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Research paper

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.

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 threating 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 and Gates, 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, 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 and Swaco, 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

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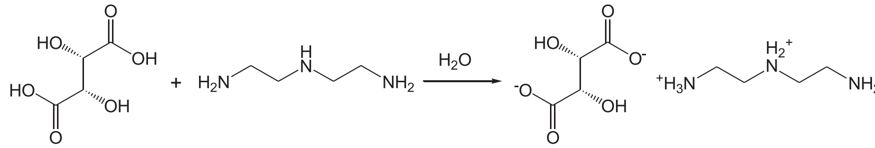

Scheme 1. Synthesis example of an amine-tartaric salts.

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: SiO_2 60.54, Al_2O_3 23.93, FeO 0.23, Fe_2O_3 4.29, MgO 2.56, CaO 2.78, K_2O 1.45 and others 4.22.

2.2. Preparation of ATS

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

2.3. Swelling inhibition and mud ball immersing test

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

2.4. Bentonite inhibition test

400 mL of water containing certain amount of inhibitor was treated by 2% (m/m) bentonite. After stirred for 20 min, the dispersion was hot rolled at 70 °C for 16 h. Then the rheological properties were measured after the samples were cooled to the room temperature. After that the equivalent amount of drilling fluid bentonite was 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., 2014a,b). 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 and 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):

$$\text{Apparentviscosity(AV)} = f_{600}/2(\text{mPa}\cdot\text{s});$$
$$\text{Plasticviscosity(PV)} = f_{600} - f_{300}(\text{mPa}\cdot\text{s});$$
$$\text{Yieldpoint(YP)} = (f_{300} - \text{PV})/2(\text{Pa}).$$

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

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

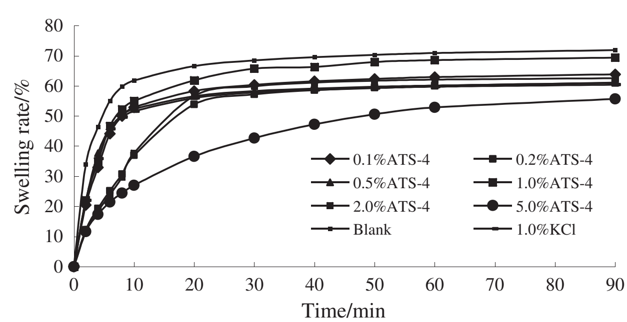

Fig. 1. The effect of inhibitor concentration on the clay-swelling rate.