Study on improving viscosity of polymer solution based on complex reaction

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Abstract. The current status of polymer flooding Technology on high salinity oil reservoir is not ideal. A method for increasing the viscosity of polymer solutions is urgently needed. This paper systematically studied the effect of ions with different mass concentrations on the viscosity of polymer solutions. Based on the theory of complex reaction, a countermeasure of increasing viscosity of polymer solution under conditions of high salinity reservoir was proposed. The results show that Ca2+ and Mg2+ have greater influence on the solution viscosity than K+ and Na+. When the concentration of divalent ions increases from 0 mg/L to 80 mg/L, the viscosity of the polymer solution decreases from 210 mPa·s to 38.6 mPa·s. The viscosity of the polymer solution prepared from the sewage treated with the Na2C2O4 increased by 25.3%. Atomic force microscopy test results show that Na2C2O4 can effectively shield the divalent metal ions, so that the polymer molecules in the solution stretch more, thereby increasing the solution viscosity.

1. Introduction
Application of polymer flooding in high salinity oil reservoirs put forward higher requirements for polymer salt resistance[1]. At present, researchers use acrylamide polymers as the basis, through polymers modification or introducing special structural units in the molecular chain, the problem of oil-repelling polymers maintaining its high effective viscosity during the process has been solved to a certain extent[2,3]. However, with the increasing depth of reservoir exploitation, the salinity of reservoir fluid also increases. Therefore, it is urgent to solve the problem of increasing viscosity of high salinity reservoir polymer solution[4-7]. This paper focuses on the effects of salinity and metal ions and their concentration on the viscosity of polymer (HPAM) solution. Based on the theory of complex, Na2C2O4 was selected as the metal complex agent to improve the viscosity performance of the polymer solution. With the help of atomic force microscopy tests, the effect of divalent metal ions on the configuration of polymer molecules in solution was qualitatively described, and the mechanism for increasing viscosity of polymer solutions based on complex reactions was clarified.

2. Experimental conditions and methods
2.1. Experimental materials
Polymer: The experimental polymer was partially hydrolyzed polyacrylamide (HPAM) supplied by Daqing Refining & Chemical Company, molecular weight 2500×10⁴, solids content 90%, degree of hydrolysis 25%;

Inorganic salts: NaCl, KCl, CaCl₂, MgCl₂, effective content ≥ 96.0%, supplied by Xi’an Chemical Reagent Factory.

2.2. Experimental apparatus
Viscosity Measurement Instruments: The viscosity of the polymer solution was measured using a Brookfield Model LVDVII+ viscometer (American Boleyfield Engineering Laboratory Co., Ltd.), selected 0# rotor at reservoir temperature to measure the viscosity of the polymer solution with the rotational speed was 6 r/min.

2.3. Polymer solution preparation

2.3.1. Simulated water. This paper mainly studied the effect of total salinity and high cation content in formation water on polymer viscosity. The main inorganic salt composition was deionized water of NaCl, CaCl₂, and MgCl₂.

2.3.2. Polymer solution. Prepared a concentration of 5000 mg/L polymer mother liquor and stir for 3 h at a speed of 100 r/min. The prepared polymer solution with a mass concentration of 5000 mg/L was used as a mother liquor, after being sealed and cured, it could be diluted to a desired solution of any concentration.

3. Effect of sewage metal cation on anti-salt polymers solution viscosity
In the field applications of polymer flooding, sewage with higher ion content polymers are generally used. The degree of salinity and ion composition of the sewage have a great influence on the polymer solution. The composition of metal ions in sewage is complex. The main monovalent metal ions include Na⁺ and K⁺, the divalent metal ions include Ca²⁺, Mg²⁺, and Fe²⁺, and the trivalent metal ions include Fe³⁺. All of above metal ions have an influence on the viscosity of polymer solution. Thus, the following experiment explores the effect of salinity and various cation concentrations on polymer viscosity.

3.1. Effects of Na⁺ and K⁺ on polymer solution viscosity
In order to verify the effect of Na⁺ and K⁺ content on the polymer solution viscosity, the influence of other cations on the viscosity was first excluded. Polymer mother liquor with a concentration of 5000 mg/L was prepared using distilled water, which was diluted with simulated water containing different concentrations of Na⁺ and K⁺ to prepare the target solution. The Na⁺ and K⁺ contents of the target solution were 0, 200, 400, 600, 800, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, and 5000 mg/L, respectively. The results of target solution viscosity are shown in figure 1.

The NaCl and KCl were added to distilled water to prepare different polymer solutions with different Na⁺ and K⁺ contents, and their viscosity was measured. The experimental results are shown in figure 1. As shown in the figure, the viscosity of the polymer solution reduced rapidly with the increase of Na⁺ and K⁺ concentrations. When the Na⁺ and K⁺ contents were >1000 mg/L, the viscosity decreases gently. Because when Na⁺ and K⁺ concentrations increase, the negative charges on -COO⁻ of the polymer molecule weaken, and the electrostatic attraction within and between polymers decreased, the friction between molecules decreased, the molecules became curled, therefore viscosity is reduced. The effect of Na⁺ and K⁺ on the viscosity of the polymer solution was due to the small radius of Na⁺ in the case of the same charge, which made it easier to access the polymer chain than K⁺, neutralized the negative charge more strongly, and had a greater effect on the viscosity.
3.2. Effects of Mg$^{2+}$ and Ca$^{2+}$ on polymer solution viscosity

In order to verify the effect of Mg$^{2+}$ and Ca$^{2+}$ content on the viscosity of the polymer solution, the influence of other cations on the viscosity was first excluded. Polymer mother liquor with a concentration of 5000 mg/L was prepared using distilled water. The polymer mother liquor was diluted to the target solution with simulated water containing different concentrations of Mg$^{2+}$ and Ca$^{2+}$. The contents of Mg$^{2+}$ and Ca$^{2+}$ in the target solution were 0, 20, 40, 60, 80, 100, 200, 300, 400 mg/L, respectively. The results of the viscosity measurement of the target solution are shown in figure 2.

Figure 1. Effects of Na$^+$ and K$^+$ on polymer solution viscosity.

Different amounts of MgCl$_2$•6H$_2$O and CaCl$_2$ were added to distilled water to prepare different polymer solutions with different Mg$^{2+}$ and Ca$^{2+}$ contents, and their viscosities were measured. As shown in figure 2, the viscosity of the polymer solution decreased drastically with the increase of Mg$^{2+}$ and Ca$^{2+}$ concentration. When the content of Mg$^{2+}$ and Ca$^{2+}$ increased from 0 mg/L to 80 mg/L, the viscosity of the polymer solution decreased from 210 mPa•s to 38.6 mPa•s, when the divalent potassium ion concentration is greater than 80 mg/L, the decrease in viscosity becomes more gentle.

Figure 2. Effects of Ca$^{2+}$ and Mg$^{2+}$ on viscosity of polymer solution.
The higher the content of Mg\(^{2+}\), Ca\(^{2+}\), the greater the loss of viscosity, and the polymer solution will precipitate and fail. This is because Mg\(^{2+}\) and Ca\(^{2+}\) have a large number of charges, and the ability to shield negative charges on Polymer -COO- is stronger. This results in polycondensation of the polymer, shrinking of the molecular chain, and dehydration. The effect of Mg\(^{2+}\) on the viscosity of the polymer solution is greater than that of Ca\(^{2+}\) due to the small radius of Mg\(^{2+}\) in the case of the same charge. The smaller radius of Mg\(^{2+}\) makes it easier to access the polymer chain than Ca\(^{2+}\), shielding the negative charge on the polymer and excluding bound water molecule on the polymer, thus making the polymer curled more in solution, which leads to a greater effect on viscosity.

4. The method of increasing the viscosity of polymer solution

Na\(_2\)C\(_2\)O\(_4\) as a complexing agent can effectively remove the Ca\(^{2+}\) and Mg\(^{2+}\) in the wastewater from the west block of Changyuan and increase the viscosity of the displacing phase. The addition of Na\(_2\)C\(_2\)O\(_4\) as a complexing agent for the removal of Ca\(^{2+}\) and Mg\(^{2+}\) eliminates the settling effect of divalent ions on polymer chains and increases the viscosity of the polymer system.

\[
Na_2C_2O_4 + M^{2+} = MC_2O_4 \downarrow + 2Na^+
\] (1)

Na\(_2\)C\(_2\)O\(_4\) was selected as the complexing agent of Ca\(^{2+}\) and Mg\(^{2+}\) and added into HPAM solution with a concentration of 1500 mg/L in different ratios. The effects of addition of 70 mg/L, 140 mg/L, 210 mg/L, 280 mg/L, 350 mg/L Na\(_2\)C\(_2\)O\(_4\) on the viscosity of the HPAM solution were measured at 45°C. The results are summarized in table 1.

| Complexing agent dosage (mg/L) | 0  | 70  | 140 | 210 | 280 | 350 |
|--------------------------------|----|-----|-----|-----|-----|-----|
| Viscosity (mPa·s)              | 53.9 | 59.6 | 65.3 | 71.8 | 68.5 | 63.1 |
| Viscosity increase rate (%)    | /  | 10.6 | 21.1 | 33.2 | 27.1 | 17.0 |

The variation of the viscosity after adding different concentrations of sodium Na\(_2\)C\(_2\)O\(_4\) to the HPAM solution was plotted as a line graph, as shown in figure 3.

![Figure 3. Effect of sodium oxalate concentration on viscosity of HPAM solution.](image)

As can be seen in figure 3, with the increase of Na\(_2\)C\(_2\)O\(_4\) concentration, the viscosity of the partially hydrolyzed polyacrylamide solution increases first and then decreases. Na\(_2\)C\(_2\)O\(_4\) is a kind of metal
complex agent for multi-coordination atoms, so it can form stable complexes with high-valence ions such as Ca$^{2+}$ and Mg$^{2+}$ in the polymer solution, and it can effectively improve the solution viscosity when the amount of Na$_2$C$_2$O$_4$ is small. When 210 mg/L Na$_2$C$_2$O$_4$ was added into the HPAM solution, the viscosity of the polymer solution reached a peak value of 71.8 mPa·s, and the viscosity increase rate reached 33.2%. Further increase of Na$_2$C$_2$O$_4$ content resulted in a large increase of Na$^+$ in the solution and a decrease in the viscosity.

5. Conclusions
As the concentration of Na$^+$ and K$^+$ increases, the viscosity of the polymer solution decreases rapidly. However, when the concentration of Na$^+$ and K$^+$ is $>$1000 mg/L, the viscosity decreases gently. The concentration of Mg$^{2+}$ and Ca$^{2+}$ has a great influence on the viscosity of polymer solution. In the low concentration range, a small increase in ion concentration can cause big drop in viscosity of HPAM solution. The selected Na$_2$C$_2$O$_4$ as Mg$^{2+}$, Ca$^{2+}$ complex agent can effectively increase the initial viscosity of HPAM. When 210 mg/L Na$_2$C$_2$O$_4$ was added to the HPAM solution, the viscosity of the polymer solution reached a peak value of 71.8 mPa·s, and the viscosity increase rate reached 33.2%.

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