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Mechanism of sodium tripolyphosphate inhibiting the syneresis of HPAM hydrogel

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Experimental investigations have been conducted to elucidate the mechanism of sodium tripolyphosphate (STPP) inhibiting the hydrogel syneresis in the aspect of the reaction between STPP and partly hydrolyzed polyacrylamide (HPAM). Viscosity measurements indicate that STPP can increase the viscosity of HPAM. The results of light scattering measurements show that STPP can improve the hydrophilicity of HPAM since both hydrodynamic radius \( R_\text{h} \) and second virial coefficient \( A_2 \) of HPAM are increased by STPP, and STPP can also increase the weight average molecular weight \( M_w \) of HPAM. FTIR and NMR measurements show that the mechanism of the above effect of STPP on HPAM is the following: STPP molecule can react with the O in \(-\text{COO}^–\) group of HPAM whereby the new bond of O-C-O-P is formed, so a large quantity of STPP molecule “adsorbs” on the molecular chains of HPAM and produces the bond of C1O1P is formed, so a large quantity of STPP molecule “adsorbs” on the molecular chains of HPAM and produces the molecular chains of HPAM and produces the hydrogel shrinkage. The rate of this separation determines the polymer solution into the oil reservoir, which performs the task of storing in the oil reservoir, or by means of mechanical energy, a solvent phase separates from the hydrogel phase as a result of share a common phenomenon, termed syneresis, in which the hydrogels typically used in profile modification applications forms a physical barrier occluding the high-permeability zones, so the fluid injected into the reservoir at a later time can be diverted to flow through the low-permeability zones. Secondary recovery techniques is essentially to inject the water or polymer solution into the oil reservoir, which performs the task of conveying the oil to the production well. Unfortunately, owing to the lack of homogeneity in the oil-bearing rock, which is constituted by zones with different permeability characteristics, such fluids tend to preferentially flow through higher-permeability zones. On the contrary, the lower-permeability zones remain non-fluxed or are only partially fluxed, and such a drawback prevents the oil contained in the lower-permeability zones from being further extracted.

Polymer hydrogels are generally employed to solve such a problem. This technology uses a flowable mixture of polymer, crosslinker and water. This mixture of relatively low viscosity is injected into the reservoir. Then, with time and temperature, it forms a physical barrier occluding the high-permeability zones, so the fluid injected into the oil field at a later time can be diverted to flow through the low-permeability zones. However, hydrogels typically used in profile modification applications share a common phenomenon, termed syneresis, in which the solvent phase separates from the hydrogel phase as a result of hydrogel shrinkage. The rate of this separation determines the lifetime of the hydrogel under any given set of circumstances. As such, syneresis is the main reason why the plugging effectiveness of the hydrogel decreases with time. Therefore, inhibiting the syneresis of hydrogel is the key to extend the validity of water-shutoff treatment.

Hydrogels formulated with HPAM and Cr have been used extensively as water-shutoff agents to reduce water production, and they also suffer syneresis problem. The common method to decrease the syneresis is increasing the HPAM concentration, but high HPAM concentration leads to the unreasonable cost and excess high injection pressure. Although a fairly wide number of new acrylamide polymers, which can be employed to prepare hydrogels, have been described in the literatures, only a relatively small number of them, including acrylamide copolymers of N-vinyl pyrrolidone (N-VP), 2-acrylamido-2-methyl-propanesulfonate (AMPS), and N-vinyl acetamide (N-VA), have been commercialized. Besides, several types of novel polymer hydrogels, such as topological (TP) hydrogels, double-network (DN) hydrogels and nanocomposite (NC) hydrogels have been developed. These polymer hydrogels were generally found to possess excellent stability, but their suitability for petroleum applications is limited by their high price. Besides, it is worth emphasizing that a more serious problem for most of the new polymers used in the hydrogel is their high adsorption on reservoir rock. Therefore, adding a simple and cost-effective stabilizer in the HPAM hydrogel may be the best method of improving the hydrogel stability to increase the validity of water-shutoff treatment.

In this paper, the sodium tripolyphosphate (STPP) was proved to be an effective syneresis inhibitor for HPAM/Cr hydrogel, and its mechanism of inhibiting syneresis was investigated in the aspect of the effect of STPP on HPAM. This investigation provides a clear understanding of the effect of STPP on HPAM, and the findings can be utilized for obtain the hydrogels with high stability.

**Experimental section**

**1. Materials.**

Sodium bichromate \((\text{Na}_2\text{Cr}_2\text{O}_7)\), sodium sulfate \((\text{Na}_2\text{SO}_4)\), sodium chloride \((\text{NaCl})\) and STPP are all analytically pure, and purchased from Sinopharm. HPAM was purchased from Beijing Hengju...

First, the polymer stock solution was prepared by dissolving solid polymer in fresh water. A container with a known amount of water was vigorously stirred to create a deep vortex. Polymer was slowly added to the shoulder of the vortex to effectively wet the polymer beads. The container was sealed to minimize evaporation and was stirred continuously for 24 h to ensure complete dissolution of polymer. The crosslinker, whose amount was carefully tuned, was dissolved in water to prepare a crosslinker solution. Finally, the gelling solution was prepared by mixing the polymer stock solution and crosslinker solution. In the gelling solutions, the concentration of HPAM, Na₂Cr₂O₇, and Na₂SO₃ was 0.2%, 0.3%, and 0.5% respectively, which were obtained through many screening procedures. After the gelling solution was prepared, it was sealed in a bottle and put into an oven at 60°C.

Syneresis rate is defined as the decrease in the hydrogel weight at a given time relative to the initial hydrogel weight.


The 0.2% HPAM solutions with different concentrations of STPP were prepared respectively (To inhibit the oxidative degradation of HPAM, the oxygen in the solution has been removed by nitrogen), and then they were sealed in a bottle and put into an oven at 60°C for different times. The viscosity of these solutions was measured at a shear rate of 1.22 s⁻¹ by the Brookfield viscometer (DV-II+Pro) at 25°C. Viscosity retention is defined as the viscosity at a given time relative to the initial viscosity of HPAM solution.


For the light scattering measurements, the polymer solutions were carried out in the light scattering vials. All glassware was kept dustfree by rinsing in hot acetone prior using. The solutions were filtered through membrane filters (pore size=0.38 µm) directly into the vials. This process was carried out in a dustfree glovebox. 

Static light scattering (SLS) and dynamic light scattering (DLS) measurements were carried out at 25°C using a commercial multi-angle light scattering BI-200SM (Brookhaven Instruments Corporation) equipped with a digital correlator BI-9000AT. The SLS intensities were recorded from angles θ=10° to 160°. The results of weight average molecular weight (Mₐ), the second virial coefficient (A₂), and the viscosity at a given time relative to the initial viscosity of HPAM solution.

5. Measurements of FTIR.

FTIR spectra were obtained on a Nicolet 6700 FTIR Spectrometer. The HPAMs (ω=0.2%) with 0 and 0.03% STPP in sealed bottles were all firstly put at 60°C for 24h, and then they were dried by the lyophilization method (vacuum freeze drying plant: Cammal-16LSC). The FTIR specimen was prepared by mixing the above dry HPAM sample with KBr, and spectral analysis was performed over the range 4000-400 cm⁻¹.

6. Measurements of NMR.

The STPP solution (ω=0.3%), the HPAM solution (ω=2%), and the composite solution composed of STPP (ω=0.3%) and HPAM (ω=2%) in sealed bottles were put at 60°C for 24h, and then they were dried by the lyophilization method. ³¹P solid state NMR spectra of the three dry samples were measured with a Bruker AVANCE III 400M instrument using a cross polarization pulse sequence, and operating at 161 MHz, with a 4 mm, 3-channel, magic angle spinning (MAS) probe. The contact time of the cross polarization/magic angle spinning experiment was set to be 100 µs. The acquisition time was 50 ms, the recycle delay was 5 s, and all NMR experiments were performed at room temperature. The spectra were processed and analyzed using Bruker Topspin V3.0.

Results and discussion

1. Effect of STPP on the hydrogel syneresis.

HPAM/Cr hydrogel has been used extensively as water-shutoff agents to reduce water production in common oilfield on account of its low price and simple preparation. However, further application of this hydrogel in difficult reservoir condition is limited due to its unsatisfactory stability. In order to decrease the hydrogel syneresis, some inorganic additives, including sodium lactate, sodium salicylate, sodium oxalate, sodium malonate, STPP etc., were employed in the hydrogel, and the results showed that only STPP could inhibit the syneresis. The effect of the concentration of STPP on the hydrogel syneresis is showed in Fig. 1. For the hydrogel without STPP, the syneresis rate on the 180th day reaches up to 35%, and it is only 10% for the hydrogel with 0.01% STPP. When the concentration of STPP is 0.03%, the syneresis rate on the 180th day decreased to 3%. When the concentration of STPP is higher than 0.03%, the syneresis rate increases, but is still lower than that of the hydrogel without STPP. Hence, STPP (about 600$/t) is an effective syneresis inhibitor for HPAM/Cr hydrogel. To clarify the mechanism of STPP inhibiting the hydrogel syneresis, the effect of STPP on HPAM was investigated in the following parts.
2. Effect of STPP on the viscosity of HPAM.

As showed in Fig. 2, the viscosity of HPAM with STPP decreases when the solutions were just prepared, and the high concentration of STPP results in the high decrease of the viscosity. It is because HPAM is susceptible to the salt, whereby STPP makes the HPAM molecule get coiled, therefore the viscosity reduces (salt sensitive effect).21 With the increase of the heating time, the viscosity of HPAM without STPP decreases continuously, which is caused by the thermal degradation of HPAM. In contrast, the viscosity of HPAM with STPP increases at first and then decreases slightly. The viscosity retention of HPAM with 0.01% STPP rises from 98.7% to 105.9% on the 1st day, whereas the one of HPAM with 0.1% STPP increases from 82.9% to 111.0% during the same time, which indicates that the high thickening rate is obtained by the high concentration of STPP. However, due to the negative “salt sensitive effect” of STPP, the highest viscosity is obtained when the STPP concentration is 0.03% rather than 0.1%.

![Fig. 2 Effect of the concentration of STPP on the viscosity of HPAM prepared with fresh water](image)

![Fig. 3 Effect of the concentration of STPP on the viscosity of HPAM prepared with 1mol/L NaCl](image)

When the fresh water was replaced by 1mol/L NaCl to prepare the HPAM-STPP solution, the STPP still had thickening effect on the HPAM solution during the heating process, as showed in Fig. 3. Closer inspection of the data in Fig. 2 and Fig. 3 indicates that the thickening effect of HPAM is facilitated by NaCl, since the highest viscosity retention can reach up to 150% whereas only 130% in the absence of NaCl. Besides, when the STPP concentration is 0.03% and 0.1%, the highest viscosity retention was obtained on the 5th day and the 1st day respectively; but the viscosity of HPAM solution without NaCl is the highest on the 10th day and the 5th day, so the presence of NaCl in HPAM solution is benefit to the thickening rate.

As it is generally accepted, the addition of common salts (NaCl, CaCl₂, etc.) reduces the viscosity of the polymer solution, since the salt can compress the twin electrical layer and decrease the hydrophilicity of polymer, leading to the decrease of the polymer viscosity. However, STPP can increase the viscosity of HPAM solution. Hence, STPP is an uncommon salt for the HPAM solution, and it must have some especial effect on the HPAM.

3. Effect of STPP on the hydrophilicity of HPAM.

![Fig. 4 Effect of STPP on the aRₜ of HPAM](image)

The syneresis is the process that the water escapes from the network structure of hydrogel. This phenomenon can be intuitively understood as the following: the binding force of the HPAM to the water molecule is reduced, that is, the hydrophilicity of HPAM is decreased. Hence, the mechanism of the effect of STPP on the hydrogel syneresis was studied by investigating the influence of STPP on the HPAM hydrophilicity. The 0.2% HPAM solution with 0%, 0.03% and 0.1% STPP was respectively heat-treated at 60°C for different days, and then the hydrodynamic radius (Rₜ) of HPAM was measured. The average Rₜ of HPAM is summarized in Fig. 4. As showed in Fig. 4, the aRₜ of HPAM without STPP decreases with time, and it reduces from 137.2nm at the initial time to 52.2nm on the 15th day. But for the HPAM with 0.03% STPP, it is interested that the aRₜ increases with time, reaching up to 162.3nm from 105.2nm during the same time. Generally, when the HPAM solution is mixed with common salts, such as NaCl, CaCl₂ and MgCl₂, the Rₜ of HPAM will decrease.21 It is because that the common salts reduce the electrostatic repulsion among HPAM molecules, and then the molecules get coiled. Obviously, the effect of STPP on the Rₜ of HPAM can’t be explained by the above “salt sensitive effect”, and some other mechanisms must be existed in the STPP-HPAM system. To our best knowledge, it can be inferred that when
STPP is exposed to the HPAM molecule, it may be “adsorbed” on the HPAM molecule chain by the electrostatic attraction or chemical reaction. Since STPP is highly hydrophilic, the hydration layer of STPP undoubtedly contributes to increase the hydration layer thickness of HPAM. As a result, the $R_g$ of HPAM with STPP is higher than that of HPAM without STPP. However, when the “adsorption” of STPP reaches its saturation value, the surplus STPP will exist in free state in water, and then it will compete with the HPAM to adsorb water molecules, leading to the decrease of the $R_g$ of HPAM. This may be the reason why the $R_g$ of HPAM with 0.1% STPP is lower than that of HPAM with 0.03% STPP.

Additional, the time dependence of the polydispersity index (PDI) affected by STPP is showed in Fig. 5. In the absence of STPP, the PDI firstly increases and then decreases, which is caused by the continuous degradation of HPAM. The PDI of HPAM sample with STPP increases with time, indicating the increase distribution width of molecular weight due to the aging process. It is also observed that the PDI with 0.1% STPP is higher than the one with 0.03% STPP. A high concentration of STPP leads to more “adsorption” of STPP onto HPAM molecule, whereby the HPAM with a high molecular weight is obtained. As a result, more STPP results in higher PDI.

4. Effect of STPP on the $M_w$ of HPAM.

HPAM is a linear polymer made of the combination of acrylamide and acrylic acid. At high temperature condition, the molecular chain is easy to be broken, which has been considered as the reason leading to the hydrogel instability. The 0.2% HPAM solution with 0%, 0.03% and 0.1% STPP was respectively heat-treated at 60°C for 24h, and then the effect of STPP on the $M_w$ of HPAM was investigated by the SLS technology. As showed in Fig. 6, the $M_w$ of the three HPAMs is about $4.70 \times 10^6$ g·mol$^{-1}$ before the heat-treatment. The $M_w$ of HPAM without STPP suffers an obvious decrease due to the heat-treatment, and reduces to $4.31 \times 10^6$ g·mol$^{-1}$. However, the $M_w$ of HPAM with 0.03% STPP increases from $4.70 \times 10^6$ g·mol$^{-1}$ to $5.08 \times 10^6$ g·mol$^{-1}$. When the STPP concentration increases to 0.1%, the $M_w$ of HPAM reaches up to $5.14 \times 10^6$ g·mol$^{-1}$. The results indicate that STPP can increase the $M_w$ of HPAM, which may be a reason why STPP can improve the $R_g$ of HPAM and thereby enhance the hydrogel stability.

5. Effect of STPP on the $A_2$ of HPAM.

The second virial coefficient ($A_2$) can be used to characterize the interaction between macromolecules and solvent molecules. When $A_2$ is positive, the net interaction between macromolecules and solvent molecules is attractive, and the macromolecule tends to dissolve; when $A_2$ is negative, the net interaction between macromolecules and solvent molecules is repulsive, and the macromolecule tends to accumulate; when $A_2$ is zero, the net interaction between macromolecules and solvent molecules equals to the interaction among macromolecules, and the macromolecule is in free status. As showed in Fig. 7, the $A_2$ of the HPAM without STPP is $2.4 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$ before the heat-treatment, and it decreases to $2.1 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$ because of the heat-treatment. When 0.03% STPP is added to the HPAM solution, the $A_2$ increases a lot, reaching up to $5.9 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$, and it even increases to $8.1 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$ after the heat-treatment. This indicates that the STPP promotes the dissolution of HPAM, and increases the hydrophilicity of HPAM. For the $A_2$ of the HPAM with 0.1% STPP, it is up to $5.1 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$, and increases to $6.6 \times 10^4$ cm$^{-3}$ mol$^{-1}$ g$^{-2}$ due to the heat-treatment. Obviously, 0.1% STPP can also improve the hydrophilicity of HPAM, but its effect is worse than that of 0.03% STPP. These results are in good agreement with the data.
obtained from the DLS measurement, so it can be deduced that increasing the hydrophilicity of HPAM is an important reason of the STPP inhibiting the hydrogel syneresis.

6. Reaction mechanism of STPP and HPAM.

STPP and pretreated HPAMs with 0 and 0.03% STPP were characterized by FTIR spectroscopy respectively. As showed in Fig. 8, the stretching peaks of the two HPAMs at 1410, 1570 and 1660 cm$^{-1}$ assigned to C-N, C=O in –COO$^-$ and C=O in –CONH$^-$ respectively are nearly identical. However, due to the effect of STPP on HPAM, the stretching frequency of C=O in –COO$^-$ group of HPAM is increased from 1119 cm$^{-1}$ to 1132 cm$^{-1}$, and a new stretching peak of the HPAM/STPP system appears at 993 cm$^{-1}$ which assigns to the C-O-P group.$^{10}$ Therefore, it can be concluded that the STPP reacts with C-O in –COO$^-$ group of HPAM, whereby the new bond of C-O-P is formed.

Hence, the mechanism of STPP affecting on HPAM is clarified: (1) Because of the crosslinking reaction between STPP and HPAM, the intramolecular or intermolecular crosslinking occurs among the HPAM molecule (showed in Fig. 10), whereby the viscosity of HPAM solution is increased. (2) This crosslinking reaction results in the increase of the macromolecular chain length and the hydration layer thickness, so the $M_w$ and $a_R$ of HPAM rise. (3) The additional crosslinking between the –COO$^-$ group of HPAM and the crosslinker (Cr), which decreases the hydrophilicity of HPAM and then reduces the water-holding capacity of hydrogel, is considered as an important reason for the syneresis of HPAM hydrogel.$^{13}$ The crosslinking between the –COO$^-$ group and STPP not only increases the hydrophilicity of HPAM (or the hydrogel network) due to the strong hydration capability of STPP, but also inhibits the additional crosslinking between the -COO$^-$ group and the Cr caused by the competition crosslinking. As a result, the hydrogel syneresis is mitigated. In conclusion, the increase of the hydrophilicity of HPAM (or the hydrogel network) improves the water-holding capacity of the hydrogel, whereby the hydrogel syneresis is decreased.

Since HPAM is easy to be degraded at high temperature, the HPAM hydrogel is generally used below 80 °C. Although a fairly wide number of new polymers were generally found to possess excellent thermal stability, the synergistic problem of the hydrogels formulated with these polymers at high temperature condition is still inevitable, since their dosage in the hydrogels is limited by their unreasonable cost. Hence, employing HPAM of low price to prepare temperature-resistance hydrogel is significantly important. On the basis of the crosslinking reaction between STPP and HPAM, a hydrogel, which is steady at 160 °C, has been developed. As showed in Fig. 11, the synergistic rate on the 30th day reaches up to 95.3 %, which means that almost all the hydrogel changes to water. Along with the increase of the STPP, the synergistic rate is decreased, and the synergistic rate can be reduced to 8.2 %. It can be seen that STPP can dramatically improve the stability of the HPAM hydrogel at high temperature. To our best knowledge, this robust and persistent gel is the first example which is prepared with HPAM and inorganic chromium.

As showed in Fig. 12, the thermostability of the hydrogel can be further improved below 160 °C, and the synergistic rate on the 30th day is all below 8.2 % at the temperature range from 90 °C to 160 °C. Therefore, this HPAM hydrogel can not only be a water shutoff agent in high-temperature oil reservoir, but also be selected as a channeling sealing agent in the thermal recovery of heavy oil.

Conclusions

STPP is an effective synergistic inhibitor for the hydrogel formulated with HPAM. The mechanism of STPP inhibiting the synergic hydrogel of HPAM is the following: STPP molecule can react with the C-O in -COO\(^-\) group of HPAM whereby the new bond of C-O-P is formed, leading to a large quantity of STPP molecule "adsorbing" on the molecular chains of HPAM. As a result, the hydrophilicity of HPAM is increased due to the strong hydrophilicity of STPP, and the degradation of HPAM is inhibited owing to the intramolecular or intermolecular crosslinking between HPAM and STPP. The increase of the hydrophilicity and stability of HPAM improves the water-holding capacity of the hydrogel, whereby the hydrogel synergic is decreased. On the basis of the crosslinking reaction between STPP and HPAM, a hydrogel prepared with HPAM and Cr\(^{3+}\) has been developed and can be successfully used in high temperature oil reservoir of 160 °C.

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Notes and references