Preparation and swelling inhibition of cation glucoside to montmorillonite

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Abstract: In this work, a cation glucoside (CG) was synthesized with glucose and glycidyl trimethyl ammonium chloride (GTA) and used as montmorillonite (MMT) swelling inhibiter. The inhibition of CG was investigated by MMT linear expansion test and mud ball immersing test. The results showed that the CG has a good inhibition to the hydration swelling and dispersion of MMT. Under the same condition, the linear expansion rate of MMT in CG solution is much lower that of methylglucoside and the hydration expansion degree of the mud ball in the CG solution was significantly inhibited. The characterizations of physic-chemical properties of particle, analysized by thermogravimetric analysis and scanning electron microscopy, revealed that CG play great role to prevent water from absorb and keep MMT in large particle size.

1. Introduction

The montmorillonite (MMT) are products of volcanism and hydrothermal activity and are composed of hydrous aluminum silicates in the form of extremely small particles, which chemical varieties that swell in water and possess high cation-exchange capacities. The theoretical formula for montmorillonite (i.e., without structural substitutions) is $(OH)_4Si_8Al_4O_{20}\cdot nH_2O$, as shown in Figure 1. Na^+, Ca^+, K^+, Fe^{3+} and other cations are common substitutes; the exact ratio of cations varies with source. MMT can take up water between their layers, causing swelling, and change the interlayer spacing according to the mineral variety. In addition to being involved in inorganic exchange reactions, they react with and absorb some organic liquids, such as amines, glycols, glycerols, and other polyhydric alcohols. The swelling of MMT gives the water greater viscosity, which is very important in keeping a drill head cool during drilling and facilitating removal of rock and dirt from within a drill hole [1,2]. On the other hand, during the drilling of oilfield, 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 [3,4]. Montmorillonite swelling is at the origin of well instability during drilling. Steiger and Low [5,6] showed that the addition of KCl can reduce the water activity of clay and consequently the swelling pressure and improve the stability of clay formations. Recently, it has been found that the use of a hydrophilic organic compound, such as methylglucoside (MEG), can also afford other characteristics similar to those of oil based mud to inhibit the swelling

[7,8]. The MEG system is easy to formulate and condition, and it is not poisonous and non-hazardous, the use of this drilling fluid could eliminate cost of oil contaminated drilled cuttings disposal [10]. But it was found that the dosage of MEG is relative high and the temperature tolerance is relative low. So the researchers have screened other organic additives with high thermostability and good capacity of swelling inhibition [9-12]. In this work, cation glucoside (CG) was synthesized as a new montmorillonite swelling inhibitor. Both the inhibitive properties of synthesized inhibitor and the inhibitive mechanism were discussed in detail.

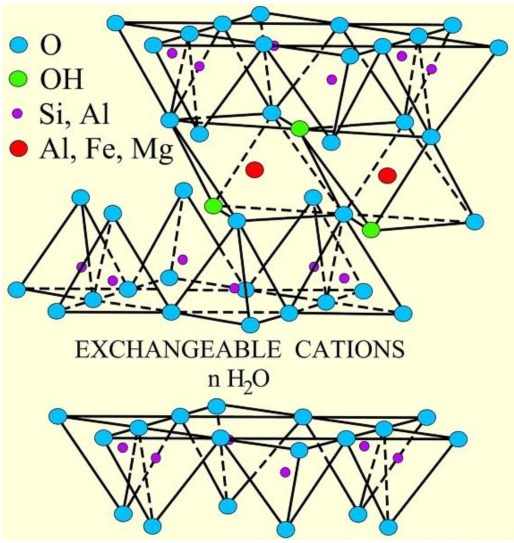
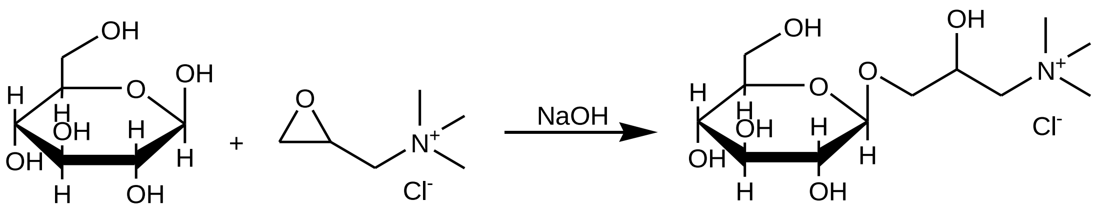


Fig. 1 The structure of montmorillonite

2. Experimental

Materials. The sodium montmorillonite (Na-MMT) SD-1005 was obtained from Zhejiang Sanding Technology Co., LTD. The chemical compositions of the sample were: SiO_2, 64.07%; Al_2O_3, 19.11%; CaO, 4.48%; MgO, 3.61%; Na_2O, 3.07%; Fe_2O_3, 2.64%; P_2O_5, 1.71%; K_2O, 0.72%. The cationic exchange capacity was 95 mmol/100g measured by the ammonium acetate method. MEG was provided by Sinopharm Chemical Reagent Co., Ltd, China. All the reagents were used without further purification.

Synthesis Of CG. Cation glucoside (CG) was synthesized with glucose and glycidyl trimethyl ammonium chloride (GTA), as shown in Scheme 1. A certain amount of glucose and 5% NaOH were dissolved in water at a certain temperature, and the GTA methanol solution was added dropwise. The reaction was stirred until the disappearance of GTA, as evidenced by thin-layer chromatography. The solvent was removed in vacuo and the residue was recrystallized in methanol, giving the title compound.



Scheme.1 Synthesis of cation glucoside

Swelling Inhibition and Mud Ball Immersing Test. The hydration swelling of shale is tested by a NP-01 shale expansion instrument according to API Procedure No.13B. Mud ball immersing test is as follows: montmorillonite (10 g) was used to make a mud ball and the mud ball was immersed in

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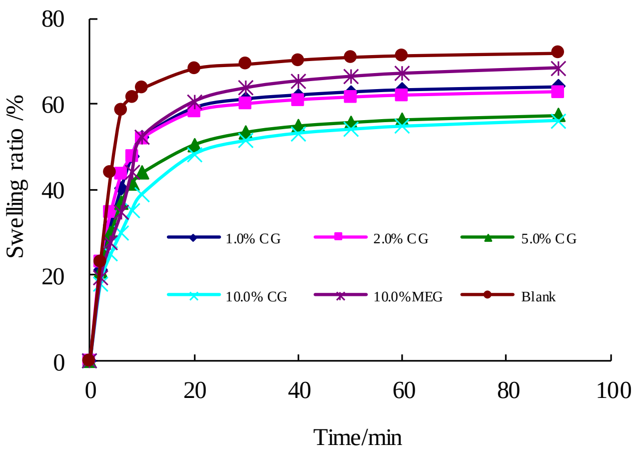
100mL tap water or other aqueous solutions for 36 h. Watch the details of the immersed mud balls, check whether there are cracks or dilapidation on the surface.

Physicochemical Property Analysis. TGA experiments were carried out using a TGA/SDTA 851^e thermal analysis machine (Mettler-Toledo, Switzerland) under a flow of nitrogen. The sample weight used was about 10 mg, and the temperature ranged from 25℃ to 930℃ with a ramping rate of 20℃/min. The surface morphology of the sample under study in the absence and presence of inhibitors was investigating using a Digital Microscope Imaging scanning electron microscope (model SU6600, serial no. HI-2102-0003) at accelerating voltage of 20.0 kV.

3. Results and discussion

Swelling Inhibition Performance Evaluation. In order to investigate the influence of CG to the swelling inhibition of MMT, the swell rate of MMT with time in different concentration of CG solution was recorded. As shown in Figure 2, the water adsorption rate increased dramatically during the initial 10 min and then followed by slow increase in any cases, while the swelling rate of MMT in CG solution (left) is much lower compared with virgin MMT indicating that the water affinity of the MMT was inhibited by CG. The influence of CG concentration to its swelling inhibition behavior is similar with all of inhibitors that low swelling rate can be obtained in presence of high inhibitor concentration because the swelling rate is a function of inhibitor dosage. In our research, the inhibition performance of MEG, a common inhibitor as suggested before, has also been added for comparison. The results show that the swelling rate of MMT, 57.4%, in presence of 5% CG was much lower than the 65.5% swelling rate in 10% MGE 90 min, while the swelling ratio is similar at the concentration of 10% and 5%, so 5% should be the optimum concentration for its application. It gives great potential to the industrial application of CG as a montmorillonite swelling inhibitor. As a contrast test, the inhibition of GTA was also investigated and the same condition (right), and the results show that at the concentration of 1.0%, 2.0%, 5.0%, 10.0% the swelling ratios of MMT are 71.67%, 65.88%, 67.05%, 68.26% respectively within 90min, which are much higher than that of CG at the same concentrations. From the inhibition of CG and GAT, it can be concluded that the inhibition can attributed to the synergistic effect of quaternary ammonium and glucoside groups.



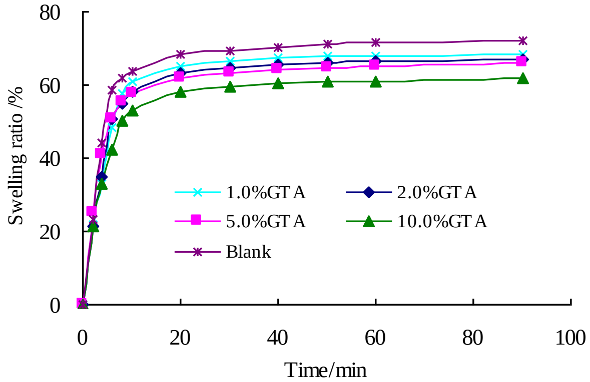


Fig. 2 The inhibition of CG (left) and GTA (right) to clay

The mud ball immersing test provides a more intuitive way to describe the inhibitive property. In our research, the mud balls were immersed into 5%CG solution and 5%MEG solution respectively. Figure 3 shows the status of the mud balls after immersed for 48 hours. From the results, it can be seen that the morphology of mud ball in presence of MEG solution is great changed and cracked into pieces due to swell of MMT. In contrast, there is almost no any status change can be found when the mud ball was immersed in CG solution indicating that the swelling of MMT by hydration is slightly so as to the smooth surface of the mud ball without any cracks. This observation could be explained by the hydrophobic film resulting from CG, which blocks the water penetration into the interlayer of MMT and then prevent it from hydrating swelling.

Fig.3 The status of mud balls immersed in water (left) and 5% CG (right) solution for 48 h

TGA Analysis. Thermogravimetric analysis (TGA) was used to describe the thermal stability of MMT after modified by different additive, and the result was shown in Figure 4. From the pattern we can see that there are several mass loss steps in the process of decomposition of MMT modified by water and CG solution. Before 200°C, the mass loss is assigned to the dehydration of physically adsorbed water and water molecules around metal cations such as Na^+ and Ca^{2+} on exchangeable sites in MMT [11,12], which is very slight in both of samples, less than 5%. The weight loss at above 200 °C is contributed to the release of structural water. In case of CG modified MMT, the mass loss at above 200 °C due to structural hydroxyl groups is much less than that of the water modified sample, which indicates the adsorption of water into the interlayer regions between silicate sheets for MMT was greatly weakened after modified with CG.

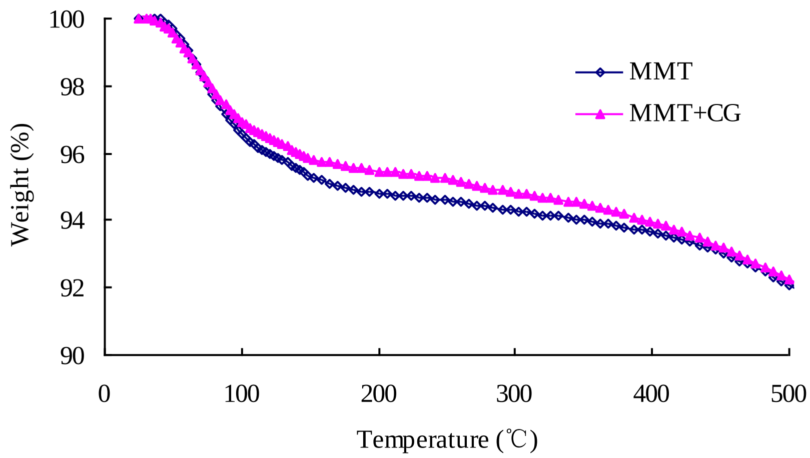
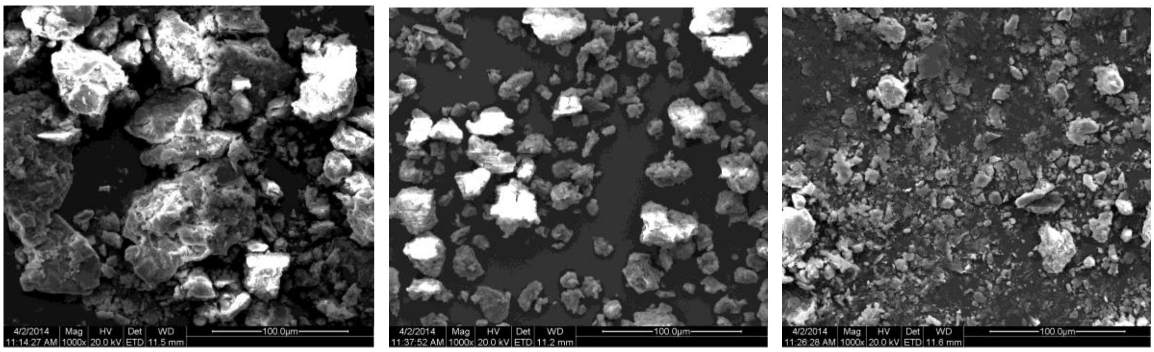


Fig. 4 The TGA of the montmorillonite treated by water and CG solution

Scanning Electron Microscopy. Scanning electron micrographs of the materials have been recorded in order to get insight into the particles morphology and texture. Figure 5(a) shows an SEM image of the virgin MMT particles without any treatment, and the morphology of the MMT particles after immersed in 1% CG solution for 12 h has been shown in Figure 5(b). For comparison the SEM image of MMT particles after immersed in water for 12 h has also been measured in Figure 5(c) shows. From the three micrographs, it can be found that large aggregates of oriented platelets mixed with smaller particles are present in the untreated montmorillonite sample. After immersed in water or CG solution, the MMT particles aggregated clusters particles still remain, which is still larger than the MMT treated immerged in water indicating the inhibition of CG to the swelling of MMT.



(a) virgin MMT (b) MMT treated with CG (c) MMT treated with water

Fig. 5 SEM of montmorillonite treated with different ways

CG containing four hydrophilic –OH groups and a quaternary ammonium group is favorable to the absorption of CG on the surface of MMT by the electrostatic attraction between quaternary ammonium and negative charge on the MMT and hydrogen bonds between the –OH groups of CG and MMT as suggested by Van Olphen [13]. As a result the space between the MMT layers was blocked by the absorbed CG molecules which inhibiting the entering of H_2O molecules into the layer of MMT. On the other hand, the stability of MMT in water was greatly enhanced by the film on the MMT surface formed from CG, which play great role to protect of MMT against water.

4. Summary

In this work, a cation glucoside (CG) was synthesized with glucose and GTA for the use as MMT swelling inhibitor. The MMT swelling tests showed that CG exhibits great inhibition to the MMT linear expansion by keeping 57.4% of swelling rate at 90 min, which is much effective than that of 10% MEG. Furthermore, the hydration expansion of the MMT mud ball in the CG solution was significantly inhibited, which consists with the results of thermogravimetric analysis and scanning electron microscopy results. It can be concluded that the high effect inhibition of CG to the swelling of MMT should be contributed to its –OH groups and quaternary ammonium group, by which CG absorbs on the MMT and prevent H_2O molecular from entering the layer.

Acknowledgments
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