Water Adsorption on Kaolinite and Illite after Polyamine Adsorption

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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 (SiO₄) of illite. Therefore, PA can be used as inhibitor while drilling shale formations mainly composed of illite, not kaolinite.

Key words: kaolinite and illite hydration; surface tension analysis; water adsorption; polyamine adsorption

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 & Leung^[1] and

27 Zhong *et al*^[2]. As reported by Lal^[3], the amount and type of clay minerals in shale
28 decide the affinity of shale for water and are directly related to wellbore stability. A
29 critical factor in designing drilling fluid is the ability to dehydrate clay minerals to
30 prevent wellbore stability problems while drilling in shale formations^[4, 5]. In recent
31 decades, various drilling fluid additives have been proposed, including relatively high
32 concentrations of inorganic salts, organic salts, and many types of polymeric additives,
33 as reported by Bruton & McLaurine^[6], Rosa *et al*^[7], Caenn & Chillingar^[8], and Souza
34 *et al*^[9]. It has been reported that poly (ethyleneoxide) (PEO) polymers,
35 PEO-PPO-PEO copolymers can adsorb strongly to clay surfaces by hydrogen bonding
36 with silanol groups on the clay surface^[10,11] to decrease hydration of minerals.
37 Nevertheless, as Young & Iskander^[12] concluded, these approaches have exhibited
38 various limitations and remained somewhat unsuccessful with regard to the
39 dehydration of clay minerals. A recent advance was the introduction of water-based
40 drilling fluids containing low molar masses of polyether amine compounds, as
41 proposed by Klein *et al*^[13], Patel *et al*^[14], and Qu *et al*^[15]. Extensive research^[2, 16-18]
42 has been conducted concerning water adsorption on Montmorillonite (MMT) after
43 PA intercalation. However, water adsorption behavior of kaolinite and illite after PA
44 adsorption has not been discussed yet and whether or not PA can dehydrate kaolinite
45 and illite remains unclear. As reported by Šolc *et al*^[19], kaolinite is a dioctahedral
46 layered aluminosilicate of 1:1 type, therefore, each layer has two different surfaces
47 parallel to the (001) plane. First one, tetrahedral, is formed from basal oxygen atoms
48 of the tetrahedral (SiO₄) sheet, while the second one, octahedral, is formed from
49 surface hydroxyl groups of the octahedral (AlO₆) sheet. As reported by Benco *et al*^[20],
50 these hydroxyl groups of octahedral surface are very flexible and allow effective
51 formation of hydrogen bonds with the polar molecules. They have amphoteric

character and are able to act as proton donors and/or acceptors, respectively^[21]. 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^[22], 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.^[23] In one configuration, two hydrogen atoms interact with the surface oxygen to form two hydrogen bonds, whereas in the other configuration, 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*^[24] 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.

Experimental

Clay and clay suspensions

Well-crystallized kaolinite was obtained from clay repository of Maoming Kaolin

Science and Technology CO. Ltd in China. The $<2\ \mu\text{m}$ 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 $100\ ^\circ\text{C}$ 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 $<2\ \mu\text{m}$ 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 $100\ ^\circ\text{C}$ for 5 h until the weight remained constant.

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 molar mass was approximately 400 g/mol and had a typical chemical formula of $\text{CH}_3\text{--[OCH}_2\text{CH}_2\text{]}_x\text{--[OCH}_2\text{(CH}_3\text{)CH]}_y\text{--NH}_2$. PEG400 was purchased from Sinapharm Chemical Reagent CO. Ltd.

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.

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 K₂SO₄ 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-K α radiation equipped with solid-state detector and operating at 40 KV and 40 mA.

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 1mm deep and 3 mm in diameter and randomly oriented.

Water, benzene, and heptane vapor adsorption isotherm measurements

The clay composites were dried at 100 $^{\circ}\text{C}$ 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 to 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.

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 to 0.2. Prior to the measurements, the samples were outgassed for at least 24 h at 105 $^{\circ}\text{C}$ under vacuum to remove adsorbed water.

Results and Discussion

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*^[25], to fit the experimental data (Table 1). Langmuir adsorption model was described by Dada *et al*^[25] in its linear form in equation 1.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (1)$$

where C_e is the equilibrium concentration of adsorbate (mmol/L), q_e is the amount of adsorbate adsorbed on adsorbent at equilibrium (mmol/g), K_L is Langmuir isotherm constant, Q_0 is maximum monolayer coverage capacity (mmol/g). The free energy change of the adsorption reaction is given by equation 2^[26].

$$\Delta G = -RT \ln K_L \quad (2)$$

where ΔG is standard free energy change (KJ/mol), R is the universal gas constant (8.314 J mol⁻¹K⁻¹), and T the absolute temperature (K). The free energy change indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption^[26].

Freundlich adsorption model was described by Dada *et al*^[25] in its linear form in equation 3.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f is Freundlich constant (mmol/g), n is adsorption intensity, C_e is the equilibrium concentration of adsorbate (mmol/L), Q_e is the amount of adsorbate adsorbed on adsorbent at equilibrium (mmol/g).

Langmuir and Freundlich model were used to fit data for PA and PEG400 adsorption on kaolinite or illite.

As is shown in Table 1, the adsorption isotherms of PA on kaolinite and illite fit the Langmuir model better. ΔG for PA adsorption on kaolinite was greater than that on illite, indicating more energetically favorable adsorption on kaolinite. According to the assumptions of the Langmuir adsorption model^[25], it can be known only a monolayer of PA adsorbed on kaolinite or illite. As is shown in Figure 1, with PA

addition, pH of clay mineral solution increased a lot and the solution was highly basic. With PA concentration increasing, more PA adsorbed on illite or kaolinite and pH of the solution exhibited no obvious variation, suggesting no obvious release of OH⁻ or H⁺ during adsorption process. With PEG400 concentration increasing, more PEG400 adsorbed on illite or kaolinite and pH of the solution increased at low concentration, which may be caused by OH⁻ release during the process of adsorption and with greater PEG400 concentration, pH of the solution became similar to that of clay mineral solution. According to Figure 1, no obvious zeta potential change of illite or kaolinite was observed after PA or PEG400 adsorption, suggesting illite or kaolinite charge changed little and no electrostatic interaction was present in the adsorption process. As reported by Xu *et al*^[27], PA NH₂/NH₃⁺ head groups can form hydrogen bonds to oxygen atoms of the tetrahedral (SiO₄) sheet and PA PPO/PEO backbone can adsorb strongly to clay surfaces by hydrogen bonding with silanol groups on the clay surface. As can be inferred that PA adsorbed on the tetrahedral (SiO₄) sheet of illite or kaolinite through hydrogen bonds between PA NH₂/NH₃⁺ and tetrahedral sheet O atoms, or hydrogen bonds between PA O atoms and silanol groups. As reported by Greenwell *et al*^[28], Na⁺ cations in MMT can be closely coordinated by the PA O, N atoms, water molecules, and the clay sheet. Similar to Na⁺, K⁺ in illite may also be coordinated in the same manner. Kaolinite octahedral surface hydroxyl groups can act as proton acceptor or proton donator^[21]. As a result, PA can adsorb onto octahedral surface of kaolinite by hydrogen bonds between PA NH₂/NH₃⁺ and O(H) of kaolinite octahedral surface or between PA O atoms and kaolinite surface hydroxyl group.

The adsorption isotherms of PEG400 on kaolinite, and illite fit Langmuir model better, indicating only a monolayer of PEG400 adsorbed on kaolinite or illite. ΔG for PEG400

adsorption on kaolinite was greater than that on illite, indicating more energetically favorable adsorption on kaolinite.

Similar to interaction between ethanol^[22] or PEO polymers^[10] and clay minerals, H(O) atom of PEG400 can form a hydrogen bond with the surface oxygen of tetrahedral (SiO₄) sheet of illite or kaolinite and O (H) atom can interact with K⁺ in illite. PEG400 can adsorb onto octahedral surface of kaolinite surface by hydrogen bonding between PEG400 (O)H and kaolinite O atoms or between PEG400 O(H) and kaolinite hydroxyl group.

ΔG for PA adsorption on kaolinite and illite was greater than that for PEG400, suggesting more energetically favorable adsorption for PA.

Clay and clay composites d-spacing variation for interlayer adsorption analysis

D-spacing of PA-kaolinite or PA-illite following PA adsorption at ~0 RH% showed that PA adsorption can cause no change of d-spacing of kaolinite or illite. The same results were also observed for PEG-kaolinite and PEG-illite. This suggests PA and PEG400 can't intercalate into the interlayers of kaolinite or illite. As seen in Figure 2, when p/p_0 increased from ~0% to 98%, the interlayer d-spacing for PA-kaolinite, PEG-kaolinite, PA-illite, or PEG-illite exhibited no increase, suggesting little water adsorption in interlayers of PA-kaolinite, PEG-kaolinite, PA-illite, PEG-illite and PA, and PEG400 adsorption caused no change to the water adsorption in interlayers of kaolinite or illite.

Vapor adsorption models and fitting of water vapor adsorption isotherms of clay composites for water adsorption mechanism analysis at different RH

This paper reports on the application of three models to generate isotherms for vapor adsorption on clay composites. The linear form of the Langmuir^[29] adsorption model is described by equation 4.

$$\frac{p}{V} = \frac{1}{V_m} p + \frac{1}{V_m K} \quad (4)$$

where p is the water vapor pressure, V is the volume of water adsorbed by the clay determined by multiplying the mass ratio of adsorbed water by the mass of the clay sample and converting the mass, V_m is the volume (cm^3) of water corresponding to one complete monolayer on the surface of the clay, and K is the adsorption equilibrium constant.

The linear form of the BET model^[30] is described by equation 5.

$$\frac{\frac{p}{p_o}}{\left(1 - \frac{p}{p_o}\right)V} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c} \left(\frac{p}{p_o}\right) \quad (5)$$

where p/p_o is the relative humidity of water vapor expressed as a ratio, V is the volume of water adsorbed by the clay determined by multiplying the mass ratio of adsorbed water by the mass of the clay sample and converting the mass and V_m is the volume (cm^3) of water corresponding to one complete monolayer on the surface of the clay. In the BET model, c is related to the enthalpy of adsorption for the first molecular layer of water and the enthalpy of adsorption for subsequent layers.

The Freundlich isotherm is described by Hatch *et al*^[28] in its linear form in equation 6.

$$\ln \left(\frac{x}{m} \right) = \ln(k) + \frac{1}{n} \ln \left(\frac{p}{p_o} \right) \quad (6)$$

where x/m is the concentration of adsorbed water at equilibrium, in g/g_{clay} , p/p_o is the relative pressure of the water vapor (i.e., the RH), and both k and n are Freundlich constants representing the adsorption capacity and adsorption strength, respectively.

PA-kaolinite and PEG-kaolinite adsorbed more water than kaolinite, indicating PA and PEG400 adsorption can enhance the water adsorption. PA-kaolinite adsorbed

246 more water than PEG-kaolinite, suggesting PA adsorption increase more water
 247 adsorption on kaolinite than PEG400 adsorption.

248 PA-illite and PEG-illite adsorbed less water than illite, indicating PA and PEG400
 249 adsorption can decrease the water adsorption. PA-illite adsorbed similar quantity of
 250 water to PEG-kaolinite, suggesting PA adsorption has similar effect as PEG400
 251 adsorption to decrease water adsorption on illite.

252 According to Zhao^[31], water adsorption isotherm of PEG-kaolinite was similar to that
 253 of Langmuir model and Langmuir model was used to fit the isotherm in addition to
 254 Freundlich and BET models. The linear Freundlich and BET models were used to fit
 255 the rest of water adsorption isotherms. The results were presented in Table 2 and
 256 Figure 3.

257 The water content curves versus RH% were fit to the linear form of the BET model.
 258 The linear region of the BET fit of the experimental data for kaolinite, PA-kaolinite,
 259 PEG-kaolinite were 0 - 40.0%, 0–40.0% and 0 - 41.0%, respectively. The linear
 260 region of the BET fit of the experimental data for illite, PA-illite, PEG-illite were 0 -
 261 25.0%, 0 - 12.6% and 0-50.5 %, respectively. According to Brunauer *et al*^[32], the
 262 major assumptions corresponding to the use of the BET adsorption model are that the
 263 adsorbent surface is composed of uniform, localized sites and that the adsorption at
 264 one site does not affect the adsorption at a neighboring site. Due to the assumptions of
 265 the BET model, nonideal, porous clay minerals with nonuniform adsorption sites
 266 make it difficult to reproduce the experimental data in the nonlinear high RH% region
 267 (Figure 3).

268 The Freundlich adsorption isotherm model has been regarded as an empirical law
 269 designed to represent the isothermal variations in gaseous adsorption on a solid
 270 adsorbent under pressure. In the work of Hatch *et al*^[28], this model was successfully

used to describe the adsorption of water onto non-swelling clay minerals. After plotting the experimental data in the linear format of the Freundlich model, there were two distinct linear regions for kaolinite and PA-kaolinite, indicating two different adsorption regimes. The low RH regimes ranged from 0 to 40.0% for kaolinite while for PA-kaolinite, it occurred at 0-6.4% RH. In the high RH regime, the linear region for kaolinite was from 40.0% to 94.6% and it was from 6.4%-94.6% for PA-kaolinite. The Langmuir and Freundlich models were used to fit the PEG-kaolinite water adsorption isotherms; in the entire RH regime, the isotherms are linear for both models. Therefore, one water adsorption mechanism is present on the PEG-kaolinite surface.

After plotting the experimental data in the linear format of the Freundlich model, there were two distinct linear regions for illite and PA-illite. The low RH regimes for illite ranged from 0 to 6.4 %, but for PA-illite, the linear regions occurred at 0- 12.6% RH. In the high RH regime, the linear region for illite was from 6.4% to 94.8% and it was 12.4%-94.6% for PA-illite. For PEG-illite, in the entire RH regime, the isotherm was linear for Freundlich model. Therefore, only one water adsorption mechanism is present on the PEG-illite surface.

In general, an n value of Freundlich model above one indicates a strong adsorption. The n values for kaolinite, PA-kaolinite, and PEG-kaolinite (4.37, 50.00, and 2.95, respectively) were all above one in the low RH% range, indicating that the clays have a strong affinity. Among those of kaolinite, PA-kaolinite, and PEG-kaolinite, n value for PA-kaolinite was the largest, suggesting PA adsorption can significantly increase the water vapor adsorption on kaolinite in low RH% range. This may result from H bonding between water and N, O, or H atoms of PA adsorbed on tetrahedral kaolinite surface. In the high RH% regimes, the n value drops below one for kaolinite,

indicating H bonding between water molecules became dominant in all the water configurations on kaolinite. However, for PA-kaolinite or PEG-kaolinite, the n values remained above one (3.04 and 2.95, respectively), indicating PA and PEG400 adsorption can increase water adsorption affinity on kaolinite in the high RH% regimes due to H bonding between water and N, O, or H atoms of PA or PEG400. The n value for illite, PA-illite, and PEG-illite is above one in the entire RH% regimes. Compared to n value (11.49) for illite in low RH% regimes, the n values for PA-illite and PEG-illite (3.69 and 1.47, respectively) were much lower, indicating PA and PEG400 adsorption can decrease water adsorption affinity on illite in the low RH% regimes. This may be due to interaction between PA or PEG400 and illite surface oxygen or K^+ to decrease water adsorption sites. In the high RH% regimes, n values for PA-illite, and PEG-illite (1.31, and 1.47, respectively) were similar to that of illite (1.20), indicating similar water adsorption affinity on illite in the high RH% regimes after PA and PEG400 adsorption.

DRIFT spectroscopy for water molecules H-bonding analysis

Although the characteristic FTIR primary amine N-H stretching modes (above 3000 cm^{-1}) were observed in the amines without clay, this region was overlain with complex O-H stretching absorptions from the clay hydroxyl groups and the interlayer water after intercalation, revealing no useful information. As reported by Greenwell *et al.*^[30], the primary amine N-H bond-bending region (1640-1560 cm^{-1}) proved to be more useful during analysis. The FTIR spectroscopy of PA in the absence of clay shows NH_2 bending mode absorptions at 1571 cm^{-1} (Figure 4). Compared to that of illite, the HOH bending vibrations of PA-illite and PEG-illite exhibited no obvious shift. The HOH bending of kaolinite at 98%RH was at $\sim 1641 \text{ cm}^{-1}$ in the DRIFT spectroscopy. Compared to kaolinite, a new band near the HOH bending (~ 1640

cm⁻¹) mode absorptions existed at $\sim 1616\text{ cm}^{-1}$, which should be assigned to be H-bonds between the ammonium groups and the interlayer water. These results suggest an increase in H-bonding interactions commensurate with the creation of interactions between the ammonium H atoms and the siloxane surface oxygen atoms of the aluminosilicate clay layer with additional H-bonds likely to form between the ammonium group and the interlayer water^[30,33]. The HOH bending of PEG-kaolinite exhibited no obvious shift.

Determination of clay composites surface tension for water adsorption thermodynamical mechanism analysis

The surface area of clay minerals was analyzed (Table 2) according to BET equations using N₂ and water adsorption data^[34]. In comparison to the results using N₂ adsorption data, kaolinite, PA-kaolinite, PEG-kaolinite, illite, PA-illite, and PEG-illite surface areas calculated using water adsorption data were lower due to their comparatively low water adsorption capacity. According to Médout-Marère *et al*^[34], the difference between specific surface areas obtained using N₂ and water adsorption data confirms that water molecules are present in the interlayer region. No obvious variation of d-spacing for these clay mineral composites was observed as RH changed from $\sim 0\%$ to 98%, suggesting few water molecules was present in the interlayer region of those samples. Consequently, the N₂ adsorption data was used to determine the surface areas of clay mineral composites.

According to Médout-Marère *et al*^[34], Médout-Marère *et al*^[35], Salles *et al*^[36], and Kwok & Neumann^[37], vapor adsorption measurements enable calculation of the adsorption free enthalpy. The film pressure π_e can be determined using Gibbs' equation, and the amount of water adsorbed at the saturated vapor pressure can be predicted using equation 7.

$$\Delta_{ads}G = -RT \int_{p=0}^{p_e} \Gamma \ln p = -\pi_e \quad (7)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), Γ is the amount adsorbed (mmol/m^2), and p is the vapor pressure (Pa). At saturation, p tends toward a maximum noted as p_e . The surface area of the clay mineral composites can be determined using N_2/BET analysis. After integrating the vapor adsorption isotherm, for high energy solids, $\Delta_{imm}G$ was calculated using equation 8.

$$\Delta_{imm}G = \gamma_{SL} - \gamma_s^o = -\pi_e - \gamma_{lv} \quad (8)$$

where γ_s^o is the surface tension of the solid in equilibrium with its own vapor. The VCG model developed by Van Oss *et al*^[24] is applied to actual solids, as was described in equations 9 and 10.

$$\Delta_{imm}G = \gamma_{lv} - 2[(\gamma_s^{LW} \cdot \gamma_l^{LW})^{1/2} + (\gamma_s^+ \cdot \gamma_l^-)^{1/2} + (\gamma_s^- \cdot \gamma_l^+)^{1/2}] \quad (9)$$

$$\gamma_s^o = \gamma_s^{LW} + 2\sqrt{\gamma_s^+ \cdot \gamma_s^-} \quad (10)$$

where γ_s^{LW} is the Liftshitz–Vander Waals contribution; specifically, the dispersive forces that exist in all cases, γ_s^+ includes the Lewis acid contributions, and γ_s^- includes the Lewis base contributions.

Surface tension of clay mineral composites was calculated and shown in Table 3. Compared with kaolinite, the surface tension of PA-kaolinite and PEG-kaolinite was higher, indicating that water adsorption ability for kaolinite increased after PA or PEG400 adsorption. Among the surface tension components of PA-kaolinite, γ_s^+ increased to be 167.52 mJ/m^2 compared with kaolinite (1.22 mJ/m^2) due to H bonding between water and N, O, or H atoms of PA while γ_s^- is reduced to 89.64 mJ/m^2 compared with kaolinite (132.32 mJ/m^2) because the H bonding between water and hydroxyl groups of octahedral surface may be reduced. Among the surface tension

components of PEG-kaolinite, γ_s^- increased to 419.29 mJ/m² compared with kaolinite because H bonding between water and O or H atoms of PEG400 existed while γ_s^- (4.88mJ/m²) was similar to that of kaolinite. As a result, surface tension of kaolinite increased due to PA or PEG400 adsorption.

Compared with illite, the surface tension of PA-illite and PEG-illite was lower, indicating that water adsorption ability for illite decreased after PA and PEG400 adsorption. Among the surface tension components of PA-illite, γ_s^+ increased to be 112.22 mJ/m² compared with that of illite (82.62 mJ/m²) due to H bonding between water and N, O, and H atoms of PA while γ_s^- is reduced to 13.34mJ/m² compared with that of illite (181.14mJ/m²) due to decreased number of water adsorption on the basal oxygen atom of tetrahedral (SiO₄). Among the surface tension components of PEG-illite, γ_s^- increased to 239.05 mJ/m² compared with illite while γ_s^+ was reduced to be 4.02 mJ/m². Therefore, surface tension of illite decreased due to PA adsorption or PEG adsorption.

Conclusions

PA adsorption can significantly increase water adsorption on kaolinite. After PA adsorption, the water vapor adsorption affinity on kaolinite in entire RH range increased and γ_s^+ of kaolinite surface tension rose due to H-bonds between the ammonium groups of PA and water molecules. PEG400 adsorption can also increase the water adsorption on kaolinite, with more water vapor adsorption affinity on kaolinite in high RH% range and higher γ_s^- of kaolinite surface tension. PA or PEG400 adsorption can decrease water adsorption on illite. After PA adsorption, water adsorption affinity on illite in the low RH% regimes was reduced and γ_s^- of surface tension of illite was decreased, for fewer water molecules were bound to the basal oxygen atom of tetrahedral (SiO₄). Surface tension of illite was reduced after

394 PEG400 adsorption due to lower γ_s^+ because K^+ in illite was coordinated by the O
395 atoms of PEG400 and less bonding between water molecules and K^+ occurred.
396 PA was more effective in the dehydration of MMT^[2,17,18] and illite and exhibited
397 many promising results for use in drilling shale formation mainly composed of MMT
398 or illite. However, for shale formation composed of large amount of kaolinite, PA
399 may be not suitable to be used during drilling.

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Water Adsorption on Kaolinite and Illite after Polyamine Adsorption

Figure 1 Adsorption isotherms of PA, PEG400 on kaolinite, and illite and pH, zeta potential variation during adsorption process

Figure 2 Relationship between clay mineral composites d-spacing at P/P0 of ~0% RH or 98% RH and the PA or PEG 400 adsorption capacity

Figure 3 Comparison of clay mineral composites experimental water adsorption data and fitting data using Langmuir, BET and Freundlich model

Figure 4 DRIFT spectroscopy of kaolinite and illite before and after PA or PEG400 adsorption at different RHs.

Water Adsorption on Kaolinite and Illite after Polyamine Adsorption

Table 1 Fitting results of the PA, PEG400 adsorption isotherms on kaolinite, and illite								
adsorbent	Clay mineral	Langmuir model constants				Frendlich model constants		
		Q ₀ (mmol/g)	K _L	R ²	ΔG(KJ/mol)	K _f	n	R ²
PA	kaolinite	0.00040	261.62	0.993	-13.79	0.000031	4.39	0.867
	illite	0.00042	135.15	0.995	-8.08	0.00077	4.13	0.898
PEG400	kaolinite	0.00014	176.39	0.980	-12.82	0.0015	4.02	0.716
	illite	0.00023	57.94	0.988	-6.69	0.00059	2.41	0.912

Table 2 Fitting parameters of Langmuir, BET, and Freundlich models applied to water adsorption isotherms

clay composites	surface area (m ² /g)	water adsorption models	RH Range (%)	R ²	Langmuir model		BET model		Freundlich model constants	
					V _m	K	V _m	c	k	n
kaolinite	26.49 (N ₂ /BET)	BET	0-40.0	0.999			0.0010	328.88		
	3.73(H ₂ O/BET-low RH)	Freundlich	0-40.0	0.971					0.0020	4.37
			40.0-94.6	0.982					0.0037	0.94
PA- kaolinite	29.40 (N ₂ /BET)	BET	0-40.0	0.995			0.006	277.5		
	21.69(H ₂ O/BET-low RH)	Freundlich	0-6.4	0.968					0.0058	50.00
			6.4-94.6	0.991					0.013	3.04
PEG- kaolinite	25.22 (N ₂ /BET)	Langmuir	0-91.3	0.999	0.0058	0.0022				
	9.65(H ₂ O/BET-low RH)	BET	0-41.0	0.972			0.0027	72.06		
		Freundlich	0-91.3	0.923					0.0055	2.95
illite	12.30 (N ₂ /BET)	BET	0-25.0	0.994			0.0020	110.52		
	7.30(H ₂ O/BET-low RH)	Freundlich	0-6.4	0.995					0.0022	11.49
			6.4-94.7	0.980					0.011	1.20
PA- illite	13.59 (N ₂ /BET)	BET	0-12.6	0.973			0.00002	32.78		
	2.33(H ₂ O/BET-low RH)	Freundlich	0-12.6	0.976					0.0012	3.69
			12.6-94.6	0.980					0.0050	1.31
PEG- illite	11.83 (N ₂ /BET)	BET	0-50.5	0.994			0.0019	13.90		
	5.25(H ₂ O/BET-low RH)	Freundlich	0-94.7	0.982					0.0062	1.47

Table 3 The surface tension components of illite and kaolinite before and after PA or PEG400 adsorption (SD error)

	γ_s^0 (mJ/m ²)	γ_s^{LW} (mJ/m ²)	γ_s^+ (mJ/m ²)	γ_s^- (mJ/m ²)
kaolinite	57.65±1.28	32.24±0.27	1.22±0.09	132.32±1.04
PA-kaolinite	289.11±5.55	44.03±0.29	167.52±3.05	89.64±2.08
PEG-kaolinite	115.43±1.75	24.98±0.10	4.88±0.08	419.29±1.56
illite	328.85±10.16	84.18±1.29	82.62±2.04	181.14±6.08
PA-illite	151.55±4.63	74.17±1.56	112.22±1.48	13.34±0.87
PEG-illite	147.88±4.01	45.78±1.12	10.05±0.48	239.05±2.21