Slow Gelation of Titanium(IV) with Partially Hydrolyzed Polyacrylamide. Crosslinking Reaction and Gel Properties

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ABSTRACT: The gelation of metallic crosslinking agent titanium(IV) (Ti(IV)) with partially hydrolyzed polyacrylamide (HPAM) is studied. Factors effecting the crosslinking reaction are discussed and the dynamic properties of gel are examined. The results indicate that crosslinking of Ti(IV) with HPAM is delayed at low concentrations of polymer and the titanium tartrate. The gelling of Ti(IV)–HPAM is a strong function of titanium/tartaric acid molar ratio, HPAM concentration, initial solution pH value, solution salinity, and hydrolysis degree of HPAM. The gel strength depends on Ti(IV) concentration in a particular way, after a maximum Ti(IV) concentration is reached gel strength decreases. The salt NaCl can accelerate the gelling rate of Ti(IV)–HPAM. The crosslinking mechanism of Ti(IV) with HPAM is proposed. Ti(IV)–HPAM gel can hold its strength at moderate temperature (50°C) for a long time which is suitable to be used in a moderate temperature oil reservoir.

KEY WORDS Titanium / Tartaric Acid / Partially Hydrolyzed Polyacrylamide (HPAM) / Metal Ion
Crosslinking Agents / Enhanced Oil Recovery /

Polymer gels have been extensively studied in the last few decades because of their great aspects in both theoretical field and industry applications.^{1–5} Particularly, in the oil industry, polymer gels are used broadly in Enhanced Oil Recovery (EOR), such as reducing water in the production of oil well,⁶ profile modification,⁷ and in depth treatment.⁸ In the *in-situ* gelation technology,^{7–8} polymer solution and the crosslinker are mixed on ground before being injected into wellbore and the porous reservoir rock. The solutions become crosslinked *in-situ* under reservoir and the formed gel is used for profile modification or depth treatment depending on the strength of the gel. The gelation time can be controlled from minutes to weeks by varying the formulation parameters. In addition, these gels are relatively inexpensive because they typically contain about 95–99.7 wt% of water, with the remainder being low cost chemicals.⁹ The representative polymers involved in this gelation system are either partially hydrolyzed polyacrylamide (HPAM) or biopolymer Xanthan gum.¹⁰ Transition metal ions such as Cr³⁺, Zr⁴⁺, Al³⁺ are often used as crosslinking agents for the gelling.^{5,11–17} The systems with Cr³⁺ and Al³⁺ as crosslinking agents receive particular attention.

The representative aluminum crosslinker is aluminum citrate, which has been on a commercial scale with both technical and economic success, but the Al³⁺/polymer gels are only stable at low pH and low temperature, hard brines and neutral pH condition in the oilfield are detrimental for sodium-aluminate/polymer system.¹² Recently, more interests are concentrated on Cr–HPAM gel system.^{13–15} Unfortunately, the negative healthy effects of chromium(VI) which is reported to be carcinogenic, is environmental unacceptable. Cr³⁺ is relatively low toxic, Cr(III) compounds such as CrCl₃ or Cr(NO₃)₃,¹³ Cr acetate,¹⁴ have been studied as crosslinking agents. But the application of this technology to in-depth treatment of

matrix rock is limited because these chromium(III)/polymer crosslinking are usually too rapid. In addition, gelation of zirconium(IV) with polyacrylamide and scleroglucan are also studied,^{16,17} the retardation and weakening of crosslinking are obtained by adding zirconium lactates into the polymer solutions.

Due to the shortcoming of Al³⁺ and Cr³⁺, metal crosslinking agents which are stable at neutral pH condition and slowly gelled with HPAM are needed. Compared to the expensive zirconium, titanium is a relatively common metal that is the ninth most abundant element in the earth crust.¹⁸ Titanium has four valence electrons and the most stable oxidation state of titanium is Ti⁴⁺. In this paper, to our knowledge, the gelation of HPAM with titanium tartrate complexes is studied for first time. Factors effecting the gelation of Ti(IV) with HPAM are discussed and the rheological properties of Ti(IV)–HPAM gel are examined. Explanations about the observed behaviors are also given out.

EXPERIMENTAL

Materials

Titanium(IV) sulfate, sodium hydroxide, sodium chloride and tartaric acid were used as received from Chengdu Chemical Agents Company (China). The HPAM(I) employed in these studies (from Daqing Petroleum Inc., China) had a M_w of 1.7×10^7 (viscosity determination) and was 22.5% hydrolyzed (titration determination). Another HPAM(II) with M_w 1.0×10^7 , with 5% hydrolysis degree was hydrolyzed further to 15%, 22%, 42% in alkaline solution (titration determination) for the study of effect of hydrolysis degree on the gelation.

Preparing Titanium Tartrate Crosslinking Agent

Titanium tartrate was prepared by reaction of tartaric acid with titanium sulfate. Tartaric acid was added into

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the titanium sulfate solution (0.1 mol/L) at appropriate stoichiometry (the mole ratios of titanium here were in TiO_2 equivalent). The solution was stored at room temperature for few days to form stable titanium tartrate complexes. The pH values of the solution were adjusted by 0.1 N NaOH solution.

Gel Synthesis

HPAM(I) stock solution was mixed with titanium tartrate crosslinking agent and sodium chloride in a tube at appropriate feed ratio, then the tube was sealed and stored in an oven at 50°C. The gel strength was characterized by the apparent viscosity of gel solution which was measured by Brookfield viscometer (6.9 s^{-1} shear rate, 25°C). In the experiments, all the mixtures were fixed with formulation of 400 ppm HPAM, 10000 ppm NaCl and 125 ppm Ti(IV)-tartrate except for special indication.

Dynamic Measurement

The rheometer RheoStress RS 100 of Haake was used to measure the viscoelastic properties of the Ti(IV)-HPAM gel and HPAM dilute solution. All experiments were conducted at 25°C.

RESULTS AND DISCUSSION

Stability of Titanium Tartrate

Titanium(IV) sulfate ($\text{Ti}(\text{SO}_4)_2 \cdot 9 \text{H}_2\text{O}$) is highly acidic, it is only stable at low pH, but at neutral and alkaline conditions, the hydrolysis of Ti(IV) ions results in precipitation from solution.¹⁸ The hydrolysis of Ti(IV) can be illustrated as below:

On the other hand, Ti(IV) can also react with oxyacids to form complexes with different shape and stability. When tartaric acid is added into the titanium sulfate solution, the organic acid will replace H_2O as a ligand to coordinate with Ti(IV), forming more stable complexes. The stability of titanium tartrate can be controlled by the feed ratio of titanium to tartaric acid.

Table I is the precipitation pH values of titanium tartrate after preparing for different times. It is shown that the coordination between Ti(IV) and tartaric acid is a thermodynamic process. It takes time to form stable complexes. With increase of tartaric acid in feed ratios, the formation of stable titanium tartrate complexes becomes faster. When the molar ratio of the Ti(IV)/tartaric acid is 1:0.8, it takes three days to form stable complexes which shows no precipitation when titrated by NaOH; as the tartaric acid in feed ratios of Ti(IV)/tartaric acid are increased to 1:1 and 1:1.2, respectively, it only takes two days to form stable complexes that show no precipitation when titrated by NaOH.

Figure 1 is the comparison of titration curves of titanium sulfate and titanium tartrate by NaOH. It is shown that the two Ti(IV) in different forms have different stability. With increase of NaOH used, the pH value of titanium tartrate solution increases sharply more early than that of titanium sulfate solution.

Table I. The variation of precipitation pH values of titanium tartrate titrated by NaOH at different time

Time/day	The molar ratios of titanium to tartaric acid mol/mol		
	1:0.8	1:1	1:1.2
0.5	3.50	4.42	5.00
1	4.10	9.80	12.60
2	5.12	—	—
3	—	—	—

—: No precipitation occurs.

Figure 1. The titration curves of titanium sulfate and titanium tartrate.

When the amount of NaOH increased from 2 to 3.25 mol NaOH/mol Ti(IV), the solution pH of titanium tartrate increases rapidly from 5.6 to 12; meanwhile, the pH of titanium sulfate solution does not change much. With further adding of NaOH, the pH of titanium sulfate solution begins to increase sharply. This is due to that titanium tartrate complexes are more stable than titanium sulfate. When NaOH is added into the titanium sulfate solution, the OH^- groups will first replace H_2O as ligands to coordinate with Ti(IV), causing hydrolysis of titanium, most of OH^- are consumed as ligands, so the pH value of the solution increases slowly. In the titanium tartrate solution, because titanium tartrate is relatively stable, exchanges between the added OH^- and tartaric acid are slow, the majority of initially added OH^- could not replace tartaric acid ligands to coordinate with titanium, these OH^- ions make the pH value of solution increase sharply more early.

Effect of Molar Ratio of Titanium/Tartaric Acid

The process of HPAM crosslinked by Ti(IV) ions is in fact a ligands exchange process between tartrate and carboxyl groups of HPAM. The crosslinking mechanism can be written schematically as follows:

where P is the polymer chain, L is the ligands, and the m should be great enough to bridge polymer chains together.

During the crosslinking reaction, Ti(IV) ions are released from titanium tartrate complexes to form new

complexes with carboxyl groups of HPAM, further causing crosslinking between polymer chains through Ti(IV) bridge. The stability of titanium tartrate complexes influence both releasing rate of Ti(IV) ions and the crosslinking rate between titanium and HPAM. By controlling the stability of Ti(IV) tartrate, the Ti(IV)-HPAM gelling rate can be controlled. In Figure 2, with decrease of tartaric acid in feed ratio of titanium/tartaric acid, the Ti(IV)-HPAM gelling rates increase. For titanium tartrate with molar ratio of titanium/tartaric acid 1:1.5, there is no obvious gelation within the first 25 h; as the ratio of titanium/tartaric acid increased to 1:0.5, the gel strength increases from 6.4 mPa s to 525 mPa s within 12 h. This confirms that the more stable the titanium tartrate, the more delayed the gelling. For convenience, all the titanium tartrate crosslinking agents used in the below experiments are fixed with molar ratio of Ti(IV)/tartaric acid as 1:0.8.

pH of the Solution

Figure 3 shows the effect of initial solution pH on the Ti(IV)-HPAM gelling rate. In the neutral solution (pH = 6.59), Ti(IV)-HPAM is gelling fast, the gel strength reaches 1520 mPa s after gelling for 60 h; while in the acidic solution (pH = 3.74), no gelation happens. In the weak alkaline solution, precipitation happens which should be due to the hydrolysis of titanium. The solution pH influences the gelling rate of Ti(IV)-HPAM by affecting Ti(IV) releasing rate from titanium tartrate complexes. In the acidic solution, (pH = 3.74), titanium tartrate complexes are very stable, there are not enough Ti(IV) ions produced to form Ti(IV)-HPAM gelation; at the weak acid solution (pH 4.95–6.59), the Ti(IV)/tartaric acid complexes become less stable, more Ti(IV) ions are released to crosslink with HPAM molecular chains, so the gel strength increases rapidly with time. The results indicate that a suitable solution pH range for Ti(IV)-HPAM crosslinking is between 3.74–6.59.

Effect of HPAM Concentration

The influence of HPAM concentration on the HPAM gelation is showed in Figure 4. The gel strength increases with increase of polymer concentration. This is due to that at high polymer concentration, it is easier to form intermolecular crosslinking through Ti(IV) bridge. In the dilute solution, polymer chains are so far away each other that it is hard to form intermolecular crosslinking. There is no obvious gelation when polymer concentration is below 300 ppm.

Influence of Titanium Concentration

The titanium concentration, C_{Ti} , influences the gelling of Ti(IV)-HPAM in a particular way. The gel strength increases first with increasing of C_{Ti} , reaching maximum at C_{Ti} of 250 ppm, then goes down at higher C_{Ti} (Figure 5). Same trend was observed for zirconium-scleroglucan system.¹⁶ During the crosslinking process, Ti(IV) ions dissociate first from titanium tartrate complexes before crosslinking with carboxyl groups of HPAM, after the dissociation, there is a competition between crosslinking with HPAM and formation of higher titanium polynuclear species through oxo-bridges.¹⁸ At higher C_{Ti} , the degree of forming polynuclear is greater, which reduces

Figure 2. Effect of molar ratio of titanium to tartaric acid on the gelling of Ti(IV)-HPAM, the pH of solution is 4.95.

Figure 3. Effect of solution pH on the gelling of Ti(IV)-HPAM.

Figure 4. The influence of HPAM concentration on the gelling of Ti(IV)-HPAM after gelled for 48 h, the Ti(IV) concentration is 110 ppm, the pH of the solution is 4.95.

Figure 5. The influence of Ti(IV) concentration on the gel strength after gelling for 24 h, the pH of solution is 4.95.

the effective crosslinkage between titanium and carboxyl groups of HPAM, thus decreasing the gel strength of Ti(IV)-HPAM.

Effect of Salinity

The gelation reaction between titanium and HPAM strongly depends on solution salinity (Figure 6). In free salt water, no gelation happens even after 80 h at 50°C. In salt solution, gelation takes place and increases with NaCl concentration. This is good for application in most of oil reservoirs which have hard brines. Equations 1 and 2 indicate that the added Na^+ can form stable sodium tartrate, which accelerates the ligand exchange rate of tartaric acid with HPAM.

Effect of Hydrolysis Degree of Polyacrylamide

In this experiment, HPAM(II) is hydrolyzed into different hydrolysis degree and then crosslinked by Ti(IV). The effect of hydrolysis degree of HPAM on the gelation of Ti(IV)-HPAM is illustrated in Figure 7. The gel strength displays an interesting dependence on the hydrolysis degree of the HPAM. After gelled for 42 h, the HPAM with 15% of carboxyl groups has highest gel strength. Higher hydrolysis degree of HPAM also leads to decrease of the gel strength. The reason can be explained as below: HPAM is mainly crosslinked through coordination of Ti(IV) with carboxyl groups, the more carboxyl groups in HPAM, the easier to form crosslinkage. But high carboxyl groups also cause intramolecular crosslinking at dilute polymer solution, which decreases the Ti(IV)-HPAM gel strength.

Influence of Gelling Temperature and Time

Figure 8 is the influence of temperature on gelling of Ti(IV)-HPAM. It appears that the Ti(IV)/HPAM gelling rate is favored when temperature increases, but Ti(IV)-HPAM gel structure is not stable at high temperature (75°C and 90°C). At 50°C, after 10 h of gelling, the gel strength reaches maximum and keeps high strength afterwards. At high temperatures (70°C and 90°C), Ti(IV) tartrate releases Ti(IV) fast, resulting in fast gelling of Ti(IV)-HPAM, the gel strength increases rapidly at beginning, but soon collapses with further heating. This is because that high temperature causes the hydrolysis of the amide groups of HPAM which leads to substantial syneresis of the formed gel.¹⁹ It is shown that after gelling at 90°C for 6 h, the Ti(IV)-HPAM gel strength increases to 59.7 mPa s, but soon collapses abruptly. At 50°C, the hydrolysis of amide groups of HPAM is slow, the gel can keep its strength for long time. Table II shows that the Ti(IV)-HPAM gel can hold its strength as 145 mPa s under 50°C for 58 days. These results suggest that the titanium-HPAM is a weak metal ion crosslinked gel that is suitable for application in a moderate temperature oil reservoir.

Dynamic Test of Titanium-HPAM Gel

Dynamic test is the rheological study of viscoelastic behavior of fluid in which the effect of oscillating stresses or strains on the behavior of the sample is studied. The complex modulus G^* represents the substance total resistance against the applied strain.

Figure 6. Effect of NaCl concentration on the gelling kinetics, the pH of the solution is 4.95.

Figure 7. The influence of the hydrolysis degree of HPAM(II) on the gel strength after gelling for 42 h, the concentration of HPAM (II) is 1000 ppm with 20000 ppm NaCl, and the pH of the solution is 5.25.

Figure 8. The variation of gel strength of Ti(IV)-HPAM with time at different temperature the pH of the solution is 5.20.

Table II. The effect of aging time on the Ti(IV)-HPAM gel strength at 50°C, the pH of the solution is 6.39

Time/day	Gel strength/mPa s
0	6.4
0.54	10.2
1.5	90.5
10	145.1
30	143.6
45	145.2

Figure 9. Comparison of viscoelastic properties of Ti(IV)-HPAM with HPAM dilute solution, (a) G^* , η^* , and ω , (b) G' , G'' , and ω .

$$G^* = \tau_o / \gamma_o \quad (3)$$

Where τ_o and γ_o are the stress and strain amplitudes, respectively. It can also be defined as

$$G^* = G' + iG'' \quad (4)$$

Where G' and G'' are the storage modulus and loss modulus, respectively. Complex viscosity η^* represents the total resistance to a dynamic shear:

$$\eta^* = G^* / \omega \quad (5)$$

Where ω is the frequency and η^* is complex viscosity.

Figure 9 is the comparison of dynamic properties of Ti(IV)-HPAM gel with HPAM dilute solution, the concentration of HPAM is 400 ppm. Figure 9a shows that the η^* of Ti(IV)-HPAM is greater than that of HPAM solution, both η^* decrease with dynamic frequency, displaying a shear-thinning behavior. Figure 9b shows that Ti(IV)-HPAM gel and HPAM solution have increasing G^* with increase of ω , the G^* of gel is greater than G^* of

HPAM solution, which suggests that the higher the applied dynamic strain, the bigger resistance of the fluid, Ti(IV)-HPAM gel has stronger resistance to strain variation than polymer dilute solution. The G' and G'' curves of HPAM solution intersect at $\omega = 26$ s⁻¹, indicating that HPAM solution has more elastic behavior at frequency higher than 26 s⁻¹. For Ti(IV)-HPAM gel, G' and G'' curves intersect at $\omega = 12$ s⁻¹, indicating that gel has predominant viscous behavior at frequency less than 12 s⁻¹, at frequency higher than 12 s⁻¹, the gel shows predominate elastic behavior.

CONCLUSIONS

The present study demonstrates that metal ion titanium(IV) can react with tartaric acid to form stable complexes. By varying the ratios of titanium to tartaric acid, the stability of titanium tartrate complexes can be controlled. The gelation between titanium(IV) and HPAM is a process of ligands exchange between tartaric acid and carboxyl groups of HPAM. Because of the slow releasing rate of Ti(IV) ions from titanium tartrate, the gelling of Ti(IV) with HPAM is delayed. Factors such as molar ratio of titanium to tartaric acid, polymer concentration, solution pH value, Ti(IV) concentration, solution salinity, and hydrolysis degree of HPAM have important influences on the Ti(IV)-HPAM gelation. The pH range for titanium-HPAM gelation is between 4.90–6.59. With increase of titanium concentration, Ti(IV)-HPAM is gelling faster. When titanium tartrate concentration is more than 250 ppm, the formation of polynuclear complexes of titanium causes less effective crosslinking between titanium and HPAM, decreasing the gel strength. Salt sodium chloride increases the gelling rate. Ti(IV)-HPAM gel shows shear thinning behavior during dynamic test. Comparing with HPAM gel crosslinked by other metal ion crosslinking agents, this titanium tartrate is adaptable to hard brine content, neutral pH condition and moderate temperature oil reservoirs.

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