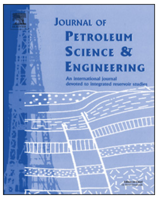
Journal of Petroleum Science and Engineering 142 (2016) 13–20

Contents lists available at ScienceDirect

Journal of Petroleum Science and Engineering

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



Water adsorption on kaolinite and illite after polyamine adsorption

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ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form
16 January 2016
Accepted 29 January 2016
Available online 30 January 2016

Keywords:
Kaolinite and illite hydration
Surface tension analysis
Water adsorption
Polyamine adsorption

ABSTRACT

Polyamine (PA) is a novel inhibitor applied to water-based drilling fluid in order to reduce clay hydration. In this paper, water adsorption behavior on kaolinite and illite after PA adsorption (PA-kaolinite, PA-illite) was characterized by X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and adsorption isotherms tests using water, benzene, and heptane. After PA adsorption, water adsorption on kaolinite was enhanced while water adsorption on illite was reduced. Water vapor adsorption affinity on kaolinite in an entire range was significantly increased due to H-bonds between the ammonium groups of PA and water molecules. As a result, kaolinite surface tension was increased. Water adsorption affinity on illite in the low relative humidity (RH) regimes was decreased after PA adsorption and illite surface tension decreased because fewer water molecules could adsorb on tetrahedral (SiO_4) of illite. Therefore, PA can be used as inhibitor while drilling shale formations mainly composed of illite, not kaolinite.

1. Introduction

During drilling, shale accounts for approximately 75% of the drilled footage and contributes to approximately 90% of the wellbore stability problems encountered, such as hole collapses, tight holes, stuck pipes, poor hole cleaning, hole enlargement, plastic flow, fracturing, and loss of well control, as reported by Steiger and Leung (1992) and Zhong et al. (2011). As reported by Lal (1999), the amount and type of clay minerals in shale decide the affinity of shale for water and are directly related to wellbore stability. A critical factor in designing drilling fluid is the ability to dehydrate clay minerals to prevent wellbore stability problems while drilling in shale formations (Rojas et al., 2006; Morton et al., 2005). In recent decades, various drilling fluid additives have been proposed, including relatively high concentrations of inorganic salts, organic salts, and many types of polymeric additives, as reported by Bruton and Mclaurine (1993), Rosa et al. (2005), Caenn and Chillingar (1996), and Souza et al. (2010). It has been reported that poly (ethyleneoxide) (PEO) polymers, PEO-PPO-PEO copolymers can adsorb strongly to clay surfaces by hydrogen bonding with silanol groups on the clay surface (Burchill et al., 1983; Nelson and Cosgrove, 2005) to decrease hydration of minerals. Nevertheless, as Young and Iskander (2006) concluded, these approaches have exhibited various limitations and remained somewhat unsuccessful with regard to the dehydration of clay minerals. A recent advance was the introduction of water-based drilling fluids containing low molar masses of polyether amine compounds, as proposed by Klein et al. (2005), Patel et al. (2001), and Qu et al. (2009). Extensive research (Zhong et al., 2011; Patel et al., 2007; Wang et al., 2011; Cui and van Jeroen, 2010) has been conducted concerning water adsorption on Montmonrillonite (MMT) after PA intercalation. However, water adsorption behavior of kaolinite and illite after PA adsorption has not been discussed yet and whether or not PA can dehydrate kaolinite and illite remains unclear. As reported by Šolc et al. (2011), kaolinite is a dioctahedral layered aluminosilicate of 1:1 type, therefore, each layer has two different surfaces parallel to the (001) plane. First one, tetrahedral, is formed from basal oxygen atoms of the tetrahedral (SiO_4) sheet, while the second one, octahedral, is formed from surface hydroxyl groups of the octahedral (AlO_6) sheet. As reported by Benco et al. (2001), these hydroxyl groups of octahedral surface are very flexible and allow effective formation of hydrogen bonds with the polar molecules. They have amphoteric character and are able to act as proton donors and/or acceptors, respectively (Tunega et al., 2004). For kaolinite octahedral surface, water molecule can only form weak hydrogen bonds with the basal oxygen atoms surrounding the ditrigonal hole. As reported by Cheng and Sun (2012), illite sheets consist of an octahedral aluminum layer sandwiched between two silica layers. In each unit cell, the K^+ ion at the surface balances the substitution of Si with Al and the position of the K^+ ion is independent of the specific Si atom being substituted. For water molecules on illite surface at low RH, two configurations exist (Malani and Ayappa, 2009). In one configuration, two hydrogen atoms interact with the surface oxygen to form two hydrogen bonds, whereas in the other configuration,

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http://dx.doi.org/10.1016/j.petrol.2016.01.040
0920-4105/

only one hydrogen atom of water interacts with the surface oxygen, the other forms hydrogen bonds with other water molecules laterally. This configuration also facilitates the hydration of K^+. With RH increased, multilayers of water molecules adsorbed on illite. In this study, XRD analyses were used to study PA adsorption or water adsorption in the interlayers of kaolinite, and illite. Water, benzene, and heptane vapor adsorption on clay minerals was also tested, and the associated surface tension was analyzed using the VCG theory developed by Van Oss et al. (1988) to study water-clay minerals thermodynamical interaction. The Langmuir, Freundlich, and BET adsorption models were used to fit the experimental data in order to characterize water adsorption on clay minerals at different RH, while DFTIR spectroscopy was used to gather bonding information regarding the water molecules adsorbed on clay minerals. For comparison, water adsorption behaviors of kaolinite and illite after polyethylene glycol (PEG400) adsorption were also discussed.

2. Experimental

2.1. Clay and clay suspensions

Well-crystallized kaolinite was obtained from clay repository of Maoming Kaolin Science and Technology CO. Ltd in China. The $< 2\ \mu m$ fraction was isolated from the bulk material by sedimentation for 8 h under ambient temperature. The kaolinite paste was then washed with deionized water 3 times until the conductivity of the supernatant equaled that of deionized water. After washing, the kaolinite was dispersed and stored as a stock solution. The solid content was measured after drying at 100 °C for 5 h until the weight remained constant.

Well-crystallized illite was obtained from clay repository of Xintai Nonmetal Material Co. Ltd. in China. The $< 2\ \mu m$ fraction was isolated from the bulk material by sedimentation for 8 h under ambient temperature. The illite paste was then washed with deionized water 3 times until the conductivity of the supernatant equaled that of deionized water. After washing, the illite was dispersed and stored as a stock solution. The solid content was measured after drying at 100 °C for 5 h until the weight remained constant.

2.2. Chemicals

Polyamines (PA) (developed by the drilling fluid research team in China University of Petroleum) contains primary amino groups attached to the ends of a polyether backbone. The block copolymer backbone is usually composed of propyleneoxide, ethyleneoxide, or a propylene oxide/ethylene oxide mixture. The PA molarmass was approximately 400 g/mol and had a typical chemical formula of $CH_3–[OCH_2CH_2]_x–[OCH_2\ (CH_3)\ CH]_y–NH_2$. PEG400 was purchased from Sinapharm Chemical Reagent Co. Ltd.

2.3. Adsorption isotherms of PA, PEG400 on kaolinite, and illite

Aqueous PA and PEG400 stock solutions were prepared and mixed with deionized water and the clay mineral suspension to prepare 0.2 wt% clay mineral suspensions with various concentrations of PA or PEG400. The samples were sealed in glass vials and rotated end-over-end for 24 h to allow the adsorption process to reach equilibrium. The samples were centrifuged at 5000*g* centrifugal force for 30 min. The supernatant was collected and pH of the supernatant was measured using a PHS-3C PH Meter (Shanghai REX Instrument Factory; China) at room temperature. The clay mineral paste was collected and redispersed in deionized water. This washing procedure was repeated twice. Then, zeta potential of the redispersed clay mineral paste was measured with a Zetasizer 3000 zeta potential analyzer (Malvern Instruments Ltd.; UK). After that, the clay mineral paste was dried, ground and sieved to generate a powder sample. Before each test, the designated sample was kept at 100 °C for 5 h until the weight remained constant. The carbon content in the dried clay-polyamine composite was analyzed using a Euro EA3000 elemental analyzer (Euro Vector S.P.A.; Italy). The adsorbed quantity of PA or PEG400 was calculated based on the carbon content in the clay-polymer composite versus the pure polymer. The data were corrected using the carbon content obtained from the untreated clay sample.

2.4. XRD measurement

The clay and clay-polymer composite solutions were washed twice and centrifuged with 5000*g* centrifugal force for 30 min. Following this, the pastes produced were applied liberally and evenly to glass slides that were subsequently placed in desiccators with a saturated K_2SO_4 solution at ~98% relative humidity (RH) and silica gel at ~0 RH for one month. XRD analysis was used to measure the d-spacings of clay composites at room temperature with an X'Pert-Pro MPD of PANalytical B.V. using a source of Cu-Kα radiation equipped with solid-state detector and operating at 40 KV and 40 mA.

2.5. DRIFT analysis

The DRIFT spectroscopy of the treated samples recorded between 1000 and 2000 cm^{-1} and summations over 30 scans was obtained using a diffuse reflectance accessory 'Collector' from Spectra-Tech with a NEXUS FT-IR Spectrometer (Thermo Nicolet Instrument Corporation; USA). The samples stored in the ~98% RH and ~0% RH desiccators were analyzed, respectively, at room temperature without any KBr dilution. The materials of interest were poured loosely into a sample cup approximately 1 mm deep and 3 mm in diameter and randomly oriented.

2.6. Water, benzene, and heptane vapor adsorption isotherm measurements

The clay composites were dried at 100 °C for 5 h before being ground and sieved to generate the powder samples used for the analytical tests. The water, benzene, and heptane vapor adsorption isotherms in the relative pressure range of 0–1 were measured using an IGA-100B intelligent gravimetric analyzer (Hiden Isochema Instrument Corporation; Warrington, UK). The results represent the average of three adsorption experiments.

2.7. Bulk specific surface area (SSA) by N_2 gas adsorption

N_2 gas adsorption was performed at 77 K in duplicate using an ASAP 2010 device (Micromeritics Instrument Corporation; USA). The SSA was calculated according to the BET equation from seven data points recorded in the relative pressure range of 0.05–0.2. Prior to the measurements, the samples were outgassed for at least 24 h at 105 °C under vacuum to remove adsorbed water.

3. Results and discussion

3.1. Adsorption models and the analysis of PA, PEG400 adsorption on kaolinite, and illite

The Langmuir and Freundlich adsorption models were used, in the same manner as described in the work of Dada et al. (2012), to fit the experimental data (Table 1). Langmuir adsorption model