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Preparation and Performance of the Hyperbranched Polyamine as an Effective Shale Inhibitor for Water-Based Drilling Fluid

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Abstract

Seeking effective solutions to control and mitigate the interaction between drilling fluids and clay formations has been a challenge for many years, and various shale inhibitors have shown excellent results in problematic shale formations around the world. Herein, the hyperbranched polyamine (HBPA) inhibitor with a higher ratio of amine groups and obvious tendentiousness in protonation was successfully synthesized from ethylenediamine, acryloyl chloride and aziridine by five steps, in which the metal-organic framework (MOF) was employed as a catalyst for ring-open polycondensation (ROP). The structure and purity were confirmed by nuclear magnetic resonance hydrogen spectroscopy and high-performance liquid chromatography (HPLC) respectively. The HBPA displays more excellent performance than EDA and KCl widely applied in the oil field. After aging at 80˚C and 180˚C, the YP of a slurry system containing 25 wt.% bentonite and 2 wt.% HBPA are just 8.5 Pa and 5.5 Pa (wt.%: percentage of mass), respectively. The swelling lengths of 2 wt.% HBPA are estimated to be 1.78 mm, which falls by 70% compared with that of freshwater. Under a hot rolling aging temperature of 180˚C, the HBPA system demonstrates a significant inhibition with more than 85% shale cuttings recovery rate and is superior to conventional EDA and KCl. Mechanism analysis further validates that the HBPA can help to increase the zeta potential.

Keywords

Water-Based Drilling Fluid, Inhibitors, Hyperbranched Polyamine, Metal Organic Framework Catalyst, Amine Groups

1. Introduction

According to the complex and numerous chemical and physical variations present in the formation, normal inhibitors don't deliver satisfactory performances for preventing shale hydration swelling and dispersion in water-based drilling fluids [1] [2], and the existence of water sensitivity would produce a series of problems such as instability and collapse of the wellbore, bit balling, stuck pipe, etc [3] [4].

The linear-chain molecular structure is a much important factor that restricts the performance of the existing inhibitors [5]. Molecules adsorbed on the surface of the electronegative clay particles have absorbing groups with low density at either end and desorption takes place most easily when subjected to every downhole factor, resulting in a sharp decline in inhibitory action [6] [7] [8].

Compared with linear polymer, hyperbranched polymer, as a kind of quasi-spherical shape polymer with dominated branched structure, can introduce numerous absorbing groups at the end of the molecular chains by the functionalization and modification of end-groups, which was propitious for the molecular chain to the adsorption on the surface of clay [5]. Excluding terminal groups, the increase of absorbing groups along the chains could also enhance the adsorption capacity. The resulting molecular is adsorbed onto the negatively charged clay mineral and enters the interlayer space to tighten the crystalline layers of clay minerals, preventing shale hydration swelling [9].

In this study, a kind of hyperbranched polymer with a higher ratio of amine groups was designed and synthesized. Benefiting from this structure, primary amine, secondary amine and amide groups would produce protonated products in serious alkaline drilling fluids, which endow the molecule with strong adsorbability and thus help boost the inhibition performance of HBPA. Attributing to the characterization results of inhibitive properties, the as-synthesized HBPA significantly performances better than currently available EDA and KCl in bentonite inhibition test, linear swelling test and shale cuttings hot-rolling dispersion test. Besides, zeta potential measurements were carried out to investigate the inhibiting mechanism. Compared to EDA and KCl, the HBPA system experiences the greatest drop and no charge reversal appears.

2. Experimental

2.1. Materials

Ethylenediamine (EDA, AR, >99%): colorless or slightly yellow viscous liquid, melting point 8.5˚C, boiling point 116˚C, relative density 0.899, belongs to alkaline material, soluble in water, ethanol, slightly soluble in ether.

Di-tert-butyl dicarbonate (Boc_2O, >98%): a new type of amino protective agent, the product is a colorless crystal or colorless liquid, melting point 22˚C, boiling point 56˚C, relative density 0.950, dissolved in tetrahydrofuran, trichloromethane and other organic solvents, slightly soluble in water.

Trifluoroacetic acid (TFA) (AR, >99%): excellent solvent for organic reaction, melting point −15.6˚C, boiling point 71.1˚C, relative density 1.5351, used in this

paper for the removal of BOC protective group.

Triethylamine (AR, >99%): an organic compound, colorless oily liquid, melting point −114.8˚C, boiling point 89.5˚C, relative density 0.728, used as an acid-binding agent.

Citric acid monohydrate (AR, >99%): organic compound, melting point −94˚C, boiling point 56˚C, relative density 0.791, used in this paper for removing impurities of the product.

KCl: white crystal powder, melting point 770˚C, boiling point 1420˚C, relative density 1.98, was used as the control experiment of inhibition performance of synthetic hyperbranched polyamine (HBPA) (**Figure 1**).

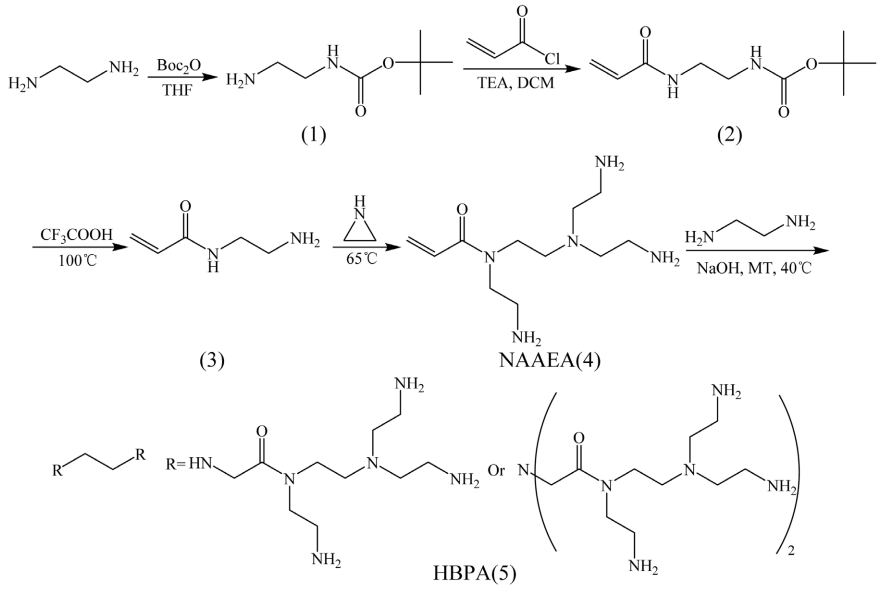


Figure 1. Schematic diagram of synthesis of the HBPA.

Aziridine was prepared based on the relevant reference [10].

The Sodium bentonite (Na-bent) was a natural smectic aluminosilicate.

2.2. Sample Preparation

2.2.1. Tert-Butyl (2-Aminoethyl)Carbamate (1)

To a solution of EDA (0.224 mol, 15 mL) and tetrahydrofuran (THF) (75 mL) was added the di-tert-butyl dicarbonate (Boc_2O) (0.04353 mol, 10 mL) at 0˚C - 5˚C. The reaction mixture was stirred at 25˚C for 24 h and then yellow oily liquid (5.57 g, 80%) was obtained through filtration, washing and concentration. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.44 (s, 9H, CH_3), 1.53 (s, 2H, NH_2), 2.54 - 2.56 (m, 2H, N-CH_2), 3.41 - 3.43 (m, 2H, CH_2-N), 6.75 (s, 1H, NH).

2.2.2. Tert-Butyl (2-Acrylamidoethyl)Carbamate (2)

Acryloyl chloride (4.5 mmol, 0.41 g) was added to a solution of 1 (4.5 mmol, 0.72 g), triethylamine (5.4 mmol, 0.55 g) and methylene chloride (DCM) (20 mL), and the acryloyl chloride (4.5 mmol, 0.41 g) dissolved in DCM (15 mL) was added slowly at 0˚C - 5˚C. The solution was stirred overnight and warmed to

25˚C during this period. and then excess solvent was removed under vacuum. The residue was diluted with saturated sodium bicarbonate solution following extraction with CH_2Cl_2, then the combined solution was dried and concentrated to give 3 (0.72 g, 75%) as a light-yellow powder. ^{1}H NMR (400 MHz, DMSO) δ: 1.37 (s, 9H, CH_3), 3.14 (s, 4H, CH_2-CH_2), 5.60 (s, 1H, CH=C), 6.07 (d, 1H, CH=C), 6.12 - 6.26 (m, 1H, C=CH), 6.81 (s, 1H, NH), 8.10 (s, 1H, NH).

2.2.3. N-(2-Aminoethyl)Acrylamide (3)

TFA (2.5 mL) was added to a solution of 2 (4.5 mmol, 0.963 g) and ethyl acetate (10 mL) at 0˚C - 5˚C. The solution was heated in an oil bath (100˚C) for 12 h, and then the excess solvent was removed under vacuum. The remains were diluted with n-butanol (15 mL) and washed with saturated sodium carbonate solution. The yellow solution was concentrated to give 4 (0.36 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 2H, NH_2), 2.52 (d, 2H, CH_2-N), 3.37 (d, 2H, N-CH_2), 5.61 (d, 1H, CH=C), 6.11 (d, 1H, CH=C), 6.23-6.25 (m, 1H, C=CH), 8.44 (s, 1H, NH).

2.2.4. NAAEA (4)

The aqueous solution with 3 (4.5 mmoL, 0.51 g) and aziridine (13.5 mmol, 0.58 g) were mixed, then the reaction mixture was stired at 65˚C for 10 h. the yellow liquid 5 (0.90 g, 82%) was obtained by alkali treatment process and concentration. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (s, 6H, NH_2), 2.55 (s, 6H, N-CH_2), 2.78 (s, 4H, CH_2-N), 3.04 (d, 2H, CH_2-N), 3.2 - 3.3 (m, 2H, N-CH_2), 3.4 (s, 2H, N-CH_2), 3.83 - 3.85 (m, 1H, CH=C), 3.99 (s, 1H, CH=C), 4.97 (s, 1H, C=CH).

2.2.5. Hyperbranched Amine Inhibitor (HBPA) (5)

A suspension of 4 (2.19 g, 9 mmol), NaOH (21 mg) and EDA (3 mmol, 0.2 mL) in methanol (20 mL) was stirred at 40˚C for 6 h under a nitrogen atmosphere. Compound 6 (1.88 g, 79%) was obtained as a light-yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10 - 1.15 (m, 1H, CH_3), 1.44 (s, 6H, NH_2), 2.54 (s, 6H, N-CH_2), 2.59 (s, 4H, CH_2-N), 2.68 (s, 2H, N-CH_2), 2.78 (s, 2H, CH_2-N), 3.22 (s, 2H, CH_2-N), 3.30 (d, 2H, CH_2-N), 3.33 (s, 1H, NH), 3.45 - 3.49 (m, 2H, N=CH_2).

2.3. Characterization

^{1}H-NMR and HPLC Analysis

The product of each step was investigated by use of nuclear magnetic resonance hydrogen spectroscopy with tetramethylsilane as an internal reference, and the measurement was performed on an advanced −400 spectrometer at 25˚C. In order to further verify the rationality and reliability of these strategies in the synthesis of HBPA, High-Performance Liquid Chromatography (HPLC) was used to characterize the high purity of the target compound.

2.4. Inhibition Property Evaluation

2.4.1. Bentonite Inhibition Test

The incorporation of highly active drilled solids into a drilling fluid is simulated in the technique, which closely resembles the process of drilling in water-sensitivity

soil. A solution of 5 wt.% bentonite (20 g) and a certain concentration of shale inhibitors dissolved in 400 mL freshwater was stirred for about 30 min, then the mixture was hot rolled for 16 h at different temperatures. After cooling to 25˚C, their rheology was measured. Then, added an equal amount of bentonite and the operation was the same as the previous. This process repeated until the data was unreadable resulting from the excessive viscosity of the sample.

2.4.2. Linear Swelling Test

The impact of inhibitor on shale cuttings exposed to the water-based drilling fluid can be assessed by linear swelling measurements which are carried out at 25˚C. A large linear swelling rate corresponds to fairly strong hydration reactivity. Firstly, bentonite powder (10 g) was compressed into bentonite pellets. Then the swelling heights of pellets soaked in a certain concentration of a solution containing various inhibitors were investigated.

2.4.3. Shale Cuttings Hot-Rolling Dispersion Test

This method is designed to evaluate exactly the ability of inhibitors to prevent shale hydration swelling and dispersion by determining the influence of inhibitors on determining the effect of an inhibitor on the structural integrity of sized cuttings at elevated temperature. Added a 350 mL solution containing 50 g shale cuttings and various concentrations of inhibitors to the aging jars for hot rolling aging for 16 h, then, the remaining shale cuttings of a certain size were screened with a 40 mesh sieve. After washing and drying to a constant mass, the recovery of cuttings can be calculated according to the formula below.

$$\text{Recovery} = \frac{\text{The constant mass}}{50} \times 100\%$$

2.5. Inhibition Mechanism Analysis

Zeta Potential Measurement

For clay particles, the trend of swelling and dispersion weakens with the absolute value of negative zeta potential decreasing. Normally, this test is used to evaluate the stability of clay dispersions via the changing trends of electrokinetic properties for bentonite affected by inhibitors. A series of bentonite suspensions of the same concentration (4 wt.%) were employed as base slurry samples and kept stirring for 24 h. Then adding various concentrations of inhibitors to these slurry samples to continue to stir for another 24 h, the supernatant was diluted to zeta potential determination.

3. Results and Discussion

3.1. Characterization

The polybasic primary amine structure of HBPA was confirmed by ^{1}H NMR analysis, which spectra were shown in **Figure 2(a)**. The ^{1}H NMR spectrum confirms the presence of primary amine in this HBPA structure with the chemical shift peaks of 1.5 ppm. It can be observed that the spectra have characteristic shifts of methylene groups, corresponding to seven kinds of protons in methy-

lene under different chemical environments on this sample. There is chemical shift peaks at 3.32 ppm, attributed to protons of NH groups. Figure 2(b) is the typical analytical HPLC (High-Performance Liquid Chromatography) chromatograms for the prepared HBPA. The results indicated that the contents of two components in the product were 72.1% and 27.9%, respectively.

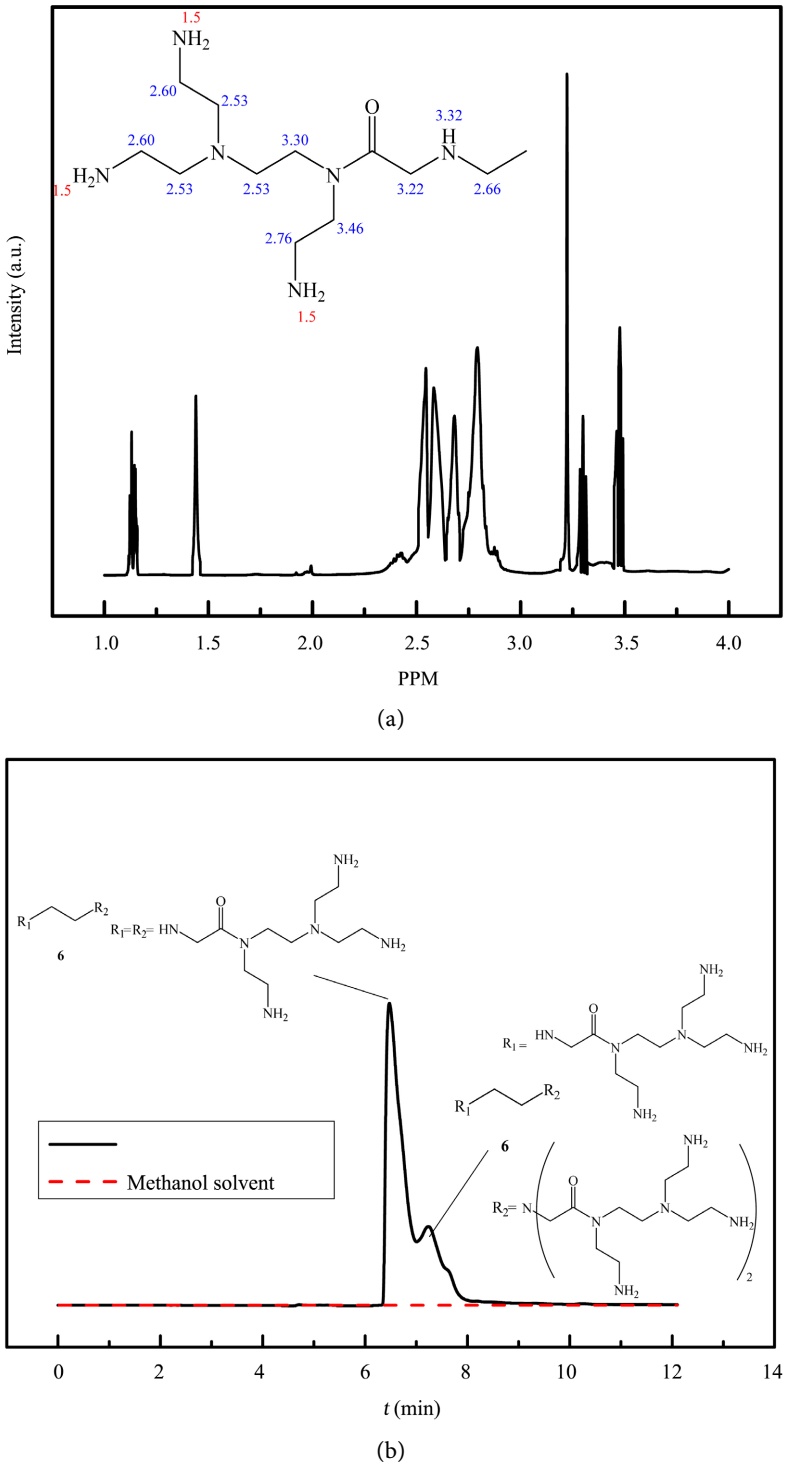
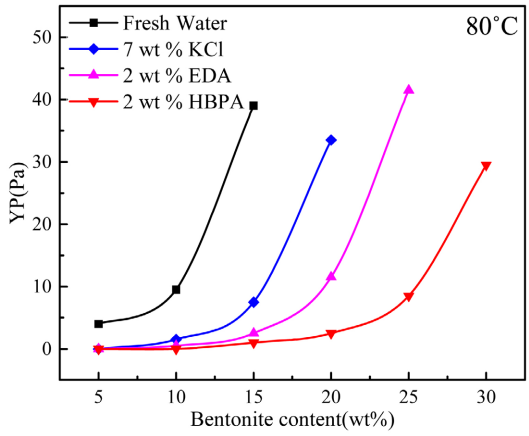


Figure 2. (a) ^{1}H-NMR of the HBPA; (b) The HPLC chromatogram of the HBPA.

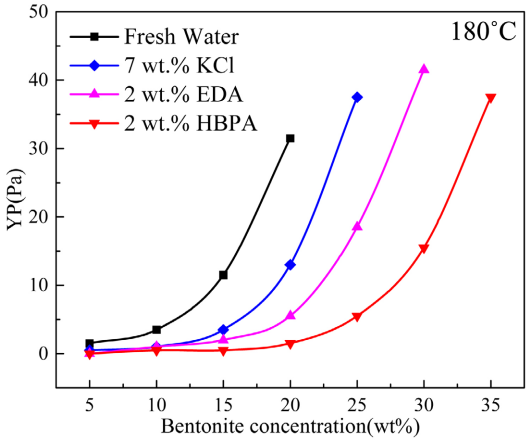
3.2. Inhibitive Properties Evaluation

3.2.1. Bentonite Inhibition Test

The ability of the inhibitor to prevent shale hydration swelling can be detected by the changing rules of yield points for bentonite slurries with various concentrations [11] [12] [13]. The evaluation results of the bentonite inhibition test were shown in Figure 3. When increasing the addition of bentonite under the absence of inhibitors, the YP shows a rapid increase, and the value quickly becomes unmeasurable as the additive content of bentonite reaches 15% of the total drilling fluid mass, suggesting the swelling behavior of bentonite [14]. By comparison, the increasing of YP of a slurry system containing different inhibitors develops slowly initially, and the value changes abruptly under higher bentonite concentration. Encouraging, compared with the two conventional inhibitors, the swelling of bentonite is inhibited by HBPA (2 wt.%) to maximum. To further evaluate the inhibition effect of these serious additives at elevated temperatures, trends in yield points for bentonite slurries with various inhibitors were examined under the conditions of 180˚C. Figure 3 reveals that the 2 wt.%



(a)



(b)

Figure 3. Variation of yield value with bentonite concentration in various inhibitor Solutions at 80˚C (a) and 180˚C (b). *apparatus: Model 900 viscometer, the data was measured at 25˚C.

HBPA displays superior performance, and the order was 2 wt.% HBPA > 2 wt.% EDA > 7 wt.% KCl for the properties of inhibition.

3.2.2. Linear Swelling Test

Linear swelling test can specifically estimate the swelling degree of rock samples with drilling fluids [15], especially for highly reactive shale formation containing abundant swelling clays [16] [17] [18]. The inhibitive durability of the prepared HBPA inhibitor was detected and the results were shown in **Figure 4**. For comparison, the EDA, KCl and freshwater systems were also tested under identical conditions. During the initial test phase, the swelling and hydration of bentonite pellet increase rapidly, and then a plateau is reached where the linear swelling lengths turn to be relatively stable. Measurement results suggest that the swelling lengths of 0.5 wt.% EDA, 1 wt.% EDA, 2 wt.% EDA, 7 wt.% KCl, 0.5 wt.% HBPA, 1 wt.% HBPA, 2 wt.% HBPA are estimated to be 3.39, 2.51, 2.09, 2.94, 2.20, 1.86 and 1.78 mm, respectively. Obviously, compared with EDA and KCl systems, the HBPA has resulted in the biggest drops in the expandability of bentonite [19].

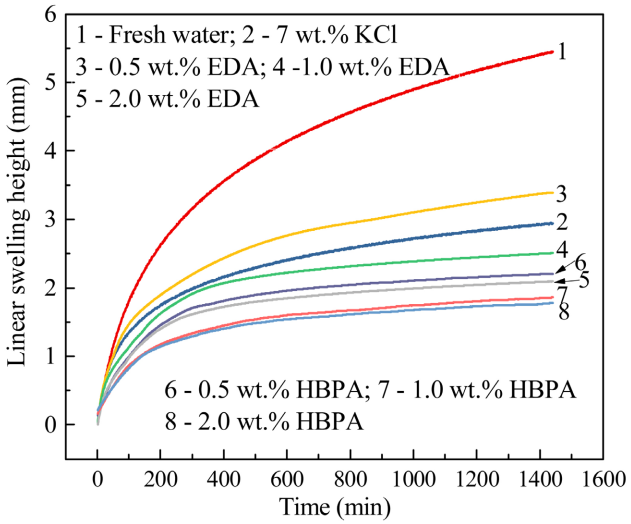


Figure 4. Linear swelling lengths of bentonite pellets in various inhibitor systems.

Ultimately, the excellent performance of the HBPA to prevent shale hydration swelling owes a great deal to the inherent characteristics [20] [21] [22] [23]: 1) the relatively more amine groups can evenly adsorb on the clay to render the clay surface more hydrophobic and promote the release of interlayer water. 2) Hyperbranched polymer, as a kind of quasi-spherical shape polymer with dominated branched structure, can introduce numerous absorbing groups at the end of the molecular chains by the functionalization and modification of end-groups.

3.2.3. Rolling Recovery Tests

According to the test standards released by ISO 10416: 2008 Petroleum and Natural Gas Industries Industries Drilling Fluids Laboratory Testing, shale recovery is the most used approach for further evaluating the inhibiting perfor-

mance of bentonite [24] [25]. By comparison of the results in **Table 1** and **Figure 5**, it can be clearly seen that the shale recovery rate is extremely low in fresh water at various hot-rolling temperatures, declining from 49.68% for 80˚C to 34.68% for 120˚C, 29.50% for 160˚C and 27.31% for 180˚C, respectively, exemplifying the hydration tendency of shale cuttings [26]. Compared to those under freshwater, the shale recovery rates which are treated by inhibitors are all satisfactory under the lower temperature of 80˚C. The recovery rates are with respect to the order of 7 wt.% KCl < 5 wt.% KCl < 0.5 wt.% EDA < 1 wt.% EDA < 2 wt.% EDA < 0.5 wt.% HBPA < 1 wt.% HBPA < 2 wt.% HBPA. At elevated temperatures, maintaining the integrity of shale becomes more difficult. The swelling and hydration of shale are strongly accelerated, and the adsorption of inhibitors on the clay surface, on the other hand, will weaken. These defects could cause rock fragments to separate from the wellbore wall during the drilling [27]. From **Figure 5** and **Table 1**, although the recovery rates for all inhibitors decline as

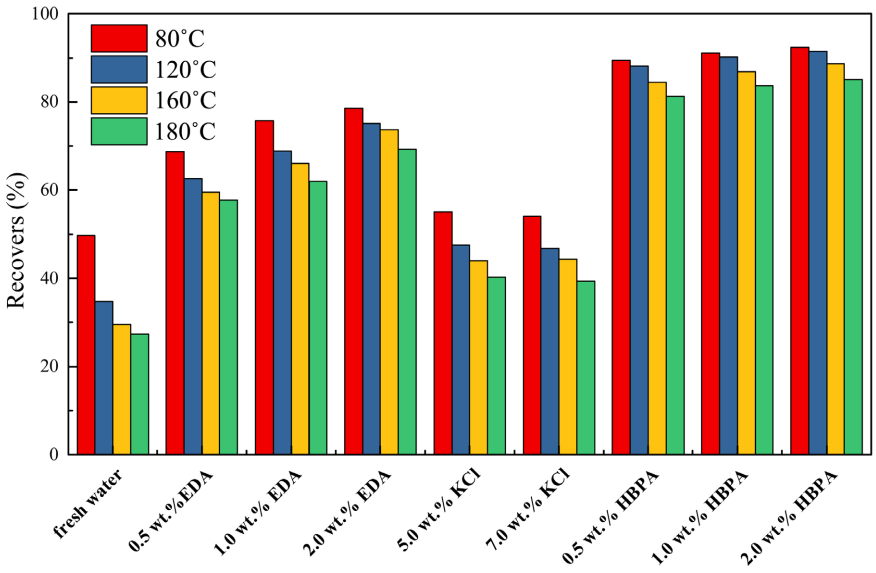


Figure 5. Shale recovery ratios of various inhibitors after hot rolling at different temperatures for 16 h.

Table 1. Shale cuttings recoveries of different inhibitor systems at different rolling temperatures.

Temperature	Inhibitors								
	Fresh Water	EDA			KCl		HBPA		
		0.5 wt.%	1.0 wt.%	2.0 wt.%	5.0 wt.%	7.0 wt.%	0.5 wt.%	1.0 wt.%	2.0 wt.%
80˚C	49.68%	68.66%	75.80%	78.60%	55.00%	54.00%	89.41%	91.13%	92.26%
120˚C	34.68%	62.56%	68.86%	75.06%	47.50%	46.72%	88.10%	90.21%	91.48%
160˚C	29.50%	59.50%	66.00%	73.66%	43.90%	44.30%	84.52%	86.90%	88.61%
180˚C	27.31%	57.72%	62.04%	69.32%	40.20%	39.32%	81.30%	83.71%	85.12%

*Rolling time: 16 h.

temperature rises, among which the 2 wt.% HBPA shows the smallest drop, only 0.8% for 120˚C and 3.9% for 160˚C. Besides, According to the data under a high temperature of 180˚C, the HBPA system remains ahead of its rivals in shale recovery with a satisfactory value of 85.12%, further confirming the excellent inhibitive and heat-resistance [28]. The above mentioned together could elucidate the prepared HBPA could effectively inhibit shale dispersion during drilling.

3.3. Mechanism Analysis

Zeta Potential Test

Electrokinetic properties of clay were performed to reveal the interactions between HBPA and clay particles, and the zeta potential pattern was displayed in **Figure 6**, with EDA and KCl inhibitor as reference. Commonly, the bentonite particle is a negative charge surface due to isomorphic replacements of ions in layers [29] [30]. The highly negative zeta potential of clay particles represents the enhanced shale hydration swelling and dispersion. As shown in **Figure 6**, the zeta potential value of sodium bentonite-based slurry is about −34 mV, implying higher discursiveness [31] [32]. Due to the diffuse electric double layer suppression by metal ions, that value decreases with the addition of KCl. As the concentration reaches 1.5 wt.%, the HBPA system experiences the greatest rise from −34 mV to −12.8 mV, about 21.2 mV, then a plateau is reached and no charge reversal appears during the whole concentration range, indicating that the adsorption of HBPA onto the clay surface reached saturation. Though the changing trend of the EDA is similar to HBPA, the latter can increase the zeta potential more positively than EDA.

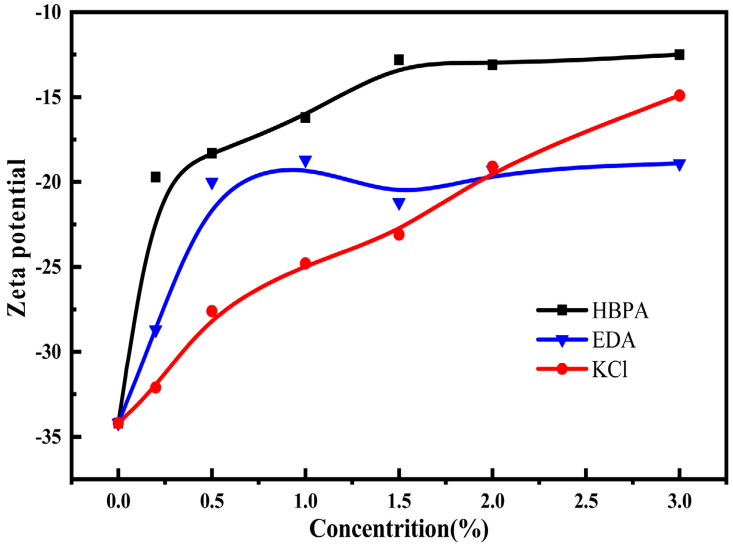


Figure 6. Zeta potential variation of different inhibitors with concentrations.

Amine group would be protonated when dissolved in an aqueous solution [33], The protonated ammonium ions neutralized the negatively charged clay surface and resulted in the increase of zeta potential. Besides, attributing to the

alkalescent property of the amine, no charge reversal was observed throughout the testing stage. Benefiting from this hyperbranched polymer with a higher ratio of amine groups, the HBPA increased the zeta potential to a higher degree than EDA and KCL, indicating the excellent performance to prevent shale hydration swelling and dispersion.

4. Conclusion

Hyperbranched polyamine (HBPA) inhibitor with a higher ratio of amine groups and obvious tendentiousness in protonation used as an effective shale inhibitor in water-based drilling fluids has been developed, and a kind of MOFs was chosen as ring-open polycondensation catalyst for this process. Compared with the traditional inhibitors, the HBPA inhibitor shows significantly inhibitive properties which can meet the demands of controlling and mitigating the shale hydrating and dispersing. In bentonite inhibition evaluation, the swelling of clay is inhibited by HBPA to maximum, and the same is true at up to 180˚C conditions. The HBPA also exhibits the lowest linear swelling lengths of 1.78 mm. Meanwhile, the shale recovery rates of HBPA for 16 h reach 92.26%, 91.48%, 88.61% and 85.12% for 80˚C, 120˚C, 160˚C and 180˚C, respectively. Further, the validity of test results was verified by analyzing the inhibiting mechanism. In a conclusion, the prepared HBPA can effectively reduce shale hydration and dispersion and apply to high-temperature wells application.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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