

Inhibiting effect of dopamine adsorption and polymerization on hydrated swelling of montmorillonite

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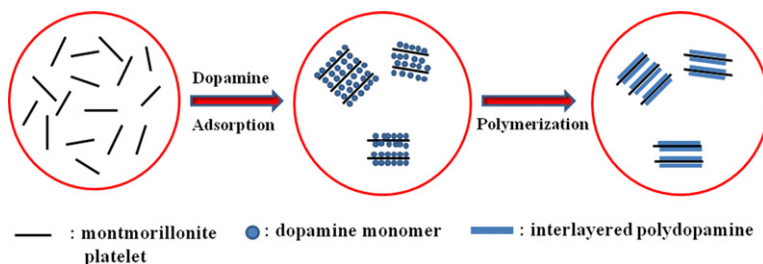
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HIGHLIGHTS

- ▶ Dopamine exhibits strong inhibiting effect on hydrated swelling of montmorillonite.
- ▶ The unique structure of interlayer polydopamine accounts for the high inhibition.
- ▶ The interlayered polydopamine has a structure of bilayer planer oligomers.
- ▶ The adsorption of positive charged dopamine plays an important role on inhibition.

GRAPHICAL ABSTRACT

The adsorption and polymerization of dopamine in the interlayer inhibit the hydrated swelling of montmorillonite.



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ABSTRACT

This paper aims at evaluating the inhibition performance of dopamine (DA) on hydrated swelling of montmorillonite (MMT) and exploring the inhibitive mechanism. The inhibition performance of DA was evaluated through the combination of linear swelling and mud making tests, and compared with three commonly used inhibitors in the field. The results show that DA performs extremely well on inhibiting the MMT swelling, within a broad temperature range even at 200 °C. Based on a combined use of FT-IR, XPS, XRD, zeta potential and TEM analysis, the probable inhibition mechanism was determined due to the identification of the structure of polydopamine (pDA) polymerized in the MMT interlayer. The results indicate that the forming of interlayered pDA that composed of bilayer planer 5, 6-dihydroxyindole (DHI) oligomers is primarily responsible for the excellent inhibition ability of DA. In addition to this, the collapse of MMT colloidal particle diffuse double layers due to the adsorption of positive charged DA monomers also contributed considerably to the inhibition effect on hydrated swelling.

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1. Introduction

The problem of well stability in water-sensitive shale formation has frustrated oil-field engineers from the beginning of the oil and gas drilling. When water-based drilling fluids encounter clay-rich shale, the resulting clay hydrated swelling can cause well instability often identified by solids build up in the mud, tight hole, stuck drill pipes and hole enlargement, which is in fact the most significant technical problem area in drilling and one of the largest sources of lost time and trouble cost [1]. Since hydrated swelling of clay is the root chemical cause of the well instability, for more than the past

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five decades various drilling fluids additives generally referred to as 'shale inhibitor' or 'clay stabilizer' that can inhibit clay swelling have been developed and utilized to overcome well instability.

Up to date, the most commonly used shale inhibitor was KCl used as the main ingredient in combination with polymer-type species, such as partially hydrolyzed polyacrylamide (PHPA) [2,3]. However, although KCl performs well due to the low hydration energy of potassium ions, the use of high concentrations can bring serious harm to the chemical and biological ecosystems [4]. Because the ammonium cation has very similar hydrated volume and hydration energy as potassium ion, ammonium and amine-based chemicals were introduced as very promising inhibitors and applied in the field with partial success in recent years, the most effective classes of which are quaternary ammonium salts and polyamine [5]. Despite the high level of inhibition, quaternary ammonium salts and polyamine still have some drawbacks, such as the toxicity of some quaternary amines (e.g., tetramethyl ammonium chloride) [5] and the relatively lower inhibition of polyamine at high temperature due to the weakening of hydrogen bonding between amino groups and tetrahedral siloxane surfaces of clay. Owing to these shortcomings, further efforts must be made to develop environmental friendly and thermostatic nitrogen-based inhibitor.

The byssus thread secreted by marine mussels can bind strongly to virtually all kinds of inorganic and organic substrates in aqueous environment via the unique adhesion ability of mussel adhesive proteins (MAPs). The MAPs contain large amounts of a particular amino acid 3,4-dihydroxy-L-phenylalanine (L-DOPA), and it has been proved that the catechol groups in L-DOPA is mainly responsible for the strong adhesion properties in aqueous environment [6–10]. Dopamine (DA), traditionally known as a hormone and neurotransmitter, is a unique compound widely used to synthesize mussel-mimetic adhesive polymers in recent years due to its very similar structure and characteristics with L-DOPA [11–13]. By virtue of the DA's simple structure mimic of MAPs [6], many researchers have studied and showed its unique ability to form spontaneous polymer films on a wide range of substrates. That is, at a weak alkaline pH [14], DA in solution will undergo an adsorption and following oxidative self-polymerization process to produce a tightly adherent polydopamine (pDA) film which is an eumelanin (black insoluble biopolymer of human skin)-like material on various substrates [15–17]. It has been suggested that the adsorption mechanism of DA on inorganic oxide substrates such as hydrophilic SiO₂ is probably double hydrogen bonding interaction [18] between the two OH groups of catechol and the O atoms on the SiO₂ surface, which is hyperstable [19], much stronger and can survive at relative higher temperature as compared with ordinary hydrogen bonding [20]. Due to the fascinating properties of high adhesion activity, thermostability and marine nontoxicity, we hypothesized that DA can act as a promising high-performance shale inhibitor in water-based drill fluids. In addition, although the interaction of DA with many substrates has been documented [15–17], the adsorption and polymerization behavior on the surface of clay as well as the hybrid structure generated have rarely been studied. In this paper, we evaluate the inhibition performance of DA on hydrated swelling of montmorillonite (MMT, 2:1 smectite clay) and explore the inhibition mechanism via a variety of characterization methods. Furthermore, we wish to relate the mechanism to inhibition performance in order to better optimize the DA containing drilling fluid.

2. Materials and methods

2.1. Materials

Pristine dioctahedral smectite clay, montmorillonite (MMT) with cation exchange capacity of 81.3 mmol/100 g, was obtained

from Xinjiang Xiazijie Bentonite Inc, China. The raw sample was characterized by X-ray diffraction and FT-IR spectroscopy. Such analyses reveal that the montmorillonite content is 73.8 wt%, and quartz, potash feldspar, anorthose, and gyp are the major impurities accompanying pristine clay. The elemental composition of the raw sample was determined by ICP-AES analysis: Si, 58.7 wt%; Al, 20.2 wt%; Na, 4.6 wt%; Fe, 8.1 wt%; Mg, 3.6 wt%; K, 3.1 wt%; Ca, 0.8 wt%; Ti 0.9 wt%. Dopamine hydrochloride (DA, 99 wt%) was purchased from Sigma-Aldrich Inc. All the other experimental chemicals were purchased from domestic reagent companies. All the materials were used without further purification.

2.2. Methods

2.2.1. Linear swelling tests

The amount of DA solutions adsorbed by MMT over time was determined in the laboratory using CPZ-2 dual channel linear swell-meter (Qingdao, China). 5 g MMT was compressed into a sized pellet by hydraulic press under 10 MPa for 5 min. Then the pellet was placed between a metal plate and a linear transducer. After immersing the pellet in the DA solution the pH of which was adjusted to 8.5 with 1 M NaOH, the change in length of the pellet was measured over time through the transducer. Both the total change in length over the whole experimental time frame and the rate of change within a certain period could be determined.

2.2.2. Mud making tests

This test determines the maximum amount of MMT that can be inhibited by a certain amount of shale inhibitor over a period of several days. 300 g deionized water or inhibitor solution with a concentration of 1 wt% was treated with 12 g MMT every day. After hot rolling at 80 °C for 16 h, the yield point of MMT/inhibitor suspension was determined before adding another portion of MMT. These daily additions of MMT and hot rolling were continued until the total loading of MMT was up to 60 g, in which case the yield point of MMT/deionized water suspension became too viscous to be measured.

For the mud making tests at constant MMT loading and variable temperatures, the addition amount of MMT was fixed at 12 g. The temperature ranged from the initial 50 °C to 200 °C, with an increase of 50 °C for each measurement.

The measurements were performed using ZNN-D6L rotational viscometer (Qingdao, China). The yield point of the MMT/inhibitor suspension was calculated from viscometer readings of 600 and 300 rpm (Φ_{600} and Φ_{300}) using the following formulas [21]: Yield point (YP) = $\Phi_{300} - \Phi_{600}/2$ (Pa).

2.2.3. Preparation of MMT/DA hybrids

DA aqueous solutions were prepared with different DA concentration (0.2 wt%, 1 wt%, 1.5 wt%), and the pH values of solutions were adjusted to 8.5 using 1 M NaOH. Then 9 g MMT was dispersed in 300 g DA solution to make 3 wt% MMT/DA suspension. The suspensions were stirred vigorously at 10,000 rpm for 20 min and then hot rolled at 80 °C for 16 h to reach the adsorption and hydration equilibrium. After cooling down to room temperature, the suspensions were centrifuged at 8000 rpm for 10 min and the solid samples were washed with deionized water to eliminate the residual DA solution. The washing and centrifugation processes were repeated several times until the supernatant was clear. Finally, the dark brown solid were dried overnight at 120 °C and ground to fine powders for the analysis of XRD, FT-IR and XPS.

2.2.4. Structure characterization techniques

2.2.4.1. Fourier transform infrared spectroscopy (FT-IR) measurements. FT-IR analyses of MMT/DA hybrids were recorded by

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