Investigation of melamine derived quaternary as ammonium salt potential shale inhibitor

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Abstract. Melamine, sodium chloroacetate and sodium hydroxide were used as raw materials to synthesize a kind of neutral quaternary ammonium salt (NQAS) as potential clay swelling inhibitor and water-based drilling fluid additive, and the reaction conditions were screened based on the linear expansion rate of bentonite. The inhibitive properties of NQASs were investigated by various methods, including montmorillonite (MMT) linear expansion test, mud ball immersing test, particle distribution measurement, thermogravimetric analysis and scanning electron microscopy etc. The results indicate that NQAS can inhibit expansion and dispersion of clay in water effectively. At the same condition, the bentonite linear expansion rate in NQAS-6 solution is much lower than those of others, and the hydration expansion degree of the mud ball in 0.5% NQAS-6 solution is appreciably weaker than the control test. The compatibility test indicates NQAS-6 could be compatible with the conventional additives in water-based drilling fluids, and the temperature resistance of modified starch was improved effectively. Meanwhile, the inhibitive mechanism was discussed through the particle distribution measurement.

1. Introduction

Montmorillonite (MMT) is a 2:1 clay, which has two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometer. Bentonite, mainly containing montmorillonite, is used in the oil drilling industry as a basic component of drilling fluid, making the drilling fluid viscous, which helps in keeping the drill bit cool and removing drilled solids[1]. However, when water-sensitive clays are exposed to the conventional water-based drilling fluids, depending on the chemical characteristics of the shale, shale has an immediate tendency to take up water from the water-based oilfield working fluid [2-3]. On the other hand, during the drilling of oilfield, great quantities of water-based mud are used, in this process, borehole stability problems such as bit balling, disintegration of cuttings, borehole wash-out and stuck pipe mostly occur in shale formations.
due to shale hydration and swelling [4]. In recent years, organic amine compounds with high performance shale inhibitor draw much attention of the researchers. This system has obtained wide application around the world with great success because of excellent inhibition, lubrication and stable rheological property and so on [5-6]. As the key additive, quaternary ammonium salt has higher inhibitory and anti-balling abilities, and it is not poisonous and non-hazardous, the use of this drilling fluid could eliminate cost of oil contaminated drilled cuttings disposal [7-8]. Currently, quaternary ammonium compound can be used in various kinds of water-based oilfield working fluid and has superior compatibility with traditional additives, and it can meet environmental protection requirements [9]. This paper developed a series of quaternary ammonium inhibitor with good comprehensive performance, and its performances were evaluated through linear expansion, mud balls, particle distribution measurement, thermogravimetric analysis and scanning electron microscopy.

2. Experimental

Materials. Melamine, sodium chloroacetate and sodium hydroxide were provided by Sinopharm Chemical Reagent Co., Ltd., Potassium chloride and sodium carbonate were purchased from Zhiyuan Chemical Reagent Factory in Tianjin. Bentonite was obtained from Changqing bentonite Group Co., Ltd., China.

Synthesis. A series of neutral quaternary ammonium salts (NQASs) was synthesized using melamine, sodium chloroacetate and sodium hydroxide as raw materials. A certain amount of melamine and sodium chloroacetate was dissolved in water with different ratio, refluxing for a certain time. After reaction, the product was added sodium hydroxide to adjust pH to 7.

Swelling Inhibition and Mud Ball Immersing Test. The hydration swelling of shale is tested by a NP-01 shale expansion instrument according to petroleum and natural gas industry standard SY/T6335-1997 of China.

Bentonite Inhibition Test and Compatibility Test. [10] The apparent viscosity, plastic viscosity and yield point were calculated from 300 and 600 rpm readings using following formulas from API Recommended Practice of Standard procedure for field testing drilling fluids (Recommended Practice, 1988):

Particle Distribution Test. 4 m/m% bentonite dispersion was prepared and prehydrated for 24 h. Inhibitors with certain concentrations were added into the dispersion and stirred for 20min, after aged for 24 h, and then the size distribution of the particles was measured by LS-13 320 laser particle size analyzer (Beckman Coulter, Inc., USA) using standard operating procedure.

3. Results and Discussion

Inhibitor Synthesis. In the reaction of inhibitor synthesis, melamine with three sp² hybridized N atoms and three sp³ hybridized N atoms, can react with sodium chloroacetate in two ways. One is sp² hybridized N atoms reacting with sodium chloroacetate, and the other is sp³ hybridized N atoms’ reaction. In fact, there is a natural selection due to the different kinds of N atoms. The sp² hybridized N atom with a pair of unconjugated free electrons can react with sodium chloroacetate in priority. Since there are three sp² hybridized N atoms, the products of NQAS may be various, as shown in Fig. 1. But with the similar structure, it is hard to separate each compound.
**Swelling Inhibition.** In order to investigate the influence of quaternary ammonium salts as swelling inhibitor for clay, the swelling rate of bentonite in different NQAS solution were evaluated by bentonite linear expansion test. As shown in Table 1, the effect of molar ratio of melamine and sodium chloroacetate on the products’ inhibition was investigated as first. The result shows that the linear expansion rate of montmorillonite in NQAS-6 solution is much lower than others within 90 min. So NQAS-6 was studied in detail.

**Table 1** Name and inhibitory activity of neutral quaternary ammonium salts.

| Material | Ratio | Nomenclature | Linear expansion Rate /% |
|----------|-------|--------------|--------------------------|
| Melamine | 1:1   | NQAS-1       | 65.54                    |
|          | 1:2   | NQAS-2       | 65.24                    |
|          | 1:3   | NQAS-3       | 65.59                    |
|          | 1:4   | NQAS-4       | 59.57                    |
|          | 1:5   | NQAS-5       | 61.53                    |
|          | 1:6   | NQAS-6       | 55.57                    |
|          | 1:7   | NQAS-7       | 60.38                    |

| Sodium chloroacetate | 1:1 | NQAS-1 | 65.54 |
|                      | 1:2 | NQAS-2 | 65.24 |
|                      | 1:3 | NQAS-3 | 65.59 |
|                      | 1:4 | NQAS-4 | 59.57 |
|                      | 1:5 | NQAS-5 | 61.53 |
|                      | 1:6 | NQAS-6 | 55.57 |
|                      | 1:7 | NQAS-7 | 60.38 |

As shown in Fig 2, the swelling rates of bentonite with time in different concentration of NQAS-6 solutions were recorded. It shows that the clay swelling rate increases dramatically at the initial 10 min, followed by slow increase. Compared with blank, the swelling rate in 0.5% NQAS-6 solution is much lower than 0.1% NQAS-6 solution with the rate of 55.57% and 61.87% respectively within 90 min, indicating that 0.5% NQAS-6 can restrain the water affinity of the MMT effectively and 0.5% should be an economical concentration.

**Mud Ball Immersing Test.** The mud ball immersing test provides a more intuitive way to describe the inhibitive property of NQAS. The mud balls were immersed into water and 0.5% NQAS-6 solution respectively. Fig 3 shows the status of the mud balls after immersed for 36 hours. The mud ball immersed
in water swelled obviously, and surface loose, while the mud ball immersed in 0.5% NQAS-6 solution swelled slightly and the surface is smoother. It is clear that NQAS-6 has significant clay swelling inhibition. These phenomena can be explained by the hydrophobic film resulting from neutral absorption of quaternary ammonium compounds on MMT, which blocks the water penetrating into the clay and prevents clay from hydrating swelling.

**Fig. 3** The status of mud balls immersed in water (left) and 0.5% NQAS-12 solution (right) for 36 h.

*Bentonite Inhibition Test.* The test was projected to simulate the relatively slow incorporation of yielding clays into a drilling fluid. This simulated process usually happens when drilling active clays in the field. As shown in Fig 4, with the amount of bentonite concentration increasing, yield point of drilling fluid keeps increasing. And yield point increased sharply with the addition of bentonite in fresh water system due to the hydration and dispersion of MMT. Comparing to blank, the lower rheological profile of 0.5% NQAS-6 proves that it performs good inhibitive capacity.

![Graph](image)

**Fig. 4** The effect of Yield point of different shale inhibitors with the base fluid.

*Compatibility Test.* The results of the compatibility test were shown in Table 2. NQAS-6 had influence obviously on the inhibitive property, rheological properties and filtrate loss of the mud systems before and after adding the shale inhibitive additives, indicating that quaternary ammonium inhibitor can effectively restrain the bentonite slurry, but apparent viscosity, yield point, dynamic plastic ratio and API filtration of polymer drilling fluid with NQAS-6 were significantly increased at the room temperature, due to flocculation effect of organic amine, and NQAS-6 can effectively improve the temperature resistance of modified starch. Thus, quaternary ammonium salts could be compatible with the conventional additives in water-based drilling fluids.

**Table 2:** Compatibility of NQAS with common additives in drilling fluid.

| T/°C | Additives         | AV/mPa·s | PV/mPa·s | YP/Pa | YP/PV | FLAPI/mL | μ  |
|------|-------------------|-----------|-----------|-------|-------|----------|----|
| 25   | Blank             | 3.5       | 2.8       | 0.7   | 0.3   | 13.3     | 0.0875 |
|      | 0.5% NQAS-6      | 5.5       | 2.0       | 3.5   | 1.7   | 19.8     | 0.1317 |
|      | 1.0% Modified starch | 6.0       | 4.0       | 2.0   | 0.5   | 7.5      | 0.0699 |
1.0% Modified starch +0.5% NQAS-6
Blank
0.5% NQAS-6
120 1.0%Modified starch
1.0% Modified starch +0.5% NQAS-6

Particle Size Distribution Test. Fig 5 depicts the particle size distribution of the bentonite dispersions treated with different ways. Compared to control sample, the average size of hydrated bentonite particles was much smaller, and the addition of NQAS-6 can only influence the particle size slightly, as shown in Table 3. But it should be noticed that it is different when NQAS-6 was added before and after the hydration of bentonite. When NQAS-6 was added with virgin bentonite into water together, the dissolved NQAS-6 can inhibit the swelling and disperse of bentonite in the way discussed above. When 0.5% NQAS-6 was added in the hydrated bentonite mud, the particle size hardly changed.

![Particle Size Distribution](image)

**Fig. 5** Effect of 0.5% NQAS-6 on particle size distribution of bentonite.

**Table 3** Mean and median of bentonite particle dealt with different ways.

| Additives                      | Mean/μm | Median/μm |
|-------------------------------|---------|-----------|
| Virgin bentonite              | 33.26   | 26.65     |
| Hydrated bentonite            | 10.97   | 6.11      |
| Virgin bentonite+0.5% NQAS-6  | 18.17   | 10.16     |
| Hydrated bentonite+0.5% NQAS-6| 34.82   | 7.33      |

4. Summary
In this work, neutral quaternary ammonium salts (NQASs) were synthesized with melamine, sodium chloroacetate and sodium hydroxide for the use of clay swelling inhibitor. The inhibitive properties were evaluated through bentonite linear expansion, mud balls immersing test, compatibility test, bentonite inhibition test, meanwhile, NQAS could be compatible with the conventional additives in water-based drilling fluids. The results showed that 0.5% NQAS-6 can inhibit the bentonite linear expansion much effective than others. In addition, the particle distribution measurement proves the efficient inhibition of NQAS-6.

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References

[1] K. H. Lv, H. Y. Zhong, G. L. Ren and Y. X. Liu, Poly(oxypropylene)-amidoamine Modified Bentonite as Potential Shale Inhibitor, J. Open Petrol. Eng., 7, 51 (2014).

[2] A. D. Patel and M. I. Swaco, Design and Development of Quaternary Amine Compounds: Shale Inhibition with Improved Environmental Profile, SPE International Symposium on Oilfield Chemistry, p. 20 (2009).

[3] R. P. Steiger and P. K. Leung, Qualitative Determination of the Mechanical Properties of Shales, SPE Drilling Engineering, p. 181 (1992).

[4] R. H. Retz, J. Friedheim, L. J. Lee and O. O. Welch, An Environmentally Acceptable and Field-practical Cationic Polymer Mud System, SPE Prepared for Presentation at the Offshore Europe Conference, p. 4 (1991).

[5] N. G. Doonechaly, K. Tahmasbi and E. Davani. Development of High-performance Water-based Mud Formulation Based on Amine Derivatives, SPE Presented at International Symposium on Oilfield Chemistry, p. 21 (2009).

[6] Y. Z. Qu, X. Q. Lai, L. F. Zou and Y. N. Su, Polyoxyalkyleneamine as Shale Inhibitor in Water-based Drilling Fluids, Appl. Clay Sci., 44, 265 (2009).

[7] J. H. Wang, J. N. Yan and T. W. Ding, Progresses in the Researches on High Performance Bater base Muds, Drill. Fluid & Complet. Fluid, 1, 1 (2007).

[8] K. Q. Zhang, L. He and S. F. An, An Introduction to the High Performance Water Base Muds Abroad, Drill. Fluid & Complet. Fluid, 3, 1 (2007).

[9] M. Amanullah, Screening and Evaluation of some Environment-friendly Mud Additives to Use in Water-based Drilling Muds, SPE E&P Environmental and Safety Conference, p. 6 (2007).

[10] H. Y. Zhong, Z. S. Qiu and W. A. Huang, Bis(hexamethylene)triamine as Potential Shale Inhibitor in Water-based Drilling Fluid, J. Petrol. Eng., 6, 55 (2013).

[11] Y. F. Xi, Z. Ding and R. L. Frost, Structure of Organoclays—an X-ray Diffraction and Thermoravimetric Analysis Study, J. Colloid Interf. Sci., 277, 119 (2004).

[12] Y. F. Xi, Q. Zhou, R. L. Frost and H. P. He, Thermal Stability of Octadecyltrimethyl- ammonium Bromide Modified Montmorillonite Organoclay, J. Colloid Interf. Sci., 311, 351 (2007).

[13] H. Y. Zhong, Z. S. Qiu, W. A. Huang and J. Cao, Poly(oxypropylene)-amidoamine Modified Bentonite as Potential Shale Inhibitor in Water-based Drilling Fluids, Appl. Clay Sci., 67, 40 (2012).