



A salt-induced viscosifying smart polymer for fracturing inter-salt shale oil reservoirs

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Abstract

Inter-salt shale oil reservoirs located between two salt layers are always accompanied by high temperature and high salinity. However, the present commonly used water-soluble polymers in fracturing fluids suffer from poor tolerance to high temperature and high salinity. Thermoviscosifying polymers (TVP) whose aqueous solution shows viscosity increase upon increasing temperature and salt concentration have received considerable attention recently, which is promising for utilization in fracturing fluids to overcome these problems. In this work, both the salt-induced viscosifying property and mechanism of a TVP solution were investigated and the performance of TVP used as fracturing fluid based on the conditions of the Jianghan inter-salt shale oil reservoir in China was evaluated. It is found that the salt-induced viscosifying property of the TVP solution decreases with temperature and shear rate, but increases with polymer concentration. The number of intermolecular hydrophobic domains increases with the salt concentration contributing to the strengthening of a 3D network structure, which results in an increase in viscosity. In addition, the TVP fracturing fluid formulated with saturated brine exhibits excellent temperature and shear resistance, sand-suspending performance, and gel-breaking performance. Its viscosity remains above 50 mPa s after being sheared for 1 h even at a high temperature of 140 °C and the sand-suspending stability can be maintained for more than 1 week at 100 °C. Furthermore, the fracturing fluid can be easily broken down within 12 h using 0.2 wt%–0.3 wt% potassium persulfate without residue.

Keywords Fracturing · Salt-induced viscosifying · Thermoviscosifying · Smart polymer · Rheological properties

1 Introduction

Shale oil and gas have been considered to be the most promising unconventional alternative energy resources in the future according to the exploration and production history in North America (Soeder 2018). However, those reservoirs

usually have low permeability and porosity that impedes the exploitation. To overcome this drawback, hydraulic fracturing is often used to create fractures to facilitate the fluid flow (gas/oil and water) in shale (Barati and Liang 2014). In the fracturing process, an aqueous solution with high viscosity is required, as it cannot only effectively transfer pressure but also carry proppants (e.g., ceramics), and thus, more fractures could be produced and kept in the reservoir. Water-soluble polymers are widely used to thicken an aqueous solution producing a fracturing fluid since the polymer chains can entangle to form 3D networks.

Located between two salt layers, inter-salt shale oil reservoirs are mostly composed of clay minerals, salt minerals, and carbonate minerals (Zha et al. 2013). These have drawn increasing attention in recent years owing to the rich shale oil and gas reserves. For example, the tight inter-salt oil reservoir in the Jianghan basin located in the central region of China contains abundant shale gas resources ($9.1 \times 10^{12} \text{ m}^3$) (Ning 2013). However, the unique sandwich-like configuration of the reservoirs results in high

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salinity, with saturated brine (Wu et al. 2016). The salt layers on both sides are thin, brittle, and easy to be eroded when applying pure water fracturing fluid, resulting in the breakdown of the whole shale. Recent research found that the use of saturated brine fracturing fluid would avoid this problem (Wu and Li 2008), because it cannot dissolve more salts. Additionally, the reuse of the produced water that contains a high concentration of salt as the base fluid will dramatically reduce the disposal of produced water and consumption of pure water (Shaffer et al. 2013). Nevertheless, most water-soluble polymers are not salt tolerant, especially in saturated brine. For example, a polyacrylamide (PAM) solution will dramatically lose its viscosity when encountering inorganic ions such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , and even worse, coagulation and precipitation will occur when the inorganic ion concentration keeps increasing (Kamal et al. 2015a, b). Moreover, some shale oil reservoirs are accompanied by high temperature, usually over 100 °C. Therefore, a polymer with both good temperature and salt resistance is highly desirable when fracturing in such high-temperature and high-salinity (HTHS) inter-salt shale oil reservoirs.

In addressing the problems associated with viscosity loss of a fracturing fluid in the HTHS environment, different types of fluids have been developed to satisfy the requirements of fracturing under such harsh conditions. Harris and co-workers (2006) developed a viscous aqueous foamed fracturing fluid mainly comprised of a foaming agent (C_8 – C_{88} alkylamidobetaines), and a terpolymer of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamide (AM), and acrylic acid (AA), which could be utilized in subterranean zones with temperatures up to and above 400 °F (204 °C), but its salinity tolerance was not described. Yegin and co-workers (2016) developed a supramolecular fracturing fluid whose viscosity is highly pH adjustable and reliable at salinity of 5 wt% (above that of sea water); however, this fracturing fluid seems not to behave so well in temperature resistance and shear stability. Lebas and co-workers (2013) took the high total dissolved solids (TDS) (over 250,000 ppm) produced water from the Delaware basin in New Mexico as the base for fracturing fluid, formulated it with carboxymethyl hydroxypropyl guar gum (CMHPG), zirconium-based cross-linker, sodium chlorite breaker, etc., and performed a field test and witnessed its success in creating a fracture network and transporting sand into the fracture network. Great efforts have been made to develop materials fit for HTHS environment, but few of them are both temperature and salt tolerant. Chemical cross-linking is necessary in most fracturing fluid regimes which usually makes the fracturing process complex. Thus, the development of an HTHS-tolerant fracturing fluid regime with simplified components and application procedures is highly desired nowadays.

Unlike most chemically cross-linked fracturing fluids, hydrophobic associative polymers can form physical cross-linking points, providing enhanced proppant suspension without the utilization of cross-linkers, and also can easily be broken down with little to no residue during the process of flowing back to the surface. Increasing interest has been shown in hydrophobic associative polymers in hydraulic fracturing applications for their stronger viscosifying ability and better temperature and salt tolerance over standard hydrophilic polymers. Heitz and co-workers (2003) synthesized a series of copolymers containing both water-soluble blocks and hydrophobic blocks, whose potential in fracturing fluid in high temperature ranges (higher than 180 °C) has been demonstrated. The same findings were also observed by Cadix and co-workers (2015). They proved the effectiveness of hydrophobic associative polymers for hydraulic fracturing applications at high temperatures (up to 190 °C) in conventional brines (2000–4000 ppm) without the addition of external cross-linkers, and also found a preliminary encouraging cleanup profile during gel breaking. However, those physically cross-linked fracturing fluids seem not as salt tolerant and no research has focused on their performance in high salinity or saturated brine.

In recent years, another kind of associate polymer has appeared whose viscosity increases with increasing temperature. This is called a “thermoviscosifying polymer” (TVP), and it is promising to be used for oil and gas exploitation (Chen et al. 2013; Xie and Liu 2017; Zaitoun et al. 2016). The thermoviscosifying effect is attributed to the hydrophobic association between the lower critical solution temperature (LCST) sidechains grafted on to hydrosoluble skeletons when heating to a critical associating temperature (T_{ass}) (Hourdet et al. 1998; L’Alloret et al. 1995). In most cases, increasing temperature will reduce the viscosity of traditional water-soluble polymers, such as PAM and PAA (polyacrylic acid), which are categorized as “thermothinning polymers” (Yang 1999). In contrast, for the TVP polymer, high temperature becomes a favorable factor to enhance its viscosity buildup ability, which makes it possible to achieve oil and gas production in high-temperature reservoirs. Moreover, some studies (L’Alloret et al. 1995; Hourdet et al. 1998, 2005, 2008) also found the addition of salts could further enhance the hydrophobic interaction between those thermoresponsive grafts, contributing to the strengthening thermoviscosifying ability. The temperature and salt-induced thickening capability of TVPs could offer a fluid for oil and gas production in high-salinity and high-temperature reservoirs.

In recent years, other salt-thickening polymers have been investigated and various salt-induced viscosifying mechanisms were discovered. Some ascribed the salt-thickening phenomenon to hydrogen bonds and hydrophobic entanglements formed among the macromolecular

chains (Wang et al. 2012); in some systems, the salt-thickening mechanism was found to be related to the reorganization of the intermolecular interactions; for example, the coordination between cations and hydroxyls makes greater intermolecular interaction than the original simple hydrogen-bond interaction (Zhao et al. 2015); some believed that the salt-induced viscosifying ability should be attributed to an increase in the solvent's polarity and also the lower solubility of the hydrophobic moieties with increasing salinity (Sarsenbekuly et al. 2017); for some amphiphilic polymers with betaine zwitterionic groups, Zhu et al. thought the salt thickening was caused by destruction of ionic bonds in the betaine monomer and the enhancement of hydrophobic association strength (Zhu et al. 2017).

In our previous work focused on TVPs, similar salt-induced viscosifying phenomena were observed in polymers bearing *N*-(1,1-dimethyl-3-oxobutyl)-acrylamide (DAAM) (Liu et al. 2012; Wang et al. 2010). For example, the T_{ass} of an anionic TVP solution decreased from 50 to 44 °C when the NaCl concentration increased from 0 to 0.85 M. Besides, the viscosifying magnitude in 0.85 M NaCl brine (8.1 times) was much greater than that in pure water (1.1 times) (Liu et al. 2012). Another new type of nonionic TVP developed by our group showed similar salt sensitivity as the anionic one and exhibited extraordinary viscosifying ability induced by divalent ions such as Ca^{2+} and Mg^{2+} . What should be pointed out is that a solution of low polymer concentration with over 10 wt% NaCl still has the thermoviscosifying effect of this TVP, and more interestingly, the viscosity of TVP solution in high-salinity brine is always higher than that in low-salinity brine in the whole temperature range from 20 to 90 °C (Li et al. 2017). This outstanding salt-thickening ability of the TVP has attracted our keen interest in explaining its salt-induced viscosifying mechanism, and exploring its application in high-salinity reservoirs, such as the Jiangnan inter-salt shale oil reservoir.

To our knowledge, there were no studies focusing on TVP used in hydraulic fracturing, especially in the HTHS environment. In consideration of the temperature and salinity doubly induced viscosifying ability of TVP, for the first time we proposed the idea of applying TVP to solve the fracturing problem in the inter-salt shale oil reservoirs with HTHS. Thus, in the present work, a small-scale factory manufacturing pilot product TVP developed by our group was chosen as the thickener to fabricate fracturing fluid used in saturated synthetic brine. Its temperature and shear resistance, sand-suspending performance, and gel-breaking performance were examined based on the conditions of the Jiangnan inter-salt shale oil reservoir. Furthermore, the rheological behavior of this TVP was presented in different brines with salinity increasing from zero to saturation and its salt-induced viscosifying mechanism was discussed.

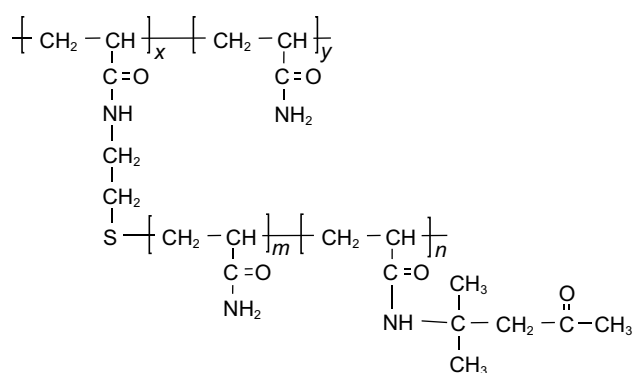


Fig. 1 Chemical structure of TVP ($x:y=9:91$)

2 Experimental section

2.1 Materials

Both commercial PAM and pilot product TVP whose molecular weight and chemical structure (Fig. 1) were described in our previous studies (Li et al. 2017) were kindly provided by Beijing Hengju Polymer Co., Ltd. The salts used for brine preparation (including NaCl, CaCl_2 , MgCl_2 , Na_2SO_4 , etc.) and gel breaker $\text{K}_2\text{S}_2\text{O}_8$ are all analytical grade and purchased from Chengdu Kelong Chemical Reagents Corporation, China. The deionized water (conductivity, $\kappa=7.9 \mu\text{S cm}^{-1}$) was treated by an ultrapure water purification system (CDUPT-III, Chengdu Ultrapure Technology Co., Ltd., China).

2.2 Preparation of polymer solution and fracturing fluid

Dry polymer powders were added to pure water at a stirring rate of 250 RPM at room temperature within 10 min to ensure that polymer powders could rapidly and uniformly disperse in water. After that, the stirring rate was lowered and kept at a speed of 100 RPM for about 24 h until a homogeneous polymer solution was formed. Then, inorganic salts were added to this polymer solution with stirring until the salts were completely dissolved. The brine formulation used for polymer fracturing fluid preparation is shown in Table 1.

2.3 Characterization of salt-induced viscosifying effect of TVP

2.3.1 Rheological test

Both static and dynamic rheological tests were performed on a Physica MCR 302 (Anton Paar, Austria) rotational rheometer equipped with a Searle-type concentric cylinder geometry CC27. The radii of the measuring bob and the

Table 1 Composition of the synthetic saturated formation water

Ions	Na ⁺ + K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	CO ₃ ²⁻	TDS
Concentration, mg L ⁻¹	102,944	138.36	13.61	274.65	932	158,121	45.01	262,469

measuring cup are 13.33 and 14.46 mm, respectively. The temperature was set to ± 0.1 °C accuracy by a Peltier temperature control device, and a solvent trap was used to minimize water evaporation during the measurements. Tests did not begin until the polymer solution was stabilized in the cylinder for 10 min. In the static rheological test, each polymer solution was sheared at a steady shear rate and temperature for 10 min, during which its viscosity was recorded every 20 s. Then, the recorded viscosity values were averaged as the final viscosity of this polymer solution at a certain shear rate and temperature.

Dynamic frequency sweeping tests were conducted in the linear viscoelastic regimes, as determined from dynamic stress-sweep measurements. All the tests were carried out using a stress-controlled mode at a constant strain of 10%, with frequency ranging from 0.01 to 100 Hz. During the dynamic rheological tests, the temperature was kept at 30 °C.

2.3.2 Temperature-variation fluorescence spectroscopy

A fluorescence spectrophotometer (Varian Eclipse, USA) was used to determine the fluorescence spectrum of pyrene in polymer solutions with different salinity. The fluorescence excitation wavelength was set at 335 nm, and the emission wavelength was arranged as 350–450 nm. The scan speed was 1200 nm min⁻¹. The excitation and emission slit width was 5 nm and 2.5 nm, respectively. Temperature was controlled at 30 °C or 70 °C by the water bath temperature control system.

2.4 Performance evaluation as fracturing fluid

2.4.1 Temperature and shear resistance evaluation

The rheological tests concerning the temperature and shear resistance of the fracturing fluid were carried out on the same rheometer (Physica MCR 302) mentioned above, but with a high-pressure and high-temperature (HPHT) measuring setup, where a concentric cylinder geometry CC25 with a measuring bob radius of 12.50 mm and a measuring cup radius of 13.56 mm was employed. Samples were stabilized for about 10 min at 20 °C to attain equilibrium before measurements. During the tests, steady shear viscosity was recorded during temperature scans going from 20 to 100 °C (or 120 °C, or 140 °C) with a heating rate of 2 °C min⁻¹ and then kept at this high temperature for 60 min. The shear rate was 170 s⁻¹ in the whole process.

2.4.2 Sand-suspending performance evaluation

Polymer fracturing fluid and ceramsite proppant with a particle size of 40–70 mesh were mixed thoroughly in a beaker with a sand ratio of 30%, which means the ceramsite volume makes up 30% of the total volume. Then, the mixture was transferred into a measuring cylinder with a sealing plug on the top and put into an incubator at 100 °C. After different aging times, the mixture was taken out to take photographs with a digital camera until the proppant was completely (> 95%) settled.

2.4.3 Gel-breaking performance evaluation

First of all, designated amounts (0.05 wt%, 0.10 wt%, 0.20 wt%, 0.30 wt%) of the gel breaker K₂S₂O₈ was added and dissolved in the polymer fracturing fluid. Then, the fracturing fluid with gel breaker was sealed in Pyrex bottles and placed inside the incubators at 60, 100, or 140 °C, respectively. After a certain interval, fracturing fluids were taken out for viscosity measurement with the same rotational rheometer as the *Rheological test* part (CC27, Physica MCR 302), at a shear rate of 170 s⁻¹ at the corresponding gel-breaking temperature. The gel-breaking test did not stop until the viscosity dropped below 5 mPa s, and the consumed time was recorded as the gel-breaking time.

3 Results and discussion

3.1 Salt-induced viscosifying behavior of TVP

3.1.1 The effect of temperature

In view of the thermoviscosifying characteristic of TVP, it is necessary to take the influence of temperature into consideration when discussing the salt-induced viscosifying effect. Thus, a non-thermoreponsive polymer, PAM, was employed to make a parallel comparison with TVP, to highlight the temperature effect on the salt-induced viscosifying ability of TVP. As shown in Fig. 2a, the viscosity of PAM stays at a high level in pure water, but decreases dramatically when increasing the salt concentration to 5 wt%, and it keeps stable at a low viscosity of around 20–45 mPa s with further increases in the salinity.

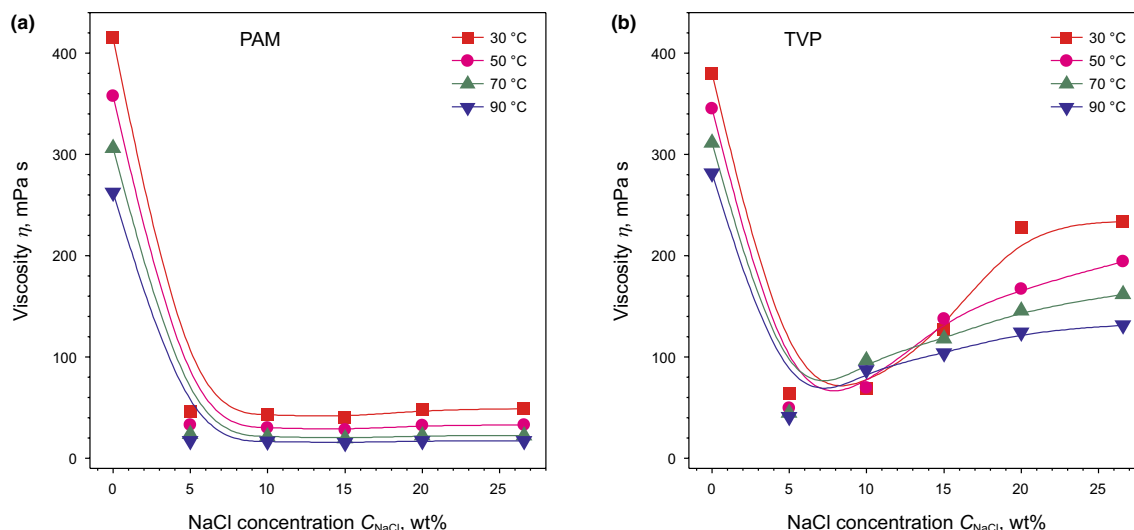


Fig. 2 Apparent viscosity plotted as a function of NaCl concentration for **a** PAM and **b** TVP aqueous solution at different temperatures ($C_p = 0.5$ wt%, $\dot{\gamma} = 10$ s $^{-1}$)

Additionally, the higher the temperature, the lower its viscosity, as thermothinning polymers do.

On the contrary, the TVP solution exhibits dominant salt-induced viscosifying ability, although it also encounters a similar viscosity decline from the pure water to brine containing 5 wt% NaCl. Specifically, the viscosity of TVP increases by 170, 145, 117, and 90 mPa s at 30, 50, 70, and 90 °C, respectively, when increasing salinity from 5 wt% to saturated salinity, 26.6 wt%. It is also easy to find that the viscosifying magnitude induced by salt decreases with ascending temperature, which indicates that high temperature is unfavorable to the salt-induced viscosifying ability of TVP.

Such unique rheological behavior of the TVP solution could be attributed to the variation of hydrophobic associated structures among TVP polymer solutions when changing the salinity and temperature. The salting-out effect of NaCl, on the one hand, destroys the hydration sheath of the polymer and shrinks the TVP coils, and thus, the apparent viscosity first decreased when adding 5 wt% NaCl into the pure water; on the other hand, this effect promotes a stronger tendency of hydrophobic aggregation among thermosensitive sidechains, stretching different polymer chains to associate into 3D networks in the solution which results in an increase in viscosity (Wang et al. 2009). Moreover, it is generally considered that the hydrophobic association interaction can be strengthened by the enhancement of solvent polarity as the solution salinity increases, which decreases the association energy among sidechains (Liu et al. 2004). Consequently, the TVP solution exhibits a viscosifying phenomenon when the NaCl concentration increases further to saturation, because the hydrophobic associations become

stronger and stronger with the increasing solution salinity. It is worth noting that the salt-induced viscosifying phenomenon cannot be observed in hydrophobically associated polymers whose high viscosity is also due to the hydrophobic associations between sidechains. The major difference between TVP and the hydrophobically associated polymer is that the side chains of TVP would undergo a process from hydrophilic to hydrophobic when increasing salinity resulting in a transition of viscosity from low to high (the viscosifying effect) with the growing amount of the hydrophobic associations, while those of hydrophobically associated polymer would form the hydrophobic associations initially but cannot avoid losing its viscosity when salinity increases because of the dehydration effect on the hydrosoluble main chain.

However, temperature, as another factor to promote the hydrophobic association among polymers, weakens the salt-induced viscosifying ability of TVP, which seems unreasonable. As a matter of fact, temperature affects the rheological behavior in another way aside from the hydrophobic interaction promotion. The formed physically cross-linked network corresponds to the “transient network” model (L’Allouet et al. 1997), which means the hydrophobic associated junctions are sufficiently weak to break and recombine in thermal fluctuations, and the networks are dynamic, rather than static. Polymer thermal motion increases with the rise of temperature, accelerating the disassociation of sidechains, and when this disassociation rate is greater than the rate of reconstruction, more and more polymer chains will escape from the micro-hydrophobic domain becoming the “free” polymer chains in solution, indicating that the amount of cross-linking points would decrease or the strength of them

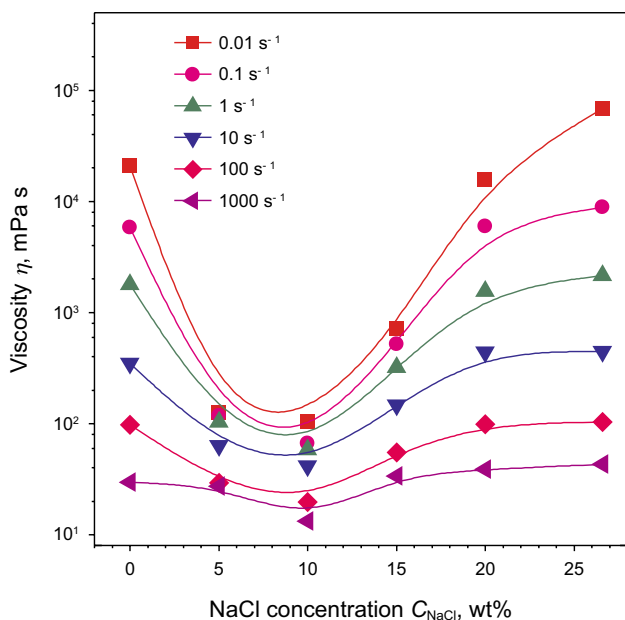


Fig. 3 Apparent viscosity of the TVP aqueous solution plotted as a function of NaCl concentration at different shear rates ($C_p=0.5$ wt%, $T=30$ °C)

would decline. Thus, the salt-induced viscosifying ability would be weakened with increasing temperature. In addition, it is easy to find that the TVP solutions with higher salt concentration are more sensitive to temperature. For example, the viscosity of the TVP solution with 20 wt% and 26.6 wt% salt concentration varies more with temperature compared to that of the TVP solution with 5 wt%–15 wt% salt concentration. This might be attributed to the more hydrophobic association structures formed in higher salinity TVP solutions which will be in return affected more broadly by the polymer chain thermal motion.

3.1.2 The effect of shear rate

The fracturing fluid will undergo relatively high-speed shearing when it is injected at a high pressure to hydraulically crack the rock open. Thus, it is important to know the rheological behavior of the TVP solution with increasing salinity at different shear rates. To avoid the disturbance of temperature when discussing the influence of shear rate on salt-induced viscosifying effect, the temperature was kept at 30 °C during which the apparent viscosity of TVP in different salinity brine was measured with increasing shear rates.

As can be seen in Fig. 3, all TVP solutions show the salt-induced viscosifying phenomenon at shear rates ranging from 0.01 to 1000 s^{-1} , and the viscosifying magnitude decreases with an increase in shear rate. For example, when the shear rate increases five orders of magnitude from the original 0.01 s^{-1} to the final 1000 s^{-1} , the viscosity of TVP

in saturated brine increased by 551, 74, 20, 6, 2.5, and 0.6 times, respectively, compared with that in the 5 wt% salt solution, indicating the formed hydrophobic associations in the TVP solution are sensitive to shear rate. Still, the TVP solution shows salt-viscosifying ability even at a high shear rate of 1000 s^{-1} .

What should be pointed out is that the salt-induced viscosifying effect is quite significant at a low shear rate of 0.01 s^{-1} where the apparent viscosity is close to the zero-shearing viscosity. As can be seen, the viscosity of TVP in saturated brine is even higher than that in pure water, owing to the increasing amount of hydrophobic associated structures induced by enhancing salinity in brine, facilitating the formation and strengthening of the physical networks. Such transient physical networks as mentioned above are unstable and easy to break and rebuild. As with the effect of temperature on viscosifying behavior, a higher shear rate will break the cross-linkers more frequently, so that the viscosity will show a decrease when reconstruction of networks cannot balance the shear destruction. In general, the more the non-linear structures in solution, the more prominent the shear thinning phenomenon will be. The TVP solution of higher salinity exhibits stronger sensitivity compared with that of low salinity, which is consistent with the hypothesis that the number of hydrophobic aggregations would rise with an increase in salt concentration.

3.1.3 The effect of polymer concentration

For most TVPs, thermothickening phenomenon would be observed only when the polymer solution reaches a certain concentration called the critical aggregation concentration (CAC) (Liu et al. 2001), which ensures the formation of enough entanglements between macromolecules. It has been well recognized that thermoviscosifying ability of TVP is positively correlated with polymer concentration (Durand and Hourdet 1999; Hourdet et al. 1994, 1997; Karakasyan et al. 2008). Likewise, the salt-induced viscosifying ability is assumed to have similar relations with polymer concentration.

Figure 4 depicts the viscosity–salinity curves varying with polymer concentration. TVP solutions show the salt-induced viscosifying ability in all polymer concentrations. Viscosity of TVP in saturated brine increased by 1.5, 1.7, 3.7, and 2.3 times, compared with that in the 5 wt% salt solution, with polymer concentration of 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1.0 wt%, respectively. It shows that a TVP solution with higher polymer concentration (0.5 wt% and 1.0 wt%) possesses more evident salt-induced viscosifying ability than that with lower polymer concentration (0.1 wt% and 0.2 wt%). Higher polymer concentration permits more hydrophobic aggregations per unit volume of

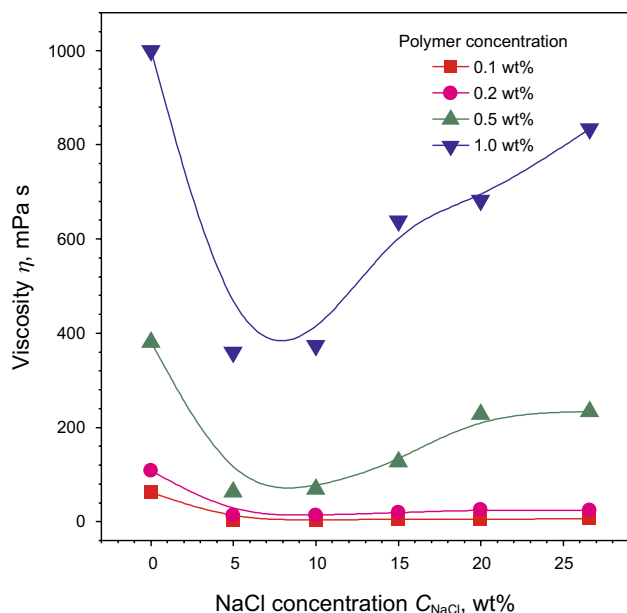


Fig. 4 Apparent viscosity of the TVP aqueous solution with different polymer concentrations plotted as a function of NaCl concentration at 30 °C ($\dot{\gamma} = 10 \text{ s}^{-1}$)

solution, contributing to denser and larger 3D hydrophobic cross-linked networks when raising the solution salinity.

3.2 Salt-induced viscosifying mechanism of TVP

From the above analysis, preliminary findings can be concluded as follows: (1) As the temperature increases, the salt-induced viscosifying ability decreases; (2) the higher the shear rate, the weaker the salt-induced viscosifying effect, and the higher the salt concentration, the more sensitive to shearing the viscosity will be; (3) TVP solutions with higher polymer concentration show a more obvious viscosifying phenomenon. It is important to reveal the mechanism of the salt-induced viscosifying behavior of this TVP for the sake of further utilization in practical applications. From the above results, we speculate that this TVP may form hydrophobic associated 3D networks in saline solution, and the number of these hydrophobic associated structures increases with the rise of salt concentration. However, increased temperature or shear rate will destabilize the hydrophobic association structures.

To verify the above hypothesis, dynamic rheological experiments were employed to examine the effect of salinity on viscoelastic properties of polymer solution and variable temperature fluorescence spectroscopy was used to verify the effect of salt concentration on the polarity of solvent and the hydrophobic association structure of TVP.

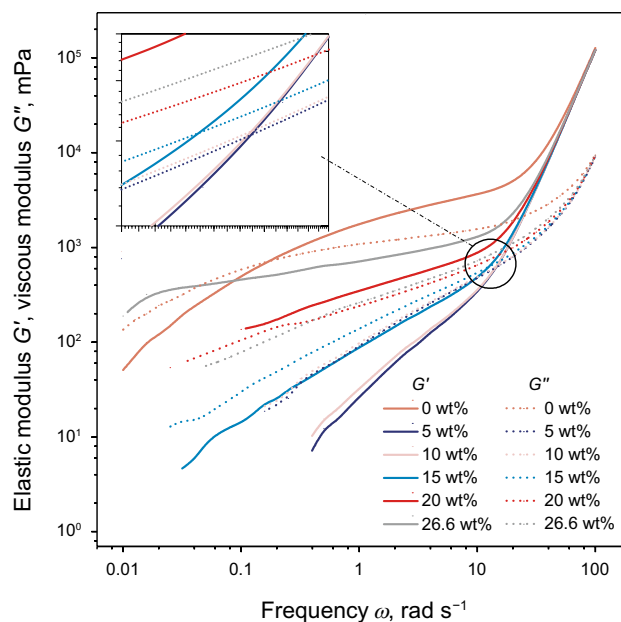


Fig. 5 Effect of NaCl concentration on the dynamic rheology of the TVP aqueous solution ($C_p = 0.5\%$, strain = 10%, $T = 30 \text{ °C}$)

3.2.1 The influence of salt on viscoelastic properties of TVP

Dynamic rheological measurements are a means of characterizing the viscoelastic properties of solutions. By comparing the storage (elastic) modulus, G' , and loss (viscous) modulus, G'' , of the polymer solution during shear deformation, or calculating the value of the loss factor, $\tan \delta$ (Eq. 1), the viscoelastic properties of the solution can be evaluated. When G' completely dominates G'' , that is, $\delta = 0^\circ$, and $\tan \delta = 0$, the fluid exhibits ideal elastic behavior. When G'' dominates G' in the whole shear range, $\delta = 90^\circ$, and $\tan \delta = \infty$, the fluid exhibits ideal viscous behavior. For viscoelastic fluids, the elastic modulus is usually lower than the viscous modulus at low frequencies, but higher at high frequencies. Sometimes, there will be an intersection where $G' = G''$, $\tan \delta = 1$ and the frequency at this intersection is denoted as ω^* . The lower the intersection frequency ω^* , the more obvious the elasticity of the solution will be (Viken et al. 2016). The elasticity also can be interpreted by the value of $\tan \delta$, that is, a higher $\tan \delta$ value suggests more prominent elasticity of the solution, at the same frequency.

$$\tan \delta = \frac{G''}{G'} \quad (1)$$

Figure 5 shows the variation of elastic modulus G' and viscous modulus G'' of different TVP saline solutions with angular frequency. The G' and G'' of solutions with 0 wt%, 5 wt%, 10 wt%, and 15 wt% salt show intersections in the range of tested angular frequency. The TVP solution in pure water has the smallest ω^* value, followed by the TVP

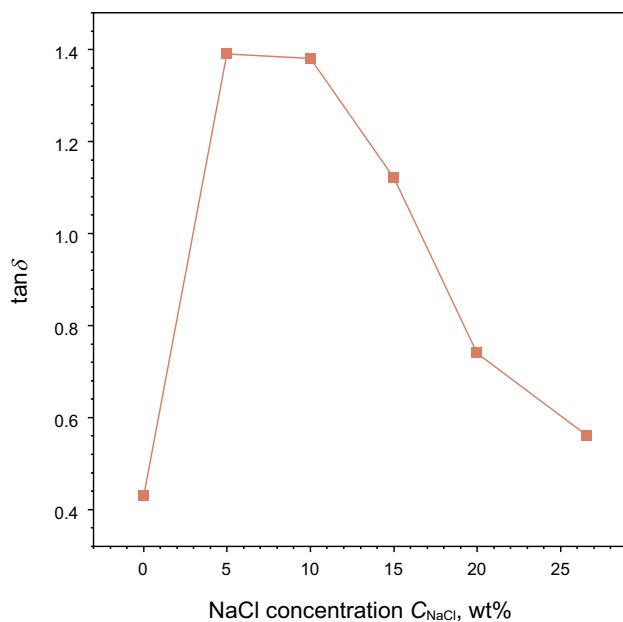


Fig. 6 $\tan \delta$ as a function of NaCl concentration ($\omega = 10 \text{ rad s}^{-1}$, $C_p = 0.5\%$, strain = 10%, $T = 30 \text{ }^\circ\text{C}$)

solution with 15 wt% salt concentration, while the solutions with 5 wt% and 10 wt% salt have the largest ω^* value. On the contrary, the solutions with 20 wt% and saturated salt concentration (26.6 wt%) have no intersection point of ω^* in the entire tested frequency scan range, but their elastic modulus G' is always higher than their viscous modulus G'' . These results can be explained as follows. For the TVP macromolecules in pure water, extended polymer chains easily form entanglements, contributing to the relatively high viscosity and conspicuous viscoelasticity (Wei et al. 2016). Accordingly, ω^* occurs at lower frequencies. When the salt concentration increases to 5 wt% and 10 wt%, the apparent viscosity and viscoelasticity experience a great loss due to the salting-out effect, resulting in higher ω^* values. As the salt concentration continuously rises to 15 wt%, the ω^* starts shifting to low frequencies. The improvement in solution viscoelasticity indicates the formation of hydrophobically associated structures in the TVP solution leading to the 3D physical networks. When further increasing the salt concentration to 20 wt% and 26.6 wt%, the elasticity of the TVP solution is always dominant over its viscous property over the tested frequency range, and its ω^* value is assumed to appear below 0.01 rad s^{-1} . As a whole, the shift of ω^* to low frequencies with increasing salinity indicates that the number of hydrophobic associated structures of TVP would increase with the enhancement of salinity in solution, promoting the building of physically cross-linked networks, giving rise to the improvement of apparent viscosity as well as the viscoelasticity.

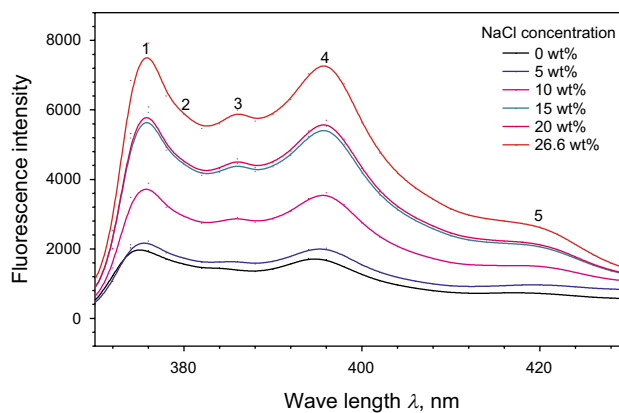


Fig. 7 Fluorescence spectra of pyrene in 0.5 wt% TVP solutions containing different NaCl concentrations at $30 \text{ }^\circ\text{C}$

When fixing a certain angular frequency, such as $\omega = 10 \text{ rad s}^{-1}$, calculating the loss factor, $\tan \delta$ from the values of G' and G'' for TVP solutions of each salt concentration, and plotting as a function of salt concentration, more obvious phenomena are presented in Fig. 6. One can find that the addition of a small amount of salt in pure water makes the value of $\tan \delta$ increase to 1.4, meaning that the elastic modulus G' is less than the viscous modulus G'' . As the salt concentration increases, the value of $\tan \delta$ gradually decreases and descends to less than 1 when the salt concentration is above 20 wt%, indicating that, at this salt concentration, the elastic modulus G' has exceeded the viscous modulus G'' . This finding is in good agreement with the salt-induced viscosifying phenomenon of the TVP solution, again suggesting that more physically cross-linked networks would form as the salt concentration increases, making the viscoelastic properties of the TVP solution more and more significant.

3.2.2 The influence of salt on the polarity of the solvent and hydrophobic association structures of TVP

Pyrene (Py) is a commonly used fluorescent probe, whose singlet spectroscopy fine structure is extremely sensitive to the polarity changes of the local environment (Kalyanasundaram and Thomas 1977; Wilhelm et al. 1991). When the concentration of Py in solution is less than $10^{-5} \text{ mol L}^{-1}$, five peaks can be observed in the spectrum (Fig. 7), where the intensity ratio of the peak 1 to peak 3 (I_1/I_3) decreases with an increase in hydrophobicity of the microenvironment. Accordingly, the changes of the I_1/I_3 value can be used to indicate the formation of hydrophobic microdomains in solution (Gao et al. 2000).

As shown in Fig. 8, one can find that the I_1/I_3 value always decreases with an increase in salt concentration at either a low temperature of $30 \text{ }^\circ\text{C}$ or a high temperature

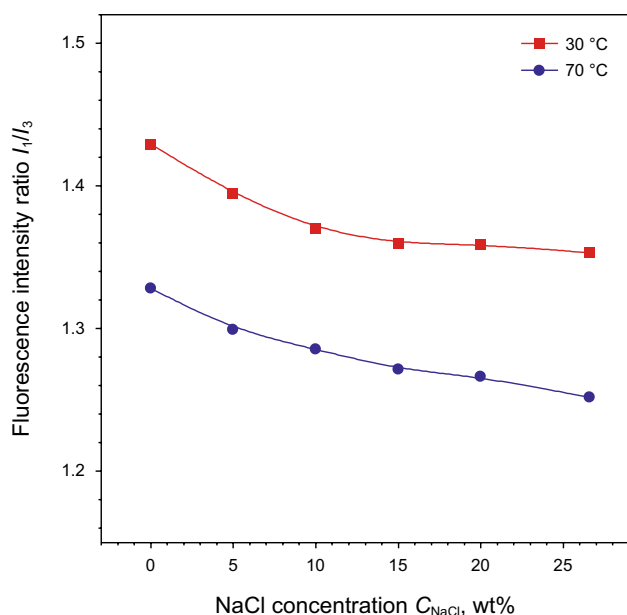


Fig. 8 Fluorescence intensity ratio I_1/I_3 as a function of salinity for TVP at 30 °C and 70 °C, respectively ($C_p=0.5$ wt%)

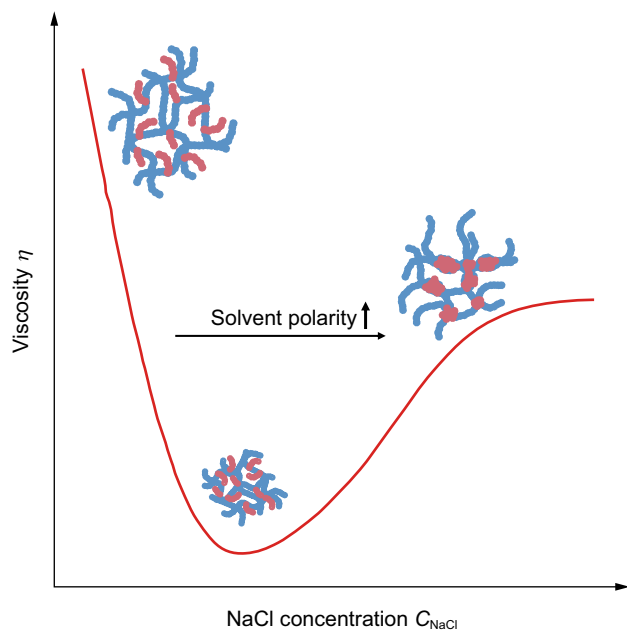


Fig. 9 Salt-induced viscosifying mechanism of TVP

of 70 °C. Besides, the I_1/I_3 values at 70 °C are all lower than those at 30 °C. These results suggest the polarity of the microenvironment of Py becomes weaker and weaker as the salinity and temperature increases, which directly suggests the temperature and salinity doubly induce the viscosifying property of TVP. On the one hand, an increase in temperature arouses the hydrophobic associations between LCST

side chains, and the higher the temperature, the more the hydrophobic associations will be. On the other hand, solvent polarity increases with the NaCl concentration, inducing more hydrophobic aggregations in the solution (Fig. 9), thus enhancing the hydrophobicity inside the aggregations. As a result, the polarity of these hydrophobic zones where Py is solubilized will decrease with an increase in both temperature and salinity, displaying a descending trend of I_1/I_3 value.

3.3 Performance evaluation as fracturing fluid

After investigating the salt-induced viscosifying property and mechanism of TVP, much attention was paid on its performance when used in fracturing fluid for the HTHS environment. Taking advantages of its temperature and salinity doubly induced viscosifying ability, TVP is assumed to be capable of turning the disadvantages of high temperature and high salinity for most water-soluble polymers into the advantages of increasing its viscosity when applied in harsh reservoirs. Moreover, the hydrophobically associated reversible 3D networks formed in high-temperature and high-salinity conditions could avoid the use of a cross-linking agent in the fracturing fluid, which will reduce the pump pressure during injection. In addition, the fluid is suspected to be able to be broken easily without residues during the gel-breaking experiment due to the lack of chemical cross-linking points in the regime.

To verify this supposition and illustrate its effectiveness when used in hydraulic fracturing in a harsh environment, the temperature and shear resistance, sand-suspending performance, and gel-breaking performance of TVP fracturing fluid were examined, based on the conditions of the Jiangnan inter-salt oil reservoir.

3.3.1 Temperature and shear resistance

Fracturing fluids are subjected to strong mechanical shear and increasing temperature during injection into the formation, which normally causes a big loss in viscosity and weakens their sand-suspending performance. Thus, how to maintain a high viscosity at a certain temperature and shear rate during the fracturing operation is very important. In other words, the fracturing fluid is required to have good temperature tolerance and shear resistance. Here, several TVP fracturing fluids with different polymer concentrations are prepared in the simulated saturated formation brine (TDS: 262,469 mg L⁻¹, salt composition is shown in Table 1). The results of fracturing fluid viscosity varying with temperature and shear time are shown in Fig. 10.

As shown in Fig. 10, all curves first decrease with increasing temperature and then tend to keep at a plateau when the temperature stays at a specified high value. After shearing for 1 h at high temperatures, the viscosity of TVP fracturing

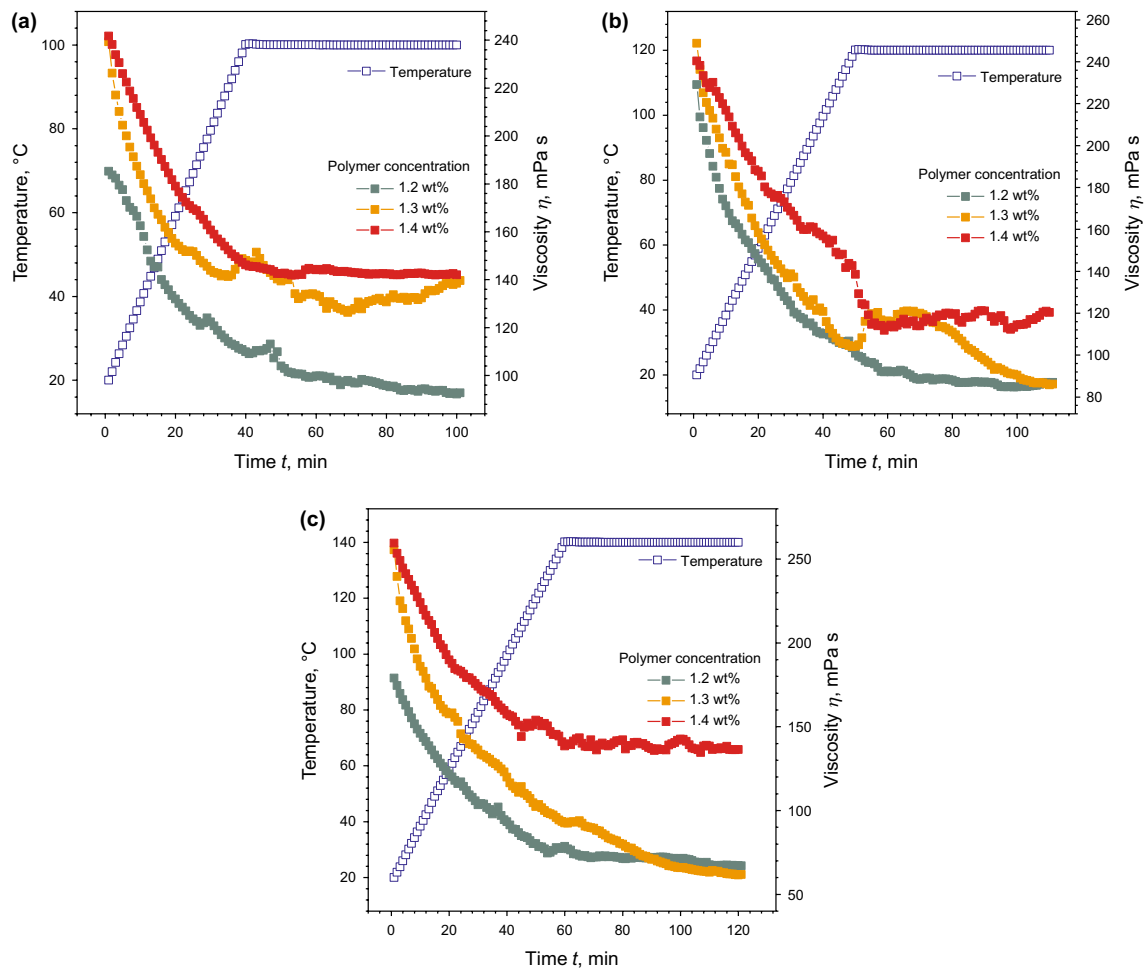


Fig. 10 Temperature tolerance and shearing resistance in saturated formation brine of TVP fracturing fluid with different polymer concentrations at **a** 100 °C, **b** 120 °C, and **c** 140 °C, respectively ($\dot{\gamma} = 170 \text{ s}^{-1}$)

Table 2 Summary of remaining viscosity of TVP fracturing fluids

Temperature, °C	TVP concentration, %	η_1 , mPa s	η_2 , mPa s	Viscosity retention rate, %
100	1.2	110	92	83.6
	1.3	147	140	95.2
	1.4	146	142	97.3
120	1.2	100	85	85.0
	1.3	105	86	81.9
	1.4	138	120	87.0
140	1.2	77	67	87.0
	1.3	92	62	67.4
	1.4	138	136	98.6

fluids is all greater than 50 mPa s, satisfying the application requirements of the fracturing fluid. For better comparison, we set the viscosity values when first reaching the maximum

temperature and the viscosity values after shearing for a further 1 h at the maximum temperature as η_1 and η_2 , respectively, and the ratio of η_2 to η_1 as the viscosity retention rate, which is summarized in Table 2.

From Table 2, it is easy to see that TVP fracturing fluids in saturated brine with various polymer concentrations all have high viscosity retention rates after constant shearing for 1 h at high temperatures. Most of the viscosity retention rates exceed 80%, and some are even close to 100%. For example, the TVP fracturing fluid with a polymer concentration of 1.4 wt% has a viscosity retention rate of 97.3%, 87.0%, and 98.6% after being sheared at constant temperatures of 100, 120, and 140 °C for 1 h, respectively, which attests to the excellent temperature and shear resistance of the TVP polymer in saturated brine at high temperatures. For practical applications, we chose the fracturing fluid with a moderate polymer concentration of 1.3 wt% for the subsequent sand-suspending performance and gel-breaking performance evaluation.

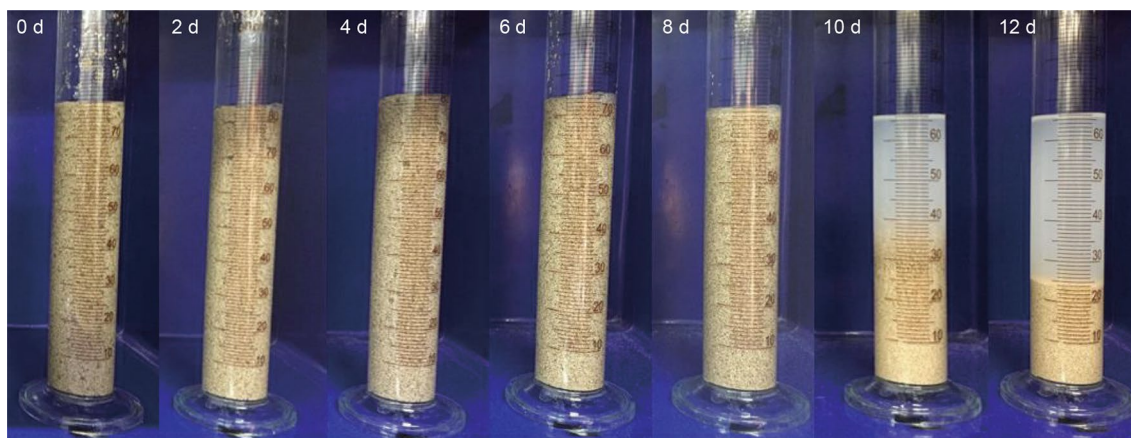


Fig. 11 Sand-carrying ability of the TVP fracturing fluid in saturated formation brine

3.3.2 Sand-suspending performance

During the fracturing process, the fracturing fluid is required to suspend and carry the proppant into the newly formed fractures for support. Therefore, fracturing fluids should have good sand-carrying performance; otherwise, the proppant will settle down too quickly and sink at the bottom of the wellbore, causing sand plugging and sand trapping problems at the bottom of the well, seriously affecting the effectiveness of fracturing (Barbati et al. 2016). Generally, the greater the viscosity of the fracturing fluid, the easier it is to suspend the sand and distribute it evenly in cracks. The previous evaluation of the temperature and shear resistance of the fracturing fluid has confirmed that it can maintain high viscosity under high-temperature and high-salinity conditions. Therefore, it is predicted that the TVP fracturing fluid should also show good sand suspending performance. In this section, proppant sedimentation experiments were performed with 40–70 mesh ceramics suspended in 1.3 wt% TVP solution at 100 °C to evaluate the sand suspending performance of TVP fracturing fluids.

Figure 11 shows the state of the suspended sand in the TVP fracturing fluid at 100 °C over time. As can be seen from the figure, the TVP sand-suspended fracturing fluid could keep stable for more than 1 week at a high temperature of 100 °C. From the 8th day onwards, clear liquid began to appear in the upper layer of the solution in the measuring cylinder, followed by the complete sedimentation of ceramic in 2 days. In the early stages, the TVP fracturing fluid exhibits quite stable sand-suspending capacity when ceramic particles were evenly distributed in the entire solution system and no delamination was found, which is ascribed to the high viscosity and excellent viscoelasticity of the TVP polymer under high temperature and high salinity. In such environments, hydrophobic associations occur between LCST sidechains of TVP, forming physically cross-linked

networks, increasing the solution viscosity, which is beneficial to slowing down the settlement of the proppants. As a result, the complete settling only took place 12 days later which is much longer than most fracturing fluid reported before. The excellent sand-suspending performance of the TVP fracturing fluid confers great potential for future practical application in HTHS reservoirs.

3.3.3 Gel-breaking performance

When the fracturing fluid completes the task of carrying proppant to support new fractures, its viscosity is required to drop rapidly and turn into a fluid with strong flowability facilitating it flowing back to the surface. This process is called gel breaking. Apart from that, the residue after this process should be as low as possible to reduce the damage to the reservoir (Barbati et al. 2016). The temperature and salt doubly stimulate the viscosifying property of TVP making it possible to achieve high viscosity without the addition of a cross-linking agent, and thus, it avoids the difficulties in gel breaking faced by most chemically cross-linked fracturing fluids. To check it, 1.3 wt% TVP fracturing fluid was used to perform the gel-breaking test at 60, 100, and 140 °C, respectively. The breaker used in this work is the commonly used oxidizing agent, potassium persulfate, and its dose was set at 0.2 wt%, 0.3 wt%, 0.4 wt%. The gel-breaking performance of each group of solutions was evaluated by the parameters of the breaking time, breaking viscosity, and residue content of the fracturing fluid.

From the results displayed in Table 3, it can be seen that: (1) At the same gel breaker concentration, the higher the gel-breaking temperature, the shorter the time required for breaking the gel. For example, the breaking time of the fracturing fluid with 0.2 wt% breaker concentration is 800, 230, and 75 min at 60, 100, and 140 °C, respectively. (2) At the same gel-breaking temperature, the higher the gel

Table 3 Gel-breaking performance of the TVP fracturing fluid in saturated formation brine

Gel-breaking temperature, °C	Breaker concentration, %	Breaking time, min	Residue content, mg L ⁻¹	Viscosity after breaking, mPa s
60	0.2	800	None	5.0
	0.3	480	None	4.6
	0.4	480	None	4.9
100	0.2	230	None	2.9
	0.3	60	None	4.2
	0.4	Gelation	Gelation	/
140	0.2	75	None	2.6
	0.3	40	None	3.2
	0.4	Gelation	Gelation	/

breaker concentration is, the shorter the gel breakage time is. For example, at 100 °C, the fracturing fluid with 0.3 wt% breaker concentration completed the gel-breaking process after 60 min, while it took 230 min to complete the process when using 0.2 wt% breaker. This is because the higher the concentration of the breaker, or the higher the temperature, the more active radicals the breaker produces and thus the greater the rate at which polymer macromolecules are degraded by free radical attacks. However, for this fracturing system, too much breaker will adversely affect the breaking process. For example, when the amount of gel breaker is 0.4 wt%, regelation occurs when the gel is broken at 100 and 140 °C, resulting in failure of gel breakage. Therefore, it is necessary to select an optimum type and amount of breaker according to different conditions of the formation (temperature, pH, etc.).

In this work, the gel breaker concentration is recommended within the range from 0.2 wt% to 0.3 wt%, and the gel would be completely broken within 12 h. Moreover, the liquid was transparent and clear and no broken residue was observed after breaking. All this demonstrates that the TVP fracturing fluid is easily broken and would not cause damage to the reservoir after breaking and flowing back to the surface.

4 Conclusion

The rheological properties of TVP solutions were systematically studied, and the effects of temperature, salinity, shear rate as well as polymer concentration were examined. This TVP shows excellent salt-induced viscosifying ability and the corresponding mechanism was revealed, and then, it was used as a thickener to prepare the fracturing fluid whose performance was evaluated based on the conditions of the Jiangnan inter-salt shale oil reservoir. It is found that this TVP shows a strong salt-induced viscosifying property, and the property is affected by several factors including

temperature, shear rate, and polymer concentration. The salt-induced viscosifying ability decreases when temperature and shear rate rise, but increases with the polymer concentration. Moreover, the salt-induced viscosifying mechanism of this TVP is ascribed to the enhanced solution polarity with the salt concentration, which promotes the formation of more hydrophobic associations between side chains. These increasing intermolecular hydrophobic domains would strengthen the 3D network structures resulting in an increase in viscosity. In addition, the TVP fracturing fluid formulated with saturated brine exhibits excellent temperature and shear resistance, sand-suspending performance, and gel-breaking performance. Its viscosity remains at a high level after being sheared for 1 h even at a high temperature of 140 °C and the sand-suspending stability can be maintained for more than 1 week at 100 °C. Furthermore, the fracturing fluid can be easily broken within 12 h using 0.2 wt%–0.3 wt% potassium persulfate without residue.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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