Applied Clay Science 166 (2018) 123–130

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research Paper

# Adsorption behavior of hydroxypropyl guar gum onto montmorillonite and reducing adsorption in the reservoir

Zichen Yin[a], Yanling Wang[a,*], Jingshan San[b]

[a] School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, PR China
[b] Harbin Topsale PetroChemicals and Enquipment New Tech Co., PR China

ARTICLE INFO

*Keywords:*
Hydroxypropyl guar gum
Montmorillonite
Adsorption behavior

ABSTRACT

Hydroxypropyl guar gum (HPG) is a kind of thickener commonly used in the field of oilfield chemistry. The adsorption behavior of HPG onto Montmorillonite (Mt) was investigated in this article. The maximum adsorption amount of HPG on Mt. was 3.6 mg/g at the HPG concentration of 2 g/L. The effect of pH, temperature, salts, alcohols and hydrolyzed polyacrylamide (HPAM) on adsorption behavior was revealed. The results showed that adsorption capacity increased with pH ranging from 3 to 13. The adsorption capacity was slightly influenced at temperature from 20 °C to 60 °C. The adsorption amount decreased at the presence of NaCl, KCl, $CaCl_2$ or $MgCl_2$, while it increased with addition of $Na_2SO_4$ or $Na_3PO_4$. The adsorption capacity was found no change at the presence of monobasic alcohol, while it significantly increased with the increasing concentration of polybasic alcohol. The adsorption density reduced with the addition of HPAM. Scanning electron microscope (SEM) and X-ray Diffraction (XRD) confirmed that adsorption behavior occurred on the exterior surface of Mt. Besides, the adsorption was attributed to Van der Waals' forces and electrostatic interaction. The Fourier Transform infrared spectroscopy (FTIR) showed that adsorption behavior occurred on Mt. surface via physisorption rather than chemisorption. The adsorption behavior of HPG on Mt. surface obeyed the Langmuir adsorption isotherm which showed that the adsorption was monolayer adsorption. The adsorption mechanism would be characterized as exterior surface adsorption, physical adsorption and monolayer adsorption.

## 1. Introduction

Hydroxypropyl guar gum (HPG) is a natural macromolecule hydrocolloids and thickener. HPG would form colloid substance when it dissolves in water, then high viscosity solutions could be prepared. Therefore, HPG is widely used in petroleum industry, biomedicine and other fields (Nayak and Singh, 2001a, 2001b; Mukherjee et al., 2018). Previous literature reported that HPG could meet the requirements of zero release in modern factories, and it was a kind of promising environmental friendly additive (Nayak and Singh, 2001a, 2001b; Zhu et al., 2016). HPG is a kind of non-ionic polysaccharose, and each mannose unit is connected to the galactose unit. It has been reported that the molecular weight of HPG is about $2 \times 10^6$ (Wang et al., 2016), and the molecular structure of HPG and cellulose are similar (Fig. 1).

HPG is commonly used to prepare fracturing fluids in oil fields, and the fracturing fluids play a vital role in the process of hydraulic fracturing (Jung et al., 2015; Vengosh et al., 2017). Nevertheless, adsorption of fracturing fluids is a vital factor leading to formation damage (Manz et al., 2016). Adsorption behavior should be fully considered in the preparation of fracturing fluids, aiming to reduce the adsorption of fracturing fluids and the formation damage. So far the most popular used fracturing fluids in oil field are emulsion polymers (Ianchis et al., 2009), viscoelastic surfactant (VES) (Hull et al., 2015; Li et al., 2016) and modified guar gum. The concentration of emulsion polymer and VES would be determined through using starch-cadmium iodide method and reinecke salt colorimetric method, respectively (Scoggins and Miller, 1979; Salem and Askal, 2002). In previous work (Yin et al., 2018), the determination method of cellulose was referred to measure the concentration of HPG, and the similar method was also used in this paper. HPG was chosen as adsorbate, and Montmorillonite (Mt) was selected as adsorbent (Mt was used to simulate formation). The adsorption behavior and mechanism of HPG onto Mt. are investigated.

* Corresponding author.
*E-mail address:* wangyl@upc.edu.cn (Y. Wang).

https://doi.org/10.1016/j.clay.2018.09.015
Received 21 June 2018; Received in revised form 16 August 2018; Accepted 9 September 2018

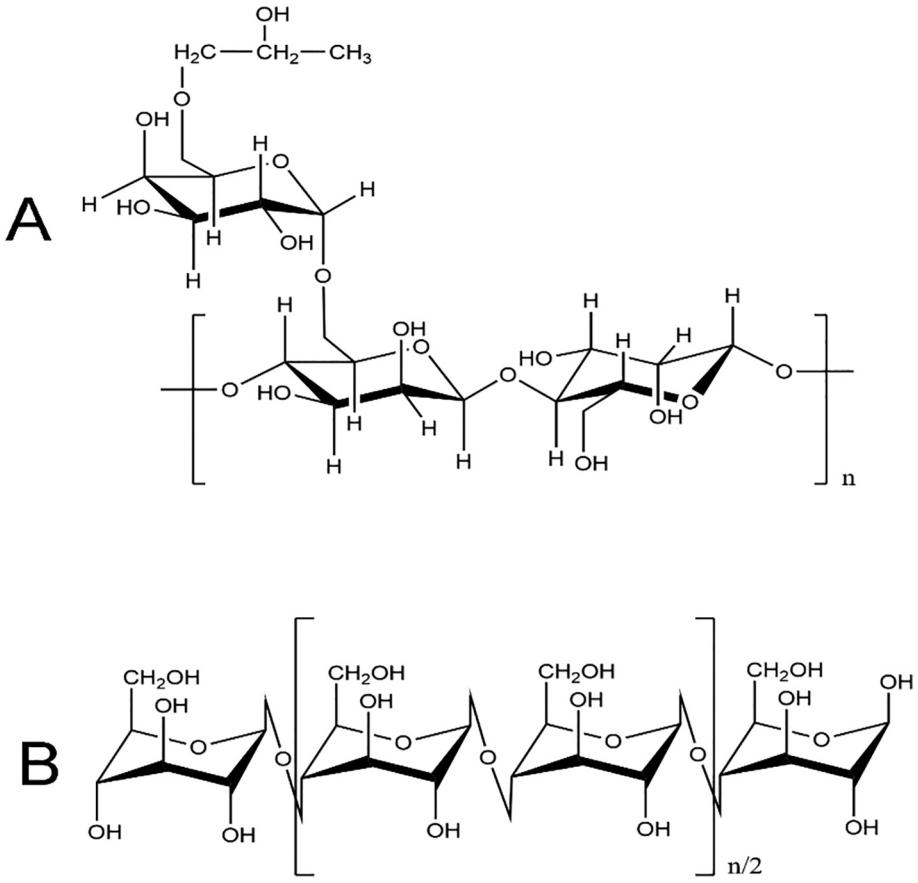


**Fig. 1.** Molecular structure of HPG (A) and cellulose (B).

**Table 1**
Chemical composition of Mt.

| Composition | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | CaO | MgO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Mt | 60.98 | 0.25 | 17.84 | 2.68 | 0.01 | 3.25 | 5.42 | 0.161 | 0.174 |

## 2. Materials and methods

### 2.1. Materials

HPG was purchased from Sinopec Shengli Oilfield. Mt. (800 mesh sieve) was provided by Petroleum Engineering Technology Research Institute of Shengli Oilfield Company. The chemical composition of Mt. was listed in Table 1. The structural formula of the Mt. sample was: $(Ca_{0.027}\,K_{0.014}\,Mg_{0.017}\;\;Na_{0.020})_{0.278}{\bullet}(H_2O)_n\;\;\{(Al_{1.346}\,Mg_{0.510}\;\;Fe_{0.131}\;Ti_{0.012}\;\;Mn_{0.001})_{2.000}\;\;[(Si_{3.975}\;\;Al_{0.025})_{4.000}\;\;O_{10}\;\;(OH)_2]\}$ (Dong et al., 2018). Partially hydrolysis polyacrylamide (HPAM, molecular weight: 10 million and 20 million, hydrolytic degree: 24%) was purchased from Adamas Reagent, Ltd. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Establishment of standard curve

The process for establishing the standard curve of HPG would be divided into two steps. The first step was the preparation of HPG standard solution. HPG was dissolved in dilute sulfuric acid for wet digestion. After wet digestion, 100 μg/mL HPG standard solution was prepared. The absorbance value was determined by spectrophotometer at 620 nm (Dubois et al., 1956). The second step was to draw HPG standard curve.

### 2.3. Measurement of adsorption capacity

The initial concentration of HPG ($C_0$) was determined according to absorbance. 4 g Mt. was dispersed into 100 mL deionized water at 20 °C and stirred for 1 h to form montmorillonite slurry. At constant temperature, Mt. was added in HPG solution for a designated time. After it, the equilibrium concentration of HPG ($C_1$) was determined. The adsorption amount of HPG adsorbed on per gram of Mt., Γ (mg/g), was calculated through formula (1) (Zhang et al., 2015):

$$\Gamma \frac{V(C_0 - C_1)}{m \times 1000} \quad (1)$$

where $V$ (mL) was the volume of solution, and m (g) was the mass of Mt. $C_0$ and $C_1$ (μg/mL) were the initial and equilibrium concentrations of HPG.

### 2.4. Characterization

The samples were characterized by Fourier infrared spectroscopy (FTIR, Thermo Nicolet Corporation, USA), which ranged from 4000 to 400 $cm^{-1}$ with 32 scans and a resolution of 4 $cm^{-1}$ in transmission by using KBr pellets. The structure of the Mt. was measured by X-ray diffraction (XRD, D/max-rB, Japan). Samples were pressed in glass sample holders and measured using diffractometer (45 kV, 40 mA). The Ni-filtered CuKa radiation (λ = 0.154 nm) was used as the X-ray source with 1.0° antiscatter slit and 0.5° divergence slit. Scans were run in the range of 3° to 15° 2θ at a scan rate of 0.197°/s and a step size of 0.0167°. The morphologies of the samples were taken using a scanning electron microscope (SEM, TESCAN VEGA/XMU, Czech Republic). Samples for surface imaging were mounted on aluminum stubs and coated with gold using a sputtering coater. The samples were examined using an accelerating voltage of 15 kV (Zhong et al., 2015; Ribeiro et al., 2018).