

Preparation and performance evaluation of small molecule ammonium salt inhibitors synthesized from mixed amines

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Abstract. This paper focuses on the synthesis of polyhydroxy small molecule amines using mixed amines as raw materials. The anti-swelling experiment, swelling shrinkage experiment, linear swelling rate and clay hydration experiments were used to evaluate the application effect of the synthesized products in oilfield water-based drilling fluids. and suitable inhibitors were selected. The inhibition mechanism was investigated by TGA, laser particle size analysis and SEM. The inhibition of clay hydration swelling was best at a concentration of 0.1% with a 1:3 mass ratio of mixed amines to phosphoric acid, i.e., the product HS-1. The results of anti-swelling, swelling shrinkage and linear expansion experiments showed that the anti-swelling rate of 0.1% HS-1 on clay was 72.97%, the swelling shrinkage rate was 54.50% and the linear expansion rate was 27.30%, which was similar to the effectiveness of 4.0% KCl. It showed good inhibition of hydration swelling dispersion of clay.

Keywords: Small molecule ammonium salt; Drilling fluids; Clay; Mixed amines.

1. Introduction

The mud shale inhibitors that are currently used in the oil and gas drilling process include: inorganic salts, bitumen, polymeric alcohols and so on. [1] They have played their respective roles in solving the well wall destabilization problems caused by mud shale hydration and swelling and dispersion in various oil fields around the world. However, the above-mentioned mud shale inhibitors still reveal some shortcomings or limitations in the process of use. For example, the massive use of inorganic salts inhibitors can cause environmental pollution in oil fields, and although potassium ions are effective in inhibiting shale swelling, they can cause environmental pollution and affect the quality of crude oil due to the high concentration.[2] The rheology of drilling fluids system become difficult to regulate after adding silicate type inhibitors, asphalt type inhibitors are not conducive to protecting the oil field environment and affect the quality of crude oil. Polyethylene glycols have limitations on the drilling problems of reactive mud shale. In contrast, small molecule amine inhibitors show good inhibition of clay. The introduction of amine functional groups in the molecular chain of amine shale inhibitors. Due to the unique adsorption of amine groups, inhibitor small molecules can be well set between the clay layers, reducing the clay layer spacing, clay layers are closely bound together, water molecules are more difficult to enter between the clay layers, reducing the tendency of clay swelling with water.[3] Therefore, it can effectively solve the problems of well wall collapse, drill bit mud pack and borehole purification caused by the hydrated swelling and dispersion of mud shale when encountering mud shale formation in the oil field. A large number of studies have been reported. [4-10] In recent years, a series of high-performance water-based drilling fluids, represented by small-molecule polyamines, have been developed as a new type of water-based drilling fluid that can replace oil-based drilling fluids. The type, dosage and application range of amine inhibitors have been better developed by continuously improving the inhibitory and environmental friendliness of amine inhibitors. [11] Low-molecular cationized amines have obvious advantages over monovalent cationic amines and polymeric quaternary amines due to their strong inhibitory properties, low biotoxicity, and good compatibility with other treatment agents. So it was expected to have effectiveness and economic benefits in subsequent oil and gas extraction.[12,13] In this research, small-molecule

ammonium salts were synthesized from industrial by-products of organic mixed amines and common acids with different raw material ratios, and the synthesized inhibitor products with excellent performance were screened by anti-swelling and swelling shrinkage experiments and linear expansion rate determination, and the changes in particle size and morphology were analyzed from microstructure by TGA, laser particle size and SEM to explore the industrial processing and application of the synthesized heteroammonium salt inhibitors.

2. Materials and methods

2.1 Materials

Calcium-based bentonite and sodium-based bentonite were purchased from Xi'an Fengyun Chemical Co. Ltd. Acids were purchased from Tianjin Shengao Chemical Reagent Co. Ltd. Mixed amines was purchased from Xi'an Yongjiu Chemical Co. Ltd. CMC and KD-03 were purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd.

2.2 Inhibitory evaluation

The hydrated expansion of bentonite was determined using a shale expander (NP01, Chuangmeng Ltd, Qingdao) according to the Chinese Petroleum and Natural Gas Industry Standards SY/T59711994 and SY/T63351997. [14]

2.3 Laser particle size measurement

The dried modified graphite sample was used to measure the particle size using laser particle size experiment, so as to obtain the median particle size and average particle size of bentonite particles in different drilling fluid treated with treatment agent. The change of bentonite particle size was analyzed according to these data. [15]

2.4 TGA and SEM

Bentonite was dispersed in different solutions for 24 h. Bentonite was separated and dried at 378 K for TGA and SEM. TGA was performed with a TGA/DSC1/1600 thermal analysis machine (Mettler Toledo Inc., Switzerland). The surface morphology of samples was investigated using a digital imaging scanning electron microscope (model SU6600, serialno. HI-2102-0003, Hitachi).[16]

3. Results and discussion

3.1 Determination of anti-swelling rate and swelling shrinkage rate

Centrifugal method was used to measure the anti-swelling rate of the synthesized products with concentration of 0.1% and material ratio of 1:3, 2:3 and 3:3. The results are shown in Table 1. It can be seen from the table that the anti-swelling rate of the synthesized products to clay is different when the ratio of different materials is used. When the mass ratio of mixed amines to common acid is 1:3, the synthesized products can inhibit the hydration and dispersion of clay. The anti-swelling rate of HF-1, HC-1 and HS-1 is 68.09%, 72.50% and 72.97%, respectively, and the anti-swelling rate of 4.0%KCl is 73.94%. The reaction product of mixed amines and concentrated sulfuric acid at the mass ratio of 1:3, namely HS-1, has the best anti-swelling effect on clay among all synthesized products.

HS-1 proof of good effect is the cause of neutral after reaction with acid mixed amine to produce the ammonium salt raised the water-soluble. Hydration of ammonium salt in the solution by ion exchange, and the roles of electrostatic and hydrogen bonding adsorption on clay surface, and organic amine molecules of hydrophobic protective layer is formed on the alkyl, slowed the osmosis water molecules to the inside clay. It showed good inhibition performance. Based on the above experimental results and analysis, the subsequent experiments were carried out by selecting the hybrid acid product synthesized by the mass ratio of 1:3 between mixed amines and common acid.

Table 1. Anti-swelling rate of synthesized inhibitors

Amines	Acid	Name	Anti-swelling rate %	Amines	Acid	Name	Anti-swelling rate %
Mixed amines	Phosphoric acid	HP-1	72.50	Mixed amines	Citric acid	HC-1	64.58
		HP-2	50.00			HC-2	48.57
		HP-3	34.09			HC-3	51.43
		HY-1	36.36			HM-1	65.96
	Hydrochloric acid	HY-2	47.62		Malic acid	HM-2	61.70
		HY-3	52.38			HM-3	43.18
		HB-1	70.41		Sulfuric acid	HS-1	72.97
	Benzoic acid	HB-2	77.50			HS-2	44.90
		HB-3	72.50			HS-3	30.61
	Formic acid	HF-1	68.09		Salicylic acid	HA-1	16.67
		HF-2	34.78			HA-2	50.00
		HF-3	28.26			HA-3	36.37
	Oxalic acid	HO-1	32.61		Tartaric acid	HT-1	52.38
		HO-2	20.51			HT-2	12.50
		HO-3	44.58			HT-3	20.83

Centrifugal method was used to evaluate the swelling shrinkage performance of clay by adding 0.1% hetero-ammonium salt. As shown in Figure 1, most hetero-ammonium salt had obvious swelling shrinkage effect on clay, and only HB-1 and HA-1 showed no effect on clay shrinkage. When 0.1% HY-1, HM-1 and HS-1 were added, the contraction rate was 36.36%, 43.18% and 54.29%, respectively. When 4.0%KCl was added, the swelling shrinkage rate was 41.46%. The swelling shrinkage rate of 0.1%HS-1 was 1.31 times higher than that of 4.0%KCl. That is the hybrid ammonium salt product obtained from the reaction of mixed amines and concentrated sulfuric acid at the mass ratio of 1:3 has the best effect on the swelling shrinkage of clay after hydration and dispersion. The anti-swelling rate of 0.1% HS-1 is 73.97%. The anti-swelling effect of clay is the best. The results of the swelling shrinkage experiment are consistent with those of the anti-swelling experiment.

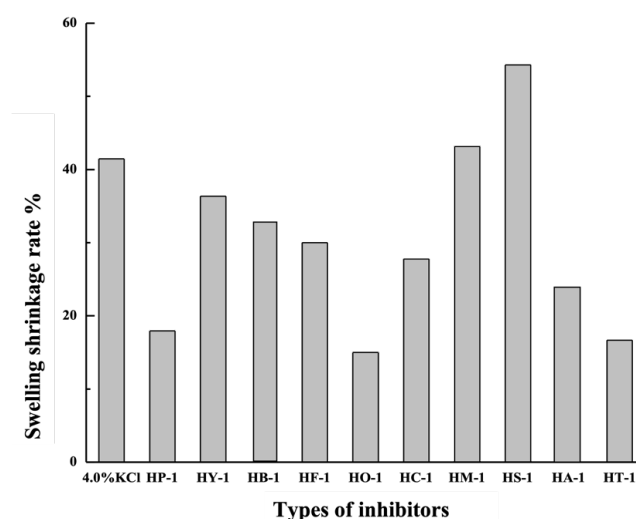


Fig. 1 Influence of products on swelling shrinkage rate of clay

HS-1 was mixed into solutions with different concentrations to investigate the effects of HS-1 concentration on the anti-swelling and swelling shrinkage of clay. The results are shown in Figure 2.

HS-1 concentration has a significant impact on the anti-swelling and swelling shrinkage of clay. When HS-1 concentration increased from 0.1%, the anti-swelling rate first decreased, but the overall change was little. When HS-1 concentration was 0.5%, the anti-inflation rate was the lowest, which was 68.60%. When the concentration increases to 1.0%, the anti-swelling rate increases to 72.50%, and HS-1 has strong anti-swelling effect on clay. When the concentration increased from 0.1%, the swelling shrinkage rate showed a trend of continuous increase, and when the concentration was 1.0%, the swelling shrinkage rate increased to 54.50%

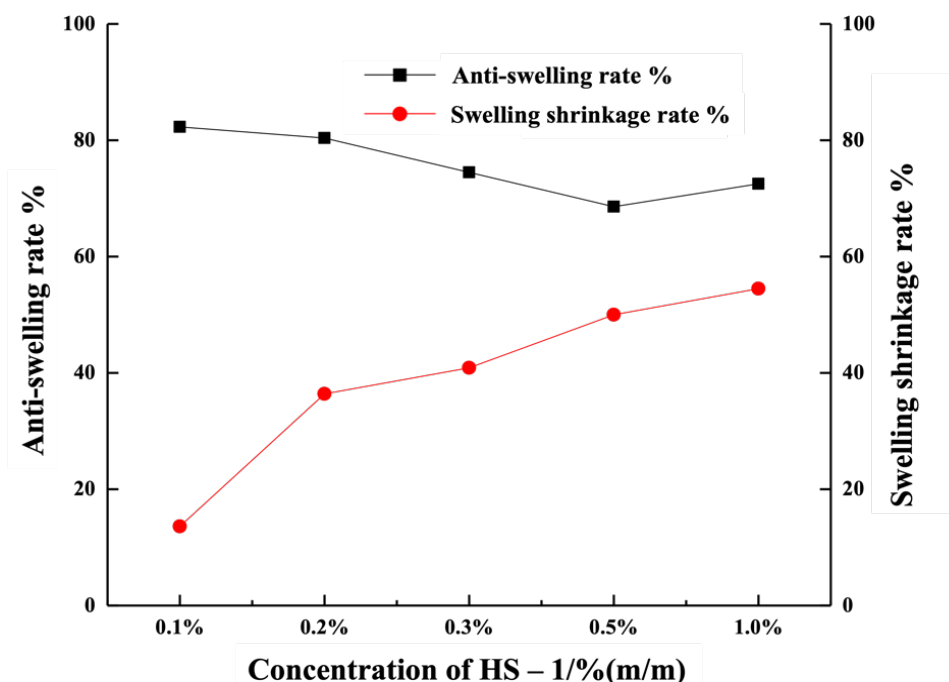


Fig. 2 Influence of HS-1 concentration on anti-swelling ratio/swelling shrinkage ratio of clay

3.2 Linear expansion experiment

In order to continue to investigate the inhibitory effect of heteroammonium salts on clay, the effect of the reaction products of mixed amines at a concentration of 0.1% with different kinds of acids (1:3 by mass) on the linear swelling rate of clay within 120 min was investigated, and the results are shown in Figure 3. As can be seen from the figure, most of the products had a significant inhibitory effect on clay within 120 min, and the clay swelled rapidly within 20 min, and the swelling rate increased after 120 min, the linear expansion rate of clay in the clear water line was 45.84%. The linear expansion rate of clay in 4.0% KCl solution was 39.42%. The inhibitory effect of HO-1 and HS-1 on clay hydration swelling and dispersion was stronger than that of other inhibitors and 4.0% KCl, and the linear expansion rate was smaller, 28.23% and 27.30%. Respectively, which were 69.25% and 71.61% of the linear expansion rate of 4.0% KCl, which indicated that HO-1 and HS-1 had better inhibitory performance on the hydration swelling and dispersion of clay. HS-1 had the smallest linear swelling rate within 120 min, indicating that HS-1 had the the reason that the ammonium salts were adsorbed on the clay surface by ion exchange, electrostatic and hydrogen bonding, while the alkyl groups on the small molecule amine molecules formed a hydrophobic protective layer, which retarded the penetration of water molecules into the clay and showed good inhibition performance. In practice, the synthesis product of mixed amines and concentrated sulfuric acid, namely HS-1, has good water solubility and stability, and the odor of the reaction product of amine and acid is lighter than that of the synthesized raw amine or acid.

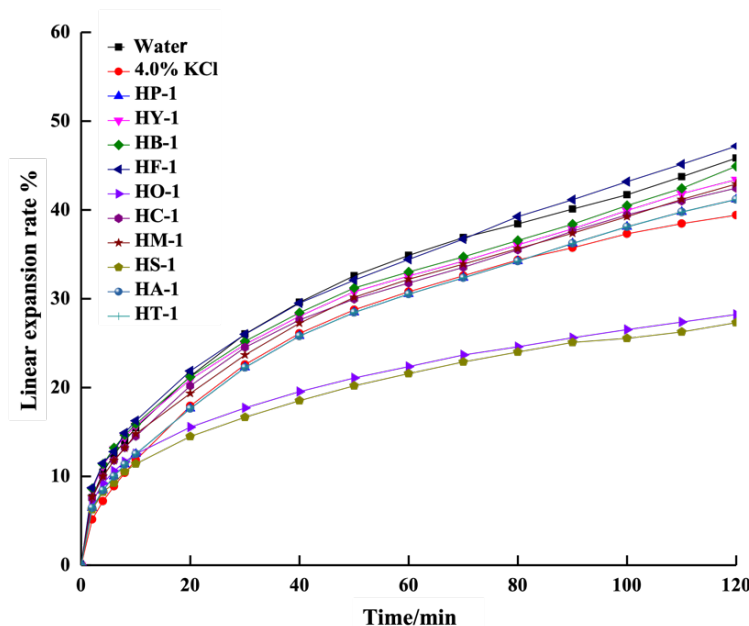


Fig. 3 Linear expansion rates of different inhibitors

3.3 Particle size measurement

The anti-swelling effect of ammonium salts on clay mainly inhibits the hydration dispersion of clay. Before the clay is hydrated, adding a certain amount of inhibitor can inhibit the disintegration of the clay sheet structure. Adding inhibitor to the already hydrated clay further inhibits the clay dispersion on the one hand, and wraps or binds the already hydrated and dispersed clay sheet on the other hand. It inhibits the disintegration of the clay particles and keeps the clay at a certain particle size. This experiment investigated the dispersion structure of bentonite before and after hydration of sodium-based bentonite by adding 0.1% HS-1. From Figure 4 and Table 3, it can be seen that the average particle size of unhydrated bentonite is $12.910\mu\text{m}$ and the median particle size is $17.410\mu\text{m}$, and the average particle size of fully hydrated bentonite in clear water is $4.800\mu\text{m}$ and the median particle size is $5.159\mu\text{m}$. After adding HS-1, the average particle size of unhydrated is reduced to 41.43% of the original average particle size, and the median particle size is reduced to 43.60% of the original median particle size. This indicates that the addition of the clay inhibitor HS-1 has a significant inhibitory effect on the hydration dispersion of both sodium-based bentonite.

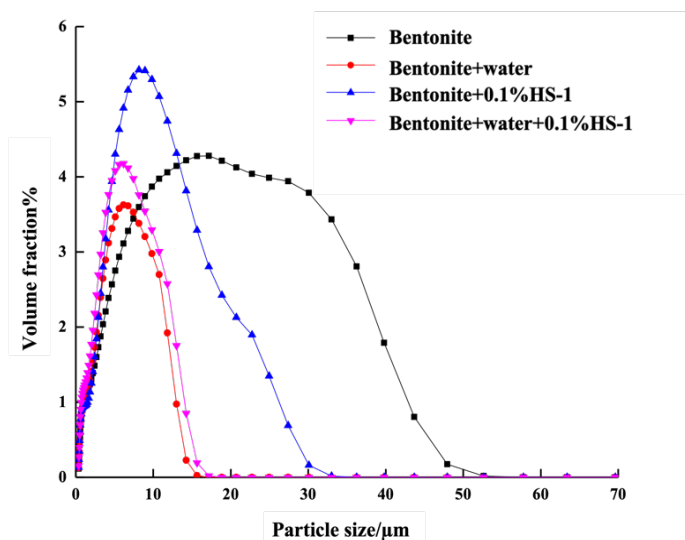


Fig. 4 Effect of HS-1 on the particle size distribution of bentonite

Table 3. Average particle size and median particle size of bentonite in HS-1 solution

Clay	Average particle size/ μm	Median particle size/ μm
Original bentonite	12.910	17.410
Bentonite + water	4.800	5.159
Bentonite +0.1%HS-1	7.561	9.819
Bentonite + water +0.1%HS-1	4.728	6.159

3.4 TGA measurement

Montmorillonite is the most easily hydrated clay mineral and is an important component of clay particles. The clay contains different forms of water: adsorbed water that is attached to the outer surface of the particles, interlayer water between layers, and hydroxyl water that is bonded to aluminum ions within the cell is called hydroxyl water. As the temperature increases, the adsorbed water, interlayer water and hydroxyl water are removed in turn. Therefore, TGA can be used to determine the weight loss rate of clay samples with different inhibitors to evaluate the effect of inhibitors to inhibit the hydration swelling and dispersion of clay. It can be seen from the figure 5 that as the temperature gradually increased, the interlayer water began to evaporate and the weight of clay particles began to decrease. When the temperature was increased from 50°C to 300°C, the weight loss rate of the treated clay in water was 4.10%, and the weight loss rate of the treated clay in HS-1 solution was 2.60%. The weight loss rate of the samples immersed in HS-1 solution was significantly smaller than that of the samples immersed in clear water, which indicated that HS-1 could more obviously prevent the penetration of water molecules into the shale and showed a significant inhibitory effect on the hydration swelling and dispersion of the clay.

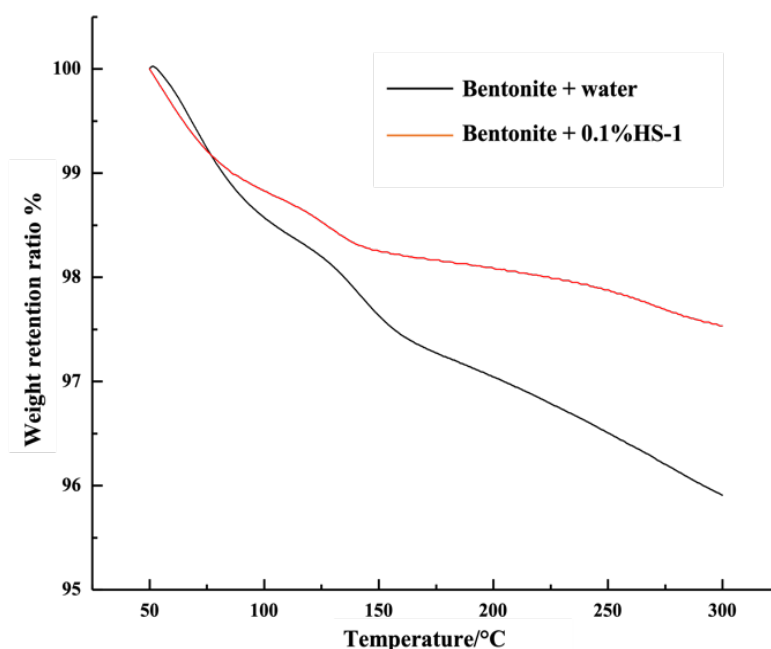


Fig. 5 TG curve of bentonite after adding different treatment agents

3.5 SEM experiment

SEM was used to analyze the microscopic morphology of bentonite particles dried by 0.1% HS-1 and water treatment to investigate the effect of HS-1 on the microstructure of clay, and the results are shown in Figure 6. Comparing the three photos, it can be seen that the addition of 0.1% HS-1 resulted in dense bentonite particles, indicating that 0.1% HS-1 had a significant inhibitory effect on the clay on a macroscopic level.

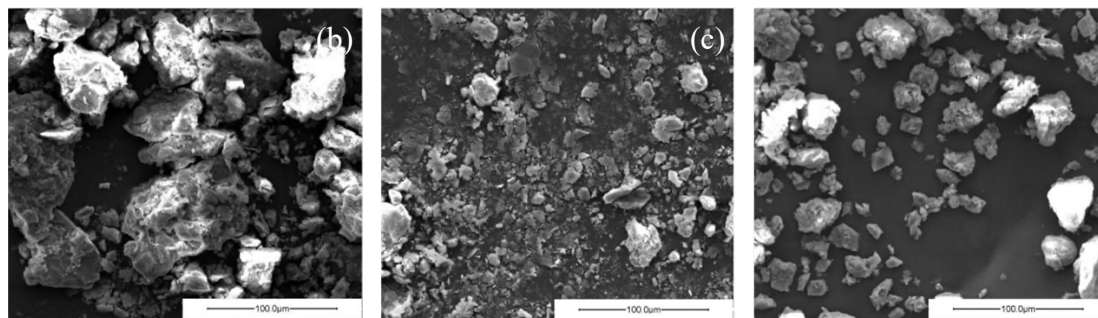


Fig. 6 SEM of Bentonite under different treatment conditions ((a) Bentonite; (b) Bentonite +0.1%HS-1; (c) Bentonite +water)

4. Conclusions

Mixed amines react with sulfuric acid at a mass ratio of 1:3 to form heteroammonium salt, namely HS-1, which has good inhibition performance on the hydration and swelling dispersion of clay. The experiments of anti-swelling rate and swelling shrinkage rate showed that when the concentration of HS-1 was 0.1%, the anti-swelling rate was 72.97% and the shrinkage rate was 54.50%; the experiments of linear expansion showed that the linear expansion rate of 0.1% HS-1 on clay was 27.30%, which was similar to 4.0% KCl. By laser particle size analysis and TGA experiments show that after the addition of 0.1% HS-1 in the hydrated bentonite, bentonite particle size significantly smaller. When the temperature increases from 50°C to 300°C, the bentonite weight loss rate of 4.10% after treatment in water, 0.1% HS-1 solution in the bentonite weight loss rate of 2.60%, indicating that the addition of 0.1% HS-1 can effectively slow down the weight loss rate of the clay and prevent the penetration of water molecules into the shale.

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