Preparation and performance of amine-tartaric salt as potential clay swelling inhibitor

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Abstract: A series of small molecular clay swelling inhibitor was prepared with tartaric acid and amines, presented as amine-tartaric salts (ATS). The inhibitor was screened based on the linear expansion rate of bentonite. The results show that the inhibitor prepared with tartaric acid and triethylenetetramine with the mole ratio of 1:1 (named as ATS-4) is the best inhibitor of the hydration expansion and dispersion of bentonite. The inhibitive properties of ATS-4 were evaluated by various methods, including clay linear swelling tests, anti-swelling tests, mud ball immersing tests, mud-making inhibition experiments and particle distribution measurements etc. The results show that ATS-4 has superior performance to inhibit the hydration swelling and dispersion of clays by controlling the particle size of clay. On the other hand, the bentonite linear expansion rate in 0.5% ATS-4 aqueous solution is much lower than that of others, and the hydration expansion degree of the mud ball in ATS-4 aqueous solution is appreciably weaker than the control test, and it is compatible with the conventional additives in water-based drilling fluids. Then, the inhibition mechanism

of the amine-tartaric salt was well discussed based on thermogravimetric analysis (TGA), scanning electron microscope (SEM), X-ray diffraction analysis (XRD), single crystal X-ray diffraction and ion exchange tests.

Key words: amine-tartaric salt; hydration expansion; inhibitor; inhibition mechanism

1. Introduction

Shales are fine-grained sedimentary rocks that can be rich sources of petroleum and natural gas. In recent years the exploration of shale oil and gas are increasing dramatically. But there are many issues threatening the drilling process such as, in the drilling, the wellbore instability and formation damage resulting from rock strength reduction, hydration expansion and dispersion of formation clay (Stamatakis et al, 1995; Retz et al, 1991). Generally, the main way to inhibit hydration expansion of shale includes the following aspects: the inhibitors can be adsorbed on clay surface through electrostatic interaction and forms a hydrophobic surface on the shale particle, thereby inhibiting the penetration of water into the interlayers (Steiger and Leung, 1992; Wang et al, 2009). And the coupling force between the clay particles and formation particles is increased through hydrogen bonds, anchoring effect etc., thus making the interlayer space impermeable for water molecules (Qiu et al., 2011; Slade et al., 2004). Consequently, a high level of shale inhibition can be achieved in drilling operations, using various additives among which KCl is very common (van Oort et al., 2003). But relatively high concentrations (up to 20 wt%) are necessary to minimize clay swelling, which is considered unfavorable to the receiving environment, limits their discharge (Patel et al, 2009). Recently, organic polymers used as clay expansion

inhibitor have been used widely, but polymers may be adsorbed on the surface of rock, reducing reservoir permeability or even blocking the formation (Jiang et al, 2016; Zhong et al, 2012). Moreover the high toxicity of cationic polymers limits their use (Ni et al, 2016; Zhong et al, 2015). In order to alleviate the problems, a series of low molecular weight ammonium salts exhibiting ideal inhibitive functions can make up for these imperfection. They are not poisonous and hazardous, and their use in drilling fluids could significantly reduce drilled cuttings disposal costs (Wang et al, 2007; Zhang et al, 2007). To seek more alternative inhibitors in this work, the properties of amine-carboxyl inhibitors are evaluated through experiments including linear expansion, mud balls and bentonite inhibition tests etc. Also, the compatibility of micromolecular ammonium salts with traditional drilling fluid additives were studied. Furthermore, the inhibitive mechanism is discussed in detail.

2 Materials and methods

2.1. Materials

The drilling fluids were formulated using several additives. Diethylenetriamine, triethylenetetramine and tetraethylenepentamine were provided by Sinopharm Chemical Reagent Co. Ltd. Tartaric acid was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Modified starch was supplied in domestic market. Bentonite was obtained from Changqing Bentonite Group Co. Ltd., China, and the chemical composition (wt.%) is: SiO₂ 60.54, Al₂O₃ 23.93, FeO 0.23, Fe₂O₃ 4.29, MgO 2.56, CaO 2.78, K₂O 1.45 and others 4.22.

2.2. Preparation of ATS

1 The series of amine-tartaric salts (ATS) was prepared using tartaric acid and organic
2 amines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine) as raw
3 materials. A certain amount of acid and amine were dissolved in water in various
4 proportions (Chen et al, 2014), after stirred for 1h, the water in the mixture was
5 evaporated, and the resident was ATS. The final product, amine-tartaric salts, was
6 abbreviated as ATS in the following text. **Scheme 1** is an example of the reaction of
7 tartaric acid and diethylenetriamine.

8 *2.3. Swelling inhibition and mud ball immersing test*

9 The hydration swelling of montmorillonite is tested by a NP-01 shale expansion
10 instrument (Haitongda, Co., Ltd., Qingdao, China), in accordance with Chinese
11 Petroleum and Natural Gas Industry Standards SY/T6335-1997 and SY/T5971-1994.
12 Mud ball immersing test is as follows: montmorillonite (10 g) was used to make a
13 mud ball, and the mud ball was immersed in 80 mL tap water or other aqueous
14 solutions for 72 h (Chen et al, 2014; Zhang et al, 2014). Then the details of the
15 immersed mud balls were evaluated, including a check whether there are cracks or
16 dilapidation on the surface.

17 *2.4 Bentonite inhibition test*

18 400 mL of water containing certain amount of inhibitor was treated by 2% (m/m)
19 bentonite. After stirred for 20 min, the dispersion was hot rolled at 70 °C for 16 h.
20 Then the rheological properties were measured after the samples were cooled to the
21 room temperature. After that the equivalent amount of drilling fluid bentonite was
22 added and the procedure was repeated until the dispersion became too viscous to be

measured (Zhong et al, 2013).

2.5 Drilling fluid properties evaluation experiment

4% (m/m) bentonite was dispersed in 350 mL of water containing a given amount of inhibitor (Zhang et al, 2014). After stirring for 20 min, aged for 16 h at room or high temperature, the rheological properties and filtration of the fluid samples were measured using a model ZNN-D6S viscometer (Haitongda, Co., Ltd., Qingdao, China), including Apparent viscosity (AV), Plastic viscosity (PV), Yield point (YP), Dynamic plastic ratio (YP/PV), API Filtration (FL) and Friction coefficient (μ) (Chen, 2006). The apparent viscosity, plastic viscosity and yield point were calculated from 300 and 600 rpm readings using following formulas from petroleum and natural gas industry standards for field testing of drilling fluids (API RP 13B-1-2009):

Apparent viscosity (AV) = $\phi_{600}/2$ (mPa·s);

Plastic viscosity (PV) = $\phi_{600} - \phi_{300}$ (mPa·s);

Yield point (YP) = $(\phi_{300} - PV)/2$ (Pa).

2.6 Particle size 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 20 min, after aged for 24 h, the size distribution of the particles was measured by LS-13 320 laser particle size analyzer based on the light scattering principle (Beckman Coulter, Inc., USA), using equipment operating procedure under the pump speed of 45%.

2.7 TGA, SEM and XRD

After the bentonite was dispersed in inhibitor solutions for 24 h, the bentonite was

1 separated and dried at 105°C for thermogravimetric analysis (TGA) and scanning
2 electron microscopy (SEM). TGA experiments were performed on a TGA/DSC 1/1600
3 thermal analysis machine (METTLER TOLEDO, Inc, Switzerland) at a ramp of 10°C
4 /min from 50°C to 400°C under a flow of nitrogen. The surface morphology of the
5 sample under study in the absence and presence of inhibitors was investigated using a
6 Digital Microscope Imaging scanning electron microscope (model SU6600, serial No.
7 HI-2102-0003) at accelerating voltage of 20.0 kV. Samples were attached on the top
8 of an aluminum stopper by means of carbon conductive adhesive tape. All
9 micrographs of the specimen were taken at 5009 times magnification. X-ray
10 diffraction analysis (XRD) analysis was performed by using an X'pert PRO MPD
11 diffractometer with Cu target at a generator voltage of 45 kV, current of 50 mA.
12 Samples were measured scanning 2θ

13 **3 Results and discussion**

14 *3.1 Preparation and swelling inhibition*

15 The series of amine-tartaric salts (ATS) was prepared using tartaric acid and organic
16 amines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine) as raw
17 materials. As shown in Table 1, the linear swelling ratio of ATS to clay was affected
18 by the type of amine, mole ratio of the functional group and the mass fraction of
19 inhibitors, and the linear expansion rate of bentonite in ATS-4 solution is much lower
20 than that of others within 30 min. So ATS-4 was selected to be studied in detail in
21 following works.

22 In order to investigate the influence of ATS-4 to the swelling inhibition of bentonite,

1 the swelling rate in different concentration of ATS-4 solutions was recorded. As
2 shown in Fig.1, the swelling rate of bentonite with time at different concentrations of
3 ATS-4 was recorded. As can be seen, the clay swelling rate increases dramatically at
4 the initial 10 min, followed by slow increase. Compared with blank, the bentonite
5 linear expansion rate in 5.0% ATS-4 aqueous solution is much lower, but the
6 concentration is larger. Under the condition of lower concentration, the swelling rate
7 in 0.5% ATS-4 solution is lower than that of others, and its effect is similar to the one
8 observed when using 1.0% KCl solution, indicating that 0.5% ATS-4 can restrain the
9 water affinity of the montmorillonite effectively, and 0.5% should be an economical
10 concentration.

11 *3.2 Mud ball immersing test*

12 The mud ball immersing tests provide a more intuitive way to describe the inhibition
13 property of ATS-4. The mud balls were immersed into water and 0.5% ATS-4
14 solution respectively. Fig. 2 shows a visual aspect of the mud balls after 72 h of
15 immersion. The mud ball immersed in water swells obviously, and surface is loose,
16 while the mud ball immersed in 0.5% ATS-4 solution swells slightly, and the surface
17 is smoother and cracked. It is clear that ATS-4 has a significantly strong clay-swelling
18 inhibition capability. The phenomena could be explained by a surface film on the clay
19 resulting from absorption of ATS-4, which blocks the water penetration into the clay
20 and prevent clay from hydrating swelling.

21 *3.3 Bentonite inhibition test*

22 The test was projected to simulate the relatively slow incorporation of yielding clays

1 into a drilling fluid. This simulated process usually happens when drilling active clays
2 in the stratum. As shown in Fig.3, with the amount of bentonite concentration
3 increasing, yield point of drilling fluid keeps increasing. And yield point increased
4 sharply with the addition of bentonite in fresh water system due to the hydration and
5 dispersion of montmorillonite. Comparing to blank, the lower rheological profile of
6 0.5% ATS-4 proves that it performs good inhibitive capacity.

7 *3.4 Effect of ATS-4 on the rheological properties and filtration of drilling fluids*

8 To evaluate the applicability in drilling fluid, the effects of ATS-4 on the rheological
9 performance of drilling fluids as measured in accordance with API RP 13B-1-2009
10 were shown in Table 2. As can be seen from Table 2, compared with the non-additive
11 control sample, addition of 0.1% ATS-4 exhibited little influence on the viscosity and
12 API filtration of drilling fluid, but the filtration rate increased dramatically as 0.5%
13 ATS-4 was used. So 0.1% ATS-4 was used to study the compatibility with common
14 drilling fluid additives. 0.1% ATS-4 and modified starch can improve viscosity and
15 reduce filtration of drilling fluid at the room temperature effectively, but are
16 incompatible with PAM. Thus, ATS-4 exhibits an excellent compatibility with the
17 modified starch in water-based drilling fluids.

18 *3.5 Particle size distribution test*

19 To study the function in the water-based drilling fluid, the effect of ATS-4 on the
20 bentonite in water was investigated. Fig. 4 shows the particle size distribution of the
21 bentonite dispersions when these are treated in different ways. Compared to the
22 un-hydrated control sample, the average size of hydrated bentonite particles is

reduced from 26.65 μm to 7.64 μm . And it should be noticed that it is different when
ATS-4 was added before and after the hydration of bentonite. When ATS-4 was
added before the virgin bentonite was dispersed into water, after 16h, the average size
of clays changed slightly, and it is just a little smaller than that of virgin bentonite.
When 0.5% ATS-4 was added to the hydrated bentonite suspension, the partials grow
up and are much larger than those of the blank suspension possibly due to flocculation.
The results confirm that ATS-4 can inhibit the bentonite swelling and dispersing, and
can aggregate the hydrated bentonite.

9 3.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) measure a mass loss of the hybrids as a function of temperature. The decomposition of organic–inorganic hybrids would take place in four steps: water desorption, dehydration, decomposition of polyammonium and dehydroxylation (Xi et al, 2004). As shown in Fig. 5, several mass loss steps are observed in the curves of bentonite immersed in tap water and ATS-4 solution. The thermal degradation of the ATS-4 treated bentonites differs significantly from that of the control bentonite between 50°C and 400°C. The weight loss of bentonite treated with tap water is 3.3% from 50°C to 225°C, while the weight loss of ATS-4 modified bentonite is no more than 1.5%, and there was obvious mass loss step from 270°C to 320°C for A line, which may be due to polymer degradation. Obviously, it can be concluded that ATS-4 can inhibit the water absorption of bentonite effectively.

21 3.7 Scanning electron microscopy

22 In order to evaluate the morphology of bentonite particles treated by different ways,

1 scanning electron microscopy (SEM) was carried out. Fig.6 (A) shows SEM image of
2 the bentonite after immersed in 0.5% ATS-4 solution. Fig.6 (B) shows the bentonite
3 after immersed in water, and Fig.6 (C) shows SEM image of the virgin bentonite
4 without any treatment. From the three photos, it is observed that after immersed in
5 water, the particles dispersed and changed to smaller particles. However, the particle
6 size of ATS-4 treated sample is similar with that of the virgin sample but much larger
7 than that of tap water treated sample. It is anticipated that, except for electrostatic
8 interaction, the hydrogen bonding between ammonium group, hydroxyl group and
9 siloxane of clay and modification of surface affinity toward water can further restrict
10 the swelling and hydration of clay minerals (Qiu et al, 2011).

11 *3.8 X-ray diffraction analysis*

12 The interlayer spacing of water immersed bentonite and ATS-4 solution immersed
13 bentonite was measured by XRD, as shown in Fig. 7. The scan for water immersed
14 bentonite indicates an intense peak at 5.908° , and an intense peak at 6.105° for 0.5%
15 ATS-4 solution immersed bentonite. The interlayer spacing can be calculated using
16 Bragg law, $2d\sin\theta=\lambda$ ($\lambda=0.154$ nm). The interlayer spacing of the water immersed
17 bentonite is 1.494nm, while 0.5% ATS-4 was used, the interlayer spacing decreased
18 to 1.446nm, indicating the effect of ATS-4.

19 *3.9 Inhibition mechanism*

20 In order to study the inhibition mechanism of amine-tartaric salts to bentonite, the
21 mud ball was immersed in 0.5% ATS-4 solution for 5d, as show in Fig.8 (left), there
22 are many crystals precipitated on the mud ball surface and at the bottom of the beaker.

1 The crystals were picked out and analyzed. The structure of the crystal was confirmed
2 by single crystal X-ray diffraction, as shown in Fig.8 (right). All the geometric
3 parameters of the crystal are in the usual ranges, as shown in Table 4. It crystallizes in
4 orthorhombic $P2_12_12_1$ space group, and the unit cell dimensions is: $a=9.631(2)$ Å
5 $b=10.573(3)$ Å $c=9.215(2)$ Å. In the crystal, each central Ca^{2+} cation was coordinated
6 with eight O atoms, among which four carboxyl O atoms and two hydroxyl O atoms
7 come from the four tartaric anions, and two hydroxyl O atoms come from two H_2O
8 molecules. The four tartaric anions behave two types of coordination with Ca^{2+} cation,
9 two tartaric anions coordinate with Ca^{2+} cation by one carboxyl O atom and one
10 hydroxyl O atom, while the other two tartaric anions coordinate with Ca^{2+} cation by
11 only one carboxyl O atom.

12 Then, the bentonite powder was immersed and stirred in 0.5% ATS-4 solution, and
13 the ion exchange was measured by EDTA method, as show in Fig.9. The result shows
14 that the concentration of Ca^{2+} in solution increases with time. So the inhibition
15 mechanism of ATS-4 to bentonite can be attributed to the ion exchange of ammonium
16 with the calcium ion in bentonite, and the exchanged ammonium in the layers of
17 bentonite can concatenate the layers by the electrostatic attraction and hydrogen bonds
18 between the ammonium and silicon hydroxyl groups. Besides, the exchanged
19 ammonium and the electrostatic adsorbed tartaric anion also can block the water
20 entering the interspaces of the layers, so as to inhibit the swelling of bentonite.

21 **4. Conclusions**

22 In this work, amine-tartaric salts were synthesized using tartaric acid and organic

amines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine). The inhibitive properties of ATS-4 towards clays swelling were investigated using linear expansion tests, mud ball immersing tests etc. The results indicate that ATS-4 shows stronger inhibition to hydration and swelling of bentonite. The hydration expansion degree of the mud ball in ATS-4 solution was significantly weaker than that of blank. The compatibility tests indicate that ATS-4 could be compatible with the conventional additives in water-based drilling fluids and that it can control the particle size of bentonite. The inhibition mechanism of amine-tartaric salt to shale may be due to the ion exchange, hydrogen bonding and modification of surface affinity toward water.

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Table 1 Name and inhibitory activity of amine-tartaric salts

Materials		Ratio	Name	Swelling ratio/%
tartaric acid	diethylenetriamine	1:1	ATS-1	69.44
		1:2	ATS-2	66.94
		1:3	ATS-3	67.88
	triethylenetetramine	1:1	ATS-4	60.37
		1:2	ATS-5	63.46
		1:3	ATS-6	68.52
	tetraethylenepentamine	1:1	ATS-7	63.20
		1:2	ATS-8	60.47
		1:3	ATS-9	60.63

Table 2 The effects of ATS-4 to the rheological performance of drilling fluids as measured in accordance with API RP 13B-1-2009 at room temperature

Additives	<i>AV</i> /mPa•s	<i>PV</i> /mPa•s	<i>YP</i> /Pa	<i>YP/PV</i> Pa/mPa•s	<i>FL</i> /mL	μ
non-additive	3.5	2.8	0.7	0.2555	13.3	0.0875
0.1%ATS-4	5.5	2.0	3.6	1.7885	15.0	0.0875
0.5%ATS-4	5.0	2.2	2.9	1.3007	125.0	0.5774
1.0%Modified starch	6.0	4.0	2.0	0.5110	7.5	0.0699
1.0%Modified starch+0.1%ATS-4	7.1	3.4	3.8	1.1122	6.8	0.0963
0.04%PAM	8.0	4.2	3.9	0.9247	12.0	0.0699
0.04%PAM+0.1%ATS-4	7.5	3.2	4.4	1.3733	20.0	0.0437

Table 3 Effect of 0.5% ATS-4 on particle size distribution of bentonite

Additives	Mean/ μm	Median/ μm
Virgin bentonite	33.26	26.65
Hydrated bentonite	11.06	7.64
Virgin bentonite +0.5% ATS-4	45.72	38.30
Hydrated bentonite +0.5% ATS-4	44.59	39.73

Table 4 The main crystal data

Item	Data
Formula sum	C ₄ H ₁₂ CaO ₁₀
Crystal system	orthorhombic
Space-group	P 21 21 21 (19)
Cell parameters	a=9.631(2) Å b=10.573(3) Å c=9.215(2) Å
Cell ratio	a/b=0.9109 b/c=1.1474 c/a=0.9568
Cell volume	938.35(39) Å ³
Z	4
Pearson code	oP108

Fig. 1 The effect of inhibitor concentration on the clay-swelling rate

Fig. 2 The status of mud balls immersed in water (left) and 0.5% ATS-4 solution
(right) for 72 h

Fig. 3 The effect of yield point of different shale inhibitors with the base fluid

Fig. 4 Effect of 0.5% ATS-4 on particle size distribution of bentonite

Fig. 5 TGA of water immersed bentonite and 0.5% ATS-4 solution immersed bentonite

Fig. 6 SEM of bentonite treated with ATS-4 solution (A), bentonite treated with water(B) and virgin bentonite (C)

Fig. 7 XRD patterns of water immersed bentonite and 0.5% ATS-4 solution immersed bentonite

Fig. 8 The analysis for crystal on the surface of mud ball (left) and the structure of the crystal (right)

Fig. 9 The change of calcium concentration in 0.5% ATA-4 solution with time