Al^{3+} involved in the reaction between HPAM and Al^{3+} is relatively increased, and then the reaction time is shortened. At the range of 0–25 000 mg/L of salinity, the cross-linking degrees are finally almost the same under the different salinities. This is because the total concentration of Al^{3+} is fixed, and the final released amount of Al^{3+} involved in the reaction are almost the same, so that the cross-linking degrees are almost the same. However, with the further increase of the salinity, the cross-linking degree and the reaction time are began to decrease drastically. There are two reasons accounting for this phenomenon. One is that a higher salinity can compress the double layer of the polymer, which is adverse to the cross-linking reaction. The other is that the release rate of Al^{3+} from the aluminum citrate complex and the velocity of molecular motion are too severe under a higher salinity, which can result in a violent cross-linking reaction with a short reaction time and an insufficient cross-linking. Therefore, we can summarize that the matching range of the salinity and the HPAM/Al^{3+} system 1 is 0–25 000 mg/L NaCl.

For HPAM/Al^{3+} system 2, within the range of salinity of 0–2000 mg/L, the absorbance difference is zero, which shows that the cross-linking reaction does not occur. With the salinity increase to over 2000 mg/L, the absorbance difference begins to increase and the cross-linking reaction begins to occur. In the range of salinity of 2000–5000 mg/L, the cross-linking degree has a large increase with the increase
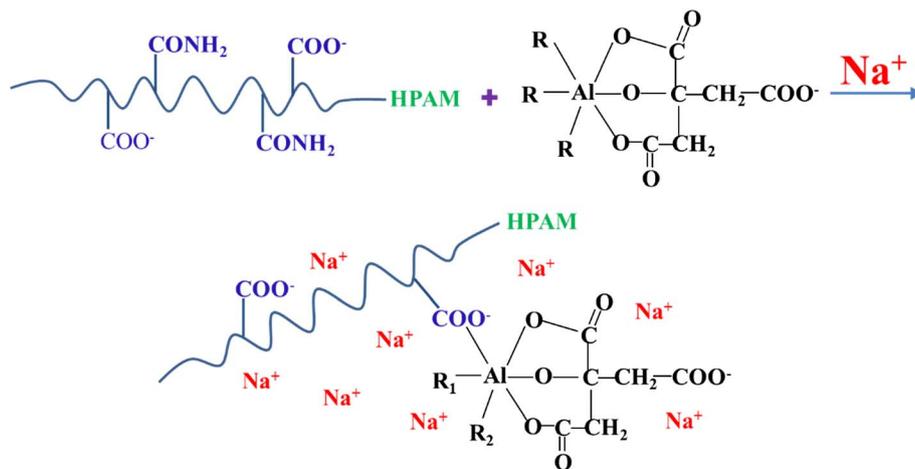
Fig. 5. Cross-linking reaction of HPAM and AlCit under the action of Na^+ (R represents citrate; R_1 and R_2 are both substitute for hydroxyl or citrate or carboxyl of HPAM molecule, which is decided by the dissociation degree of the aluminum citrate complex).

of salinity. In the range of salinity of 5000–35 000 mg/L, the cross-linking degree remains stable with the increase of salinity. Subsequently, the cross-linking degree and the reaction time drastically decreased with the increase of salinity. In addition, it can be observed that the reaction time is shortened with the increase of salinity after the cross-linking reaction occurs, especially when the salinity increases to a certain value, the reaction time is greatly shortened.

For the structure of aluminum citrate 2, the coordinate bonds are formed due to the interaction of Al^{3+} and citrate ligand instead of the interaction of Al^{3+} and the hydroxyl groups. Due to a higher polarity of the citrate ligand than that of the hydroxyl group of HPAM, the citrate ligand of aluminum citrate 2 cannot be replaced by the carboxyl group of HPAM when the aluminum citrate 2 is mixed with HPAM under a low salinity. With the increase of salinity, the ionic action in the solution becomes stronger and stronger, and the aluminum citrate 2 begins to release the aluminum ions, so that the cross-linking reaction can occur. The process of cross-linking reaction of HPAM and AlCit under the action of Na^+ is shown in Figure 5. With the increase of salinity and the action of Hofmeister salt effect, more and more Al^{3+} are released, so that the cross-linking degree is getting higher and the absorbance difference is greatly increased. When the salinity increases to a certain value, all of the aluminum ions from the aluminum citrate 2 can be released at that point, and the cross-linking degree is maximized, so that the absorbance differences are no longer changed. With the further increase of salinity, the cross-linking degree and the reaction time are began to decrease drastically. This trend and reasons are the same to the HPAM/Al^{3+} system 1 under too high salinity.

For HPAM/Al^{3+} system 3, comparing to those of HPAM/Al^{3+} system 2, the two curves of reaction time and absorbance difference have the same characteristic of variation but have the different range of salinity. Within the range of salinity of 0–5000 mg/L, the cross-linking reaction does not occur. With the salinity increase to over 5000 mg/L, the cross-linking reaction begins to occur.

In the range of salinity of 5000–20 000 mg/L, the cross-linking degree has a large increase. In the range of salinity of 20 000–50 000 mg/L, the cross-linking degree remains stable. Thus, with the increase of salinity, the cross-linking degree and the reaction time drastically decreased.

For the structure of aluminum citrate 3, after the coordinate bonds are formed, Al^{3+} is more tightly packed by the citrate ions than that in aluminum citrate 2. Therefore, a stronger ionic action is required to dissociate and release Al^{3+} from the aluminum citrate complex. As the salinity increases, and the action of Hofmeister salt effect, more and more Al^{3+} is released and the cross-linking degree is getting higher and higher, so that the absorbance difference is greatly increased. When the salinity increases to a certain value, all of Al^{3+} has been released from the aluminum citrate complex, and the cross-linking degree has reached the maximum, so that the absorbance has no longer changed. As the salinity further increases, the cross-linking degree and the reaction time begin to decrease drastically. This trend and reason are consistent with those of the HPAM/Al^{3+} system 2. In summary, the system of aluminum citrate 2 and 3 can be best applied to cross-link HPAM at the range of salinity of 5000–35 000 mg/L and 20 000–50 000 mg/L, respectively.

3.2.2 Process of cross-linking reaction of the three HPAM/Al^{3+} systems

Based on the results in Section 3.2.1, the HPAM/Al^{3+} systems can be used for conformance control of heterogeneous reservoirs in the appropriate salinity range. Next, a suitable simulated formation water with the salinity of 10 000 mg/L, 20 000 mg/L, and 30 000 mg/L NaCl are selected for the preparation of the HPAM/Al^{3+} system 1, 2, and 3, respectively. Under this condition, the effect of salinity on the cross-linking degree and the viscosity of the HPAM/Al^{3+} systems are shown in Figure 6, which can be used to analyze the process of the cross-linking reaction. From Figures 6a–c, it can be observed that the trends of changes in the
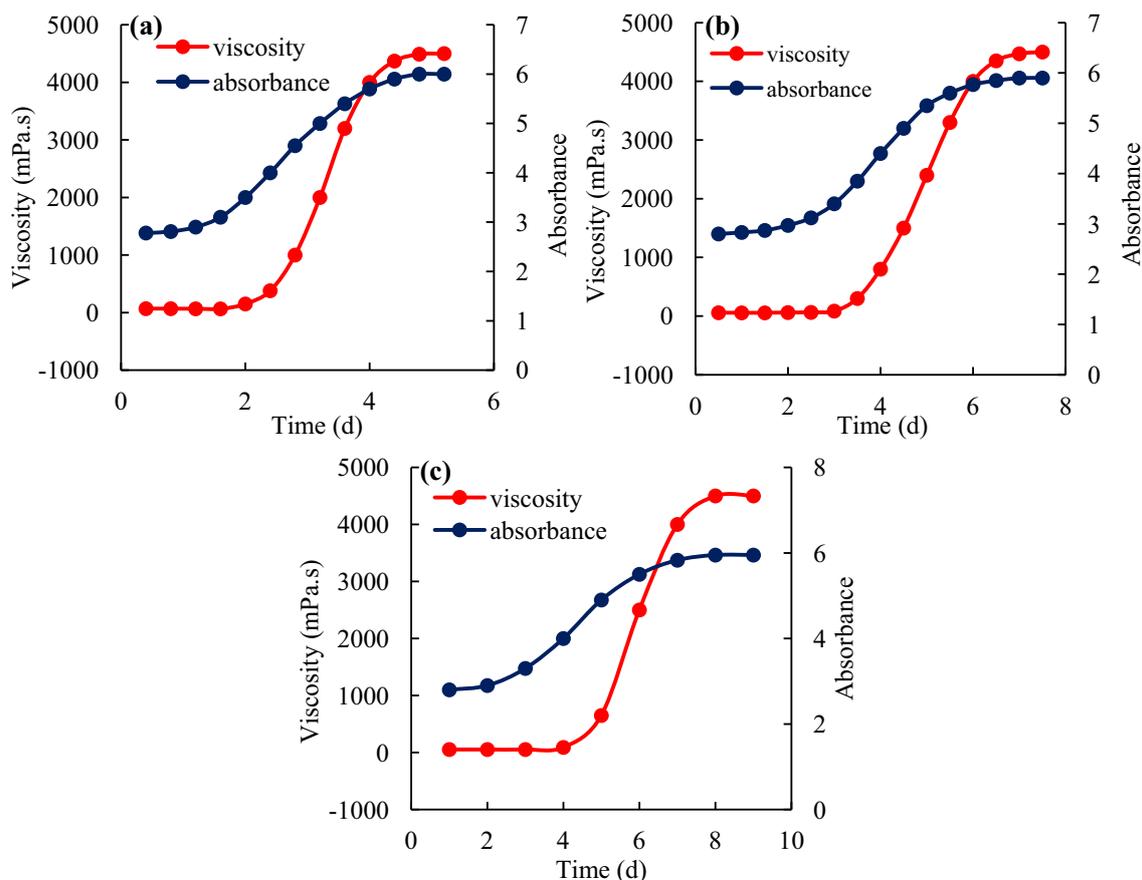
Fig. 6. Changes in the viscosity and absorbance of the HPAM/Al^{3+} systems with reaction time. (a) The system 1 under the salinity of 10 000 mg/L NaCl; (b) The system 2 under the salinity of 20 000 mg/L NaCl; (c) The system 3 under the salinity of 30 000 mg/L NaCl.

absorbance of the three with the reaction time are consistent, which are both increased with the increase of the reaction time. It can indicate that the cross-linking reactions of the three occur. In addition, the trends of changes in the viscosities can be divided into two stages. The first stage is that the viscosity almost keeps stable, which undergoes intramolecular cross-linking reaction. The second is that the viscosity is rapidly increased with the increase of the reaction time until stable, which undergoes cross-linking reactions between molecules. Intramolecular cross-linking allows the viscosity to be remained substantially unchanged and the absorbance to be increased [46]. Intermolecular cross-linking can both allow the viscosity and the absorbance to be increased. This conclusion has been verified in Zhang *et al.*'s article [42, 47]. We can conclude that the process of the cross-linking reactions of the three is the same and the difference is only that the reaction time corresponding to each stage is different.

3.3 Effect of salinity on the thermal stability of the HPAM/Al^{3+} gels

Based on the results of the matching range of the salinity and the HPAM/Al^{3+} system 1, 2, and 3, the

HPAM/Al^{3+} systems are prepared and then be gelatinized at 60 °C for DSC measurement. Thus, the DSC curves are shown in Figures 7a–c, where a single peak on each curve is observed. When the temperature is lower than the inflection point, the heat flow is increased with the increase of temperature due to the evaporation of water by trapping heat in the gel sample. When the temperature is higher than the inflection point, the heat flows began to decrease sharply due to the loss of water during evaporation. After that, the structure of the gel is destructed. Therefore, the inflection point can represent the maximum temperature resistance of a gel. Figure 7 shows that the temperature resistance of the three HPAM/Al^{3+} systems are all decreased with the increase of salinity. This is because the increase of Na$^+$ can compress the double electric layer of polymer to thin the hydration film and reduce the zeta potential, which can lead to weaken the ability of polymer to bind water molecules. Thus, more free water and less bound water are stored in the gel, so that the gel has a faster endothermic rate and a lower temperature resistance. In addition, under the same salinity, the three HPAM/Al^{3+} systems have the same temperature resistance. This is because although the ratio of Al^{3+} to citrate ion is different for the three HPAM/Al^{3+} systems, the process of cross-linking reactions between
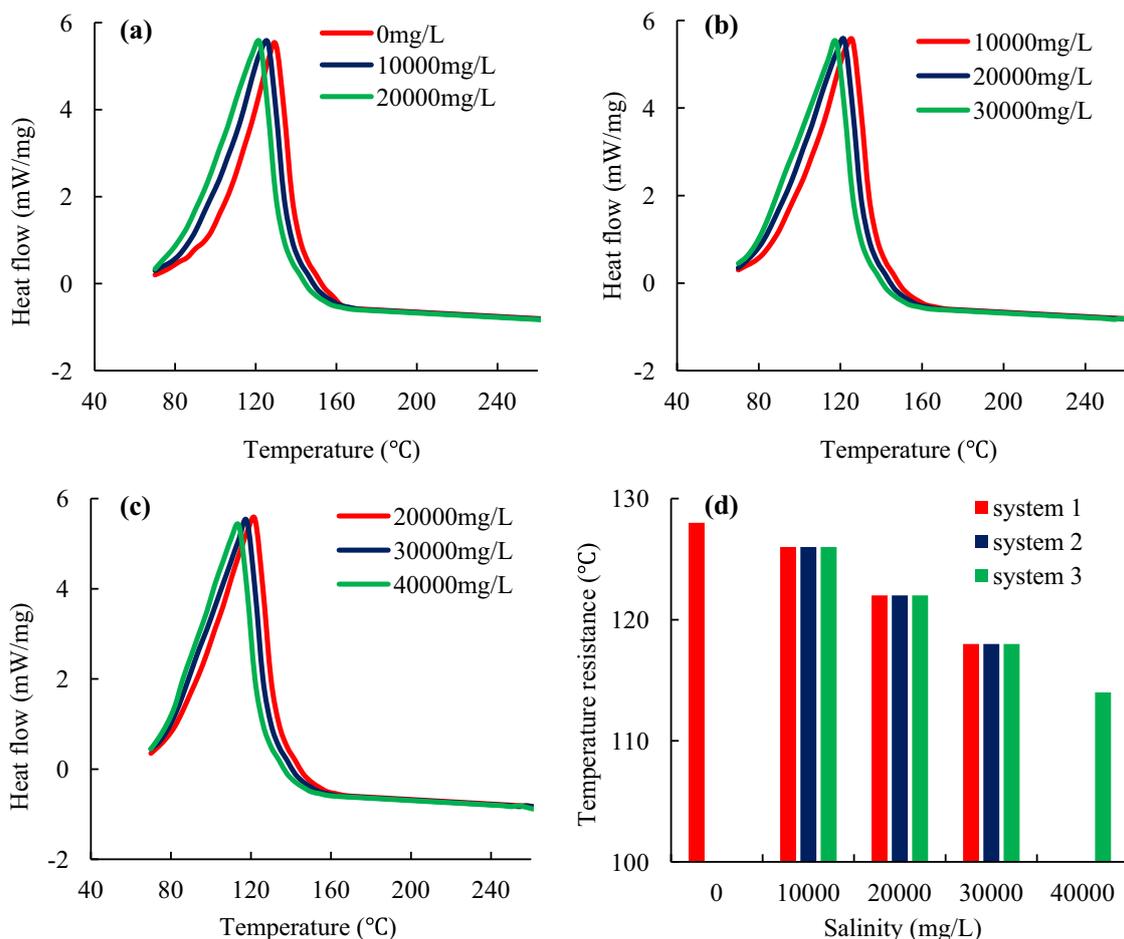
Fig. 7. DSC curves and temperature resistance of HPAM/Al^{3+} gel samples under the different salinities. (a) DSC curve of HPAM/Al^{3+} system 1; (b) DSC curve of HPAM/Al^{3+} system 2; (c) DSC curve of HPAM/Al^{3+} system 3; (d) Temperature resistance of HPAM/Al^{3+} systems.

HPAM and Al^{3+} are the same, and the structure of the formed gels are the same, so that their temperature resistance are the same.

4 Conclusion

1. Salinity has a great influence on the cross-linking reaction of the three, of which an important factor is that the salinity has an important influence on the morphology of aluminum citrate. At the temperature of 60 °C, aluminum citrate 1 is suitable for the range of salinity of 0–25 000 mg/L, aluminum citrate 2 is suitable for the range of salinity of 5000–35 000 mg/L, and aluminum citrate 3 is the range of salinity of 20 000–50 000 mg/L.
2. Due to the different ratios of citrate ligands to Al^{3+} in the three aluminum citrates, after the cross-linking reaction occurs, the characteristics of change of the reaction time and the cross-linking degree of the three are different. However, the process of the cross-linking reactions of the three are the same. In addition, the thermal stability of the formed gels is decreased with the increase of salinity regardless of the ratio of citrate ligands to Al^{3+}.
3. The reaction time of the HPAM/Al^{3+} system is a very important parameter for conformance control, which provides an important guidance for the design and adjustment of the operation scheme. For a given reservoir, the temperature and salinity are determined, so that the cross-linking reaction time can be controlled by adjusting the composition of aluminum citrate due to a simple and flexible operation.

Competing interest

The authors declare no competing financial interest.

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