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Interactions between Smectites and Polyelectrolytes

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Abstract

Interactions between smectite and polyelectrolyte play an essential role in exclusive adsorption, flocculation, and thixotropic properties of aqueous smectite/polyelectrolyte system. The materials are widely used in many industries such as drilling fluids, pharmaceuticals, paints and dyes, ceramics, papermaking and water treatment. This review focuses on the interaction between different types of polyelectrolytes and smectite, and their applications in flocculation and industrial wastewaters. The effect of several parameters related to polyelectrolyte such as charge density, charge type and molecular weight, as well as to smectite such as type, particle size, composition, pH and concentration in the aqueous system, were examined. The interactive forces between smectite and polyelectrolyte including hydrophobic interaction, ion binding, hydrogen bonding, van der Waals forces and electrostatic were thoroughly discussed. The interactive forces between smectite and cationic polyelectrolyte, anionic polyelectrolyte and amphoteric polyelectrolyte influence the flocculation of colloidal smectite-polyelectrolyte dispersions such as settling and floc dispersion. However, the interaction between smectites and polyelectrolytes and their subsequent behaviors in adsorption, flocculation, and thixotropy along with inherent mechanisms have not yet fully understood. Future in-depth work on interactions between smectites and polyelectrolytes has great implications for developing functional materials and expanding applications of other polyelectrolyte/ smectite mineral system.

Keywords: Smectites; Polyelectrolytes; Interaction; Adsorption; Flocculation; Rheology.

1. Introduction

Smectite refers to a family of layered aluminosilicate that possesses peculiar cation exchange capacity (CEC), surface reactivity and adsorption. Typically, smectite's layered structure is composed of -Si-O-Mg (Al or Li)-O-Si- layers separated by hydrated cations (e.g. Na^+ , NH_4^+ , Li^+ , K^+ and Mg^{2+}) in the interlayer space where each layer consists of two Si-O-Si tetrahedral sheets sandwiching an octahedral sheet (**Fig. 1a**). According to how much the center space of the octahedron is occupied with metal cation, clay minerals in smectite family are divided into dioctahedral ones such as montmorillonite, and trioctahedral one such as saponite and hectorite (Bergaya and Lagaly, 2013; Ismadji et al., 2015). A commercially available synthetic hectorite is known as laponite[®]. Montmorillonite, saponite and hectorite have physical and chemical properties in swelling and delamination. The layers have amphoteric properties and carry a permanent negative charge and localized positive charges (or negative charges at high pH, $\text{pH} > 9$) (Sposito et al., 1999; Dawson and Oreffo, 2013) (**Fig. 1b**). The layers and relevant smectite particles readily give rise to interactions between the smectite particle surfaces and polyelectrolytes including hydrogen bonding, hydrophobic interactions, ion binding, van der Waals forces, electrostatic attraction, and electrostatic repulsion (Song et al., 2010).

Fig.1. Smectite and its surface properties (a) The structure of smectite: layer is composed of two tetrahedral silica sheets sandwiching an octahedral sheet (with Al^{3+} , Li^+ , Mg^{2+} , and Fe^{2+} or Fe^{3+} as octahedral cations). Charge deficiencies in the octahedral and/or tetrahedral sheets yield a negative surface charge balanced by exchangeable cations in the interlayer space. (b) Smectites possess a permanent negative surface charge arising from isomorphic substitutions in the crystal structure and a pH dependent edge charge from unsatisfied valences in the disrupted

crystal lattice. Reprinted from. (Reprinted by permission from John Wiley and Sons: (Dawson and Oreffo, 2013), copyright 2013).

Smectites and polyelectrolytes are widely used in pharmaceuticals, drilling fluids, water treatment, ceramics, papermaking, paints and dyes (Carli et al., 2015; Xiao et al., 2016). Polyelectrolytes are a class of specific polymers of which repeating units bear electrolyte groups. They can be categorized into cationic, anionic and amphoteric polyelectrolytes. These polyelectrolytes can coexist with smectite in water and can vary their properties such as the adsorption, flocculation rheology and thixotropy primarily due to interaction between aqueous smectite and polyelectrolytes (Kim and Carty, 2016; Shaikh et al., 2017a). Hence, the interaction between smectite and polyelectrolyte has captured many researchers' interest and attention. The relevant applications and implications have been significantly widened (**Fig. 2b**).

The interactions between smectite and polyelectrolyte depend on the physical and chemical properties of smectites, polyelectrolytes, and medium. The polymeric structure of the polyelectrolyte, the chemical structure of monomer in the backbone, the charge distribution in monomeric groups and their distribution along the polyelectrolyte chains, are influential (Shaikh et al., 2017b). The polyelectrolyte concentration in water, molecular weight and functional groups are also critically important for the interactions between smectite and polyelectrolyte. In addition, the smectite–polyelectrolyte interactions in aqueous medium also depend on the size, shape, surface charge, and concentration of the smectite particles. Besides the pH and the temperature, the medium also has an impact on the smectite–polyelectrolyte interactions in water (Alemdar et al., 2005; Oliyai et al., 2015).

Addition of polyelectrolytes into aqueous smectite dispersion remarkably modifies the surface properties of the smectite and consequently changes the smectite particle–particle interactions. This might lead to exclusive adsorptive (Abdullah et al., 2013), flocculent (Mansri et al., 2019), rheological and thixotropic properties (Abu-Jdayil, 2011; Aalaie, 2012; Aydin et al., 2015). These interactions between smectites and polyelectrolytes can be utilized in pharmaceuticals (Viseras et al., 2010), oil and gas drilling fluids (Falode et al., 2008; Karagüzel et al., 2010; Vipulanandan and Mohammed, 2014), paints and dyes (Wang et al., 2014), paper-making industry (Zhang et al., 2013b), environmental remediation (Ismadji et al., 2015) and water treatment of smectites (Lee et al., 2014; Santhosh et al., 2016). For example, smectites as adsorbents and polyelectrolytes as flocculants are used for separation to treat industrial wastewaters (Marchuk et al., 2016) due to their cost- effectiveness (Sievers et al., 2015), versatility (Silva et al., 2016), high efficiency (Vereb et al., 2017) and relatively low toxicity (Van Haver and Nayar, 2017). In drilling fluid, smectite nanoparticles, along with polyelectrolytes, has been widely used to improve the rheology and filtration properties (Yu et al., 2018; Zhou et al., 2016).

It is evident that interactions between smectites and polyelectrolytes are of great scientific and technological significance (**Fig. 2a**). The study of such interactions has become greatly

multidisciplinary involving colloid and interface science, rheology, materials science, mineralogy and chemistry. Current research primarily focuses on the interaction between smectites and polyelectrolytes. Studies clearly reveal that the adsorption of polyelectrolytes to smectites affects their structure and chemical properties, flocculation and rheological behavior. Traditionally, the interaction between smectites and polyelectrolytes is used for developing adsorbent, flocculants, rheological additives and catalysts (**Fig. 2b**). Recently, this interaction is increasingly used for making hierarchical materials, tissue engineering materials, biosensors and drug carriers. For example, halloysite-polyelectrolytes interactions and illite-polyelectrolytes interactions has been intensively used for making biomedical composites (Zhao et al., 2015; Zhen et al., 2016; Tarasova et al., 2019).

Fig. 2. (a) Annual number of peer-reviewed papers (published from 2009 to 2019) relevant to the topic of interactions between polyelectrolytes and smectites. Data from Web of Science Core Collection and by searching for terms in topic: smectites, polyelectrolytes and interactions; (b) Data from Web of Science Core Collection and by searching for terms in topic: montmorillonite, polyelectrolytes and application, saponite, polyelectrolytes and application, hectorite or laponite, polyelectrolytes and application, and Results Analysis according to peer-reviewed scientific papers indexed in Web of Science Core Collection (published from 2009 to 2019).

In the present paper, the interactions between smectites (montmorillonite, saponite, and hectorite) and polyelectrolytes (cationic, anionic, and amphoteric) are overviewed. The insights into the effects of the interactions on adsorption, flocculation, and rheology and related applications are critically examined. Then, the existing problems and challenges are analyzed and discussed.

2. Cationic polyelectrolytes

2.1 Montmorillonite

Montmorillonite layer possesses negative charges while the layer edges have variable charges at different pH whereas cationic polyelectrolytes bear positively charged functional groups. Kraft lignin-acrylamide (KAD), polyacrylamide (PAM), tertiary amine methacrylate (TAM), poly(acrylamide-co-(N-octyl-4-vinylpyridinium bromide)) and chitosan are typical cationic polyelectrolytes which can readily interact with smectite (**Fig. 3**). The interactions subsequently influence the adsorption, flocculation and rheological behavior of montmorillonite in water (**Table 1**). Generally, cationic polyelectrolytes induce flocculation via charge neutralization, patching, polymer bridging, or combination of these interactions (Petzold and Schwarz, 2013, Zhou et al., 2019a). Charged polyelectrolytes adsorbed on the surface of micro or nano form of montmorillonite mainly through electrostatic interactions (Shaikh et al., 2017a). The amount of adsorption mainly depends on the surface charge density of montmorillonite and the type of charge of polyelectrolyte (Sakhawoth et al., 2017). Montmorillonite-polyelectrolyte system is mostly used in agriculture (Ismadji et al., 2015), construction, drilling fluid (de Figueiredo et al., 2014), and paints (de Figueiredo et al., 2014). It is also known to use in other fields such as pharmaceuticals (Viseras et al., 2010), environmental remediation (Ismadji et al., 2015) and water treatment (Beisebekov et al., 2014, Lee et al., 2014).

(a) Kraft lignin-acrylamide (Hasan and Fatehi, 2018)

(b) polyacrylamide (Craciun et al., 2015)

(c) Tertiary Amine Methacrylate (Alemdar and Bütün, 2005) (d) poly(acrylamide-co-(N-octyl-4-vinylpyridinium bromide)) (Mansri et al., 2019)

(e) Chitosan (Postnova et al., 2015)

(f) xylan-METAC (Wang et al., 2016)

Fig. 3. Chemical structures of the cationic polyelectrolytes used in recent studies relevant to the interaction between smectites and non-ionic polyelectrolytes

The surface charge density of montmorillonite and the molecular weight of cationic polyelectrolytes influence the adsorption and flocculation behavior of aqueous montmorillonite dispersion (Shaikh et al., 2017b). The floc sizes increased with increasing surface charge density and molecular weight of cationic polyelectrolytes. For example, interactions between the two kinds of cationic kraft lignin-acrylamide (KAD), of molecular weight 168,200 g/mol (KAD-1) and 103,000 g/mol (KAD-2) with montmorillonite has proved to be interact differently (Hasan and Fatehi, 2018). Although the two KADs had similar charge density (1.15 mmol/g), KAD-1, with a higher molecular weight, resulted in higher adsorption and bigger floc sizes than KAD-2. The KAD-1 and KAD-2 reached the saturation adsorption levels of 1.08 and 0.99 mg/g on montmorillonite, respectively. The KAD-1 would have a longer chain, therefore higher chance for tail and loop configuration on montmorillonite particles during adsorption of particles from the dispersion, which would in turn promote KAD-1 bridging. In addition, higher the charge density

of cationic KAD, greater is the adsorption and flocculation. For instance, an increase in the charge density of a cationic KAD (KAD-1=2.13 meq/g, KAD-2=1.29 meq/g) promoted its adsorption onto montmorillonite due to stronger electrostatic interactions between KAD and montmorillonite particles. In case of montmorillonite, the adsorption for KAD-1 and KAD-2 was 1.83 and 1.63 mg/g, respectively. Similar phenomenon have been observed in the interactions for other polyelectrolytes interacting with montmorillonite in water. (Wang et al., 2016) The flocculation efficiency of cationic xylan-2-(methacryloyloxy)ethyl trimethyl ammonium chloride (xylan-METAC) copolymers with different charge density and different molecular weights were compared where CMX1 and CMX2 has +1.8 and +2.4 meq/g with their molecular weights 88986 and 102545 g mol⁻¹, respectively. CMX2 was acted as a more efficient flocculant than CMX1 as CMX2 adsorbed and removed more efficiently by montmorillonite particles from the aqueous dispersion. The adsorption of CMX1 and CMX2 was 0.73 and 0.85 mg/g on montmorillonite particles, respectively. It was reported that polymers with a higher charge density would adsorb more on clay particles. CMX2 also changed the zeta potential and turbidity of the aqueous montmorillonite dispersion more remarkably than CMX1, which was attributed to its higher charge density and molecular weight.

In addition, different polyelectrolytes have different interactions with montmorillonite in water. Polyelectrolytes such as 3,6-ionene (Campos and Tcacenco, 2015) interaction with the montmorillonite surface takes place by Coulombic forces between the positively charged sites of 3,6- and negatively charged montmorillonite surface. The 3,6-ionene caused the basal spacing of the commercial montmorillonite to increase from 1.5 to 3.5 nm. Polyelectrolytes such as polycationic quaternary amine polymer F25 (Blachier et al., 2009), polyethyleneimine (PEI) (Oztekin, 2017) and poly(acrylamide-co-(N-octyl-4-vinylpyridinium bromide)) (AM5/VP5C8Br) were used to flocculate aqueous montmorillonite dispersion. The interactions between AM5/VP5C8Br and montmorillonite particles in dilute aqueous dispersions (Mansri et al., 2019) allowed the adsorption of the montmorillonite particles on the AM5/VP5C8Br chains, that occurred initially by the hydrophobic interaction. The electrostatic attraction between the positively charged sites on the AM5/VP5C8Br and the negative montmorillonite particles dispersion can eventually lead to patches and flocculation. The AM5/VP5C8Br chain conformation was affected by the pH of medium, thereby influencing the flocculation. The AM5/VP5C8Br chains adopted a flat conformation at pH < 4 due to important repulsive electrostatic forces by the cationic 4VP moieties (**Fig.4**). In the range of 4 < pH < 8, the charge density of the AM5/VP5C8Br related to acid addition is very low, preventing the extension of the AM5/VP5C8Br chains. At pH > 8, a turbidity removal becomes smaller than for pH < 4 and 4 < pH < 8, which was related to the compact pelote conformation adopted by the AM5/VP5C8Br chains. The hydroxide groups (OH) of aqueous medium played an important role in screening phenomena of positively charged sites on the AM5/VP5C8Br chains. Thus, the flat conformation

assists the formation of flocs by adsorption between AM5/VP5C8Br and montmorillonite particles, where the best flocculation was observed for dilute aqueous dispersions at pH <4.

Fig.4 Proposed conformation of the AM5/VP5C8Br chain at different pH in aqueous medium. (Reprinted by permission from Taylor & Francis: (Mansri et al., 2019), copyright 2019).

2.2 Saponite

Chitosan, a natural linear cationic polysaccharide containing free amino groups, has been intercalated into saponite (Shchipunov et al., 2012a; Shchipunov et al., 2012b; Budnyak et al., 2016; Mishchenko et al., 2016). Budnyak et al. (2016) demonstrated an effective way to produce chitosan-saponite composites by impregnating 20g of saponite in 285ml of chitosan solution, with a concentration of 7 mg/ml in acetic acid (pH 2.6). Chitosan has higher affinity for the surface of saponite due to the interaction between protonated amino groups of chitosan and dissociated saponite hydroxyl groups in water. The interactions also involve the electrostatic interaction and hydrogen binding (**Fig. 5a**). The interaction between saponite and chitosan gradually increased the viscosity and finally hydrogelation, leading to forming saponite/chitosan hydrogel nanocomposites (**Fig. 5b**) (Zhou et al., 2019b). Budnyak et al. (2016) studied the adsorption properties of chitosan-saponite composites for metal ions such as Cu(II), Zn(II), Fe(III), Cd(II), and Pb(II). The results shows that the interactions between saponite and cationic chitosan improved the adsorption of cations Cu(II), Zn(II), Fe(III), Cd(II), and Pb(II) due to excellent sorption properties of chitosan-saponite composites and available adsorption sites in the interlayer space, large surface area with narrower channels inside. Therefore, chitosan-saponite composites were employed to adsorb the heavy metals and toxic dyes in wastewater treatment.

Fig. 5. (a) Schematic diagram showing that the interactions between chitosan and saponite involve the electrostatic interaction and hydrogen bonding (Budnyak et al., 2016); (b) Schematic drawing of main stages of formation of monolithic hydrogel by chitosan and saponite. (Shchipunov et al., 2009) – Reproduced by permission of The Royal Society of Chemistry.

Table 1

Recent typical studies on the interaction between smectites and cationic polyelectrolytes

Cationic polyelectrolytes	Smectite	Conditions	Interaction	References
PAM	Montmorillonite	PAM: 2.0% v/v; Montmorillonite: 100 ml; The system: pH 9.	Strong adsorption affinity; Cause montmorillonite surface charge reversal; Floc sizes increased.	(Shaikh et al., 2017b)
AM5/VP5C8Br	Montmorillonite	AM5/VP5C8Br: 1–5 ppm; Montmorillonite: 400 ml; The system: pH 2.	Flocculation; Hydrophobic.	(Mansri et al., 2019)
xylan–METAC	Montmorillonite	Xylan–METACL: 2 or 3 mol mol ⁻¹ ; Montmorillonite concentration: 1 g L ⁻¹ ; pH 7.	Zeta potential and turbidity were changed; Higher charge density and molecular weight.	(Wang et al., 2016)
Chitosan	Saponite	Chitosan content: 285 ml; Saponite content: 20 g; Acetic acid concentration: 7 mg/ml; pH 2.6.	Electrostatic; Hydrogen binding.	(Budnyak et al., 2016)
RhPEG	Saponite	RhPEG content: 0.05–0.25wt%; Saponite 0.1 g L ⁻¹ ;	Irreversible adsorption; Two types of bonding between the	(Sas et al., 2017)

Poly(NIPAm)	Saponite	Saponite/Poly(NIPAm: 11wt%.	Dispersion; Adsorption.	(Nakamura and Ogawa, 2013)
PS	Na- saponite	PS: 1.2 g in 100 ml water; Saponite content: 4–30 wt%; Co-stabilizer: hexadecane and AIBN.	Formation of asymmetric PS/saponite composite nanoparticles; Hydrophobically.	(Tong and Deng, 2013)

AM5/VP5C8Br: poly(acrylamide-co-(N-octyl-4-vinylpyridinium bromide))
PAM: Polyacrylamide
poly(NIPAm): poly(N-isopropylacrylamide);
PS: polystyrene;
RhPEG: rhodamine B (RhB) modified polyethylene glycol (PEG);
xylan–METAC: xylan-2-(methacryloyloxy)ethyl] trimethyl ammonium chloride

3. Anionic polyelectrolytes

3.1 Montmorillonite

Anionic polyelectrolytes are bearing negatively charged functional groups, commonly $-\text{COO}^-$, $-\text{O}-\text{SO}_3^{2-}$, $-\text{SO}_3^{2-}$, $-\text{O}-\text{CS}^{2-}$, $-\text{O}-\text{PO}_3^{2-}$, $-\text{PO}_3^{2-}$. The interaction between smectites and anionic polyelectrolytes seems impossible as both entities are bearing negatives charges. Yet researchers have explored that the interactions of smectite and anionic polyelectrolyte. The anionic polyelectrolyte includes copolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid (AM-AMPS) and a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and N-Vinylpyrrolidone (AM-AMPS-NVP) (Ahmad et al., 2018), anionic polyacrylamide (APAM) (Heller and Keren, 2002), sulfonated polyacrylamide (SPA) (Oliyaei et al., 2015), anionic polyacrylamide–acrylate copolymer (Mpofu et al., 2004) (**Fig. 6**). The interactions can be divided into two types: an electrostatic interaction between the anionic polyelectrolyte chains and the positive charges on the edges of the smectite particles; a repulsive interaction between the negative smectite charge and the polyelectrolytes (Gumfekar and Soares, 2018). The smectite-anionic polyelectrolyte interactions in aqueous dispersion depend on molecular weight, polyelectrolyte concentration, size, surface charge and concentration of the smectite particles in water (Shaikh et al., 2017b).

(c) Sulfonated polyacrylamide (Ehsan et al., 2017)

(d) Polymethacrylic acid

(e) Polyvinyl sulfonic acid

(f) Poly(styrenesulfonic acid)

(g) Styrene-maleic acid copolymer

(h) Methyl vinyl ether-maleic acid copolymer

(i) Acrylic acid-maleic acid copolymer

(j) Polyphosphoric acid

Fig.6. Chemical structures of the non-ionic polyelectrolytes used in recent studies relevant to the interaction between smectites and non-ionic polyelectrolytes

The interaction between smectites and anionic polyelectrolytes is often used for altering adsorption, flocculation, and rheological behavior (Kafashi et al., 2017; Diouri et al., 2018) (Table 2). The addition of anionic polyelectrolyte into water-based drilling fluids can compensate for deficiencies of montmorillonite-based drilling fluids that can lead modification of the rheological properties. For example, polyanionic cellulose (PAC) (Kelessidis et al., 2013), sodium carboxymethyl cellulose and xanthan gum (XG) (de Souza et al., 2017) have been added into water-based drilling fluids to obtain the desired rheological properties. The addition of copolymer and terpolymer, a copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid

(AM-AMPS) (P1) and a terpolymer of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and N-vinylpyrrolidone (AM-AMPS-NVP (P2)) into aqueous montmorillonite dispersion can enhanced their rheological properties (viscosity and shear stress). The montmorillonite/polymer dispersions has higher viscosity and shear stress compared to the montmorillonite dispersions at 1/s shear rate at 25°C in deionized water (Ahmad et al., 2018). And the montmorillonite/P2 dispersion has higher viscosity and shear stress compared to the montmorillonite/P1 dispersion at 1/s shear rate at 25°C in deionized water. This is because the polymer P2 has three different moieties with negative charges along the backbone whereas the polymer P1 has two moieties with negative charges (**Fig.7**). Therefore, there were stronger electrostatic repulsive interactions between polymer P2 and montmorillonite layers than for polymer P1, this stronger electrostatic repulsion gives the montmorillonite/P2 dispersion better rheology. In addition, Chalah et al. (2018) shows addition of the anionic polyelectrolyte xanthan gum into the 5% aqueous montmorillonite dispersion increased the viscosity of the water-montmorillonite dispersion. These recent findings prove the rational usage of different types of anionic polyelectrolytes additives in water-based drilling muds.

Fig. 7. Schematic diagram of montmorillonite/Polymer (P2) interactions. Reprinted from (Ahmad et al., 2018), copyright (2018), with permission from Elsevier.

High molecular weight and high degrees of hydrolysis of anionic PAM in aqueous montmorillonite dispersion could be more effective in stabilizing montmorillonite aggregate than those with lower molecular weight and degrees of hydrolysis (Heller and Keren, 2002). Three possibilities for the interaction between PAM and montmorillonite particles may existing: (i) by anion exchange between the surface hydroxyl group of the montmorillonite and the carboxyl anion of PAM; (ii) by hydrogen bonding between the surface hydroxyl group and C = O of the PAM; (iii) by making a bridge involving divalent ions derived from electrostatic forces. Güngör (2001) found that in FT-IR spectra, PAM exhibit adsorption bands at 1660 and 3450 cm^{-1} (N-H,

strong bond), while PAM with Ca-montmorillonite and Na-montmorillonite shows additional adsorption bands at 1653 and 3433 cm^{-1} which indicating that PAM molecules and montmorillonite particles were interacting. The PAM molecule were loosely bound and interacts near the surface and/or into the interlayers of the montmorillonite. The dominant electrostatic repulsions between the anionic PAM functional groups and the negative surface charge of montmorillonite were responsible for the lower adsorption affinity of anionic PAM towards montmorillonite particles (Barany et al., 2009; Shaikh et al., 2017b). The same amounts of anionic PAM was added to the aqueous Na-montmorillonite dispersion and the aqueous Ca-montmorillonite dispersion under the same conditions (2% Ca- and Na- montmorillonite–water systems), the aqueous Na-montmorillonite dispersion and the aqueous Ca-montmorillonite dispersion showed different rheological behaviors (N. Güngör, 2001). The anionic PAM has a flocculation effect in the aqueous Ca-montmorillonite dispersion whereas it has a de-flocculation effect in aqueous Na-montmorillonite dispersion as Ca^{2+} has a strong tendency to form face/face contacts, which can cause defects in the edge (+)/face (-) network that promote its fragmentation. In the absence of Ca^{2+} , the “house of cards” would decompose at edge charge densities, so Ca^{2+} ions can help the formation of bridging flocculation.

PAM/montmorillonite dispersion has important role in several industries, including paper, water treatment, enhanced oil recovery and drilling (Khoshniyat et al., 2012). Sulfonated polyacrylamide (SPA) has higher thermal stability than standard hydrolyzed PAM and is commercially used as stabilizer in oil fields up to 120°C (Oliyai et al., 2015). The stability of aqueous Na-montmorillonite dispersions in the absence of SPA, were due to the electrostatic interactions. The preaseance of SPA, modified the Na-montmorillonite particle–particle interactions as few SPA chains can be adsorbed onto the Na-montmorillonite particles surface via hydrogen bonds between the oxygen atoms of Na-montmorillonite and the protons of the amide groups of SPA, resulting in steric stability. However, there were repulsion between the negative layers of Na-montmorillonite and the anionic groups of SPA, therefore, the two interactions, adsorption and repulsion, result in dispersion stability.

Earlier, anionic polyacrylamide–acrylate copolymer proved effective in flocculating montmorillonite dispersions (Mpofu et al., 2004). Both montmorillonite particles and PAM molecules are negatively charged ($\text{pH}=7.5$), and the main driving force for adsorption was hydrogen bonding between the silanol and aluminol OH groups at the montmorillonite particle surfaces, particularly the edge faces and the amide ($-\text{CONH}_2$) groups (Lewis base) of the copolymer. The longer the length of the copolymer, the higher flocculation efficiency of the montmorillonite dispersion. The concentration of the anionic polyacrylamide–acrylate copolymer flocculant increases, the size of the particles decreases, and the affinity and adsorption density increase. Hence, polyacrylamide–acrylate copolymer is normally used as a flocculant in industry for montmorillonite dispersions.

Table 2

Recent typical studies on the interactions between smectites and anionic polyelectrolytes

Anionic polyelectrolytes	Type of smectite	Conditions	Interaction	References
PAM	Montmorillonite	PAM: 2.0% v/v; Montmorillonite: 100 ml; The system: pH 9.	Lower adsorption capacities; Floc sizes increased.	(Shaikh et al., 2017b)
AM-AMPS	Montmorillonite	Montmorillonite content: 5 wt%; AM-AMPS content: 0.25 wt%; Temperatures: 25°C, 85°C	Electrostatic repulsive forces; Enhanced the rheological properties.	(Ahmad et al., 2018)
AM-AMPS-NVP	Montmorillonite	Montmorillonite content: 5 wt%; AM-AMPS-NVP content: 0.25 wt%; Temperatures: 25°C, 85°C	Electrostatic repulsive forces; Enhanced the rheological properties.	(Ahmad et al., 2018)
SPA	Montmorillonite	Montmorillonite content: 0.5~3 wt%; SPA content: 0~0.4 wt%.	Increased the Z-average particle sizes.	(Oliyai et al., 2015)
SPA	Hectorite	----	Hydrogen bonding; Ionic interaction.	(Ehsan et al., 2017)
PAAS	Hectorite	Hectorite content: 10 wt%; PAAS content: 3.5 wt% ; Molecular mass: 2.3×10^5 ; Dispersant: 0.25 wt% TSPP;	Adsorbed.	(Takeno and Nakamura, 2019)

AM-AMPS: acrylamide and 2-acrylamido-2-methylpropane sulfonic acid

AM-AMPS-NVP: acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and N-Vinylpyrrolidone

PAM: Polyacrylamide

PAAS: Polyethylene oxide

SPA: Sulfonated polyacrylamide

3.2 Saponite and hectorite

Saponite can easily delaminate in water to form a sol or hydrogel and has been widely used in many products ranging in cosmetics, paints and adhesives (Zhou et al., 2019b). In most cases of formation of saponite sols or hydrogels, the key point is the interactions between saponite particles

and polyelectrolytes in their system. However, details on such interactions remain unclear. Li et al. (2019a) studied the rheological behaviors of saponite sol-gel system, and reveal the interaction between saponite particles and the sodium polyacrylate (NaPA) by preparing saponite hydrogels with polyelectrolyte NaPA (**Fig.8a**). It was found that the NaPA incorporated saponite hydrogel was transformed to a sol due to the destruction of the house-of-card structure, and the saponite was well dispersed (**Fig. 8aVI**). A possible mechanism was also reported to explain the transformation of saponite hydrogel to sol. Firstly, the PA^- instantaneous polarized in the electric field, which was formed near the saponite particles due to the surface charge. Then, it enters the saponite hydration layer to replace some of the original hydrated ions (Gong et al., 2018). Further, a strong chemical bond formed between the polarized PA^- and the saponite particles due to stronger electrostatic attraction (**Fig. 8bII**). They also found that the stacking order of saponite particles was promoted after drying from the saponite-NaPA dispersion (**Fig. 8aVII**). This work suggested interactions between saponite particles and polyacrylates which might provide a help to tune the rheological performance of saponite sol-gel products and explore more functional saponite-based nanomaterials (Del Gaudio et al., 2018).

Fig.8. (a) Schematic illustration of saponite dispersion with/without added NaPA and reaggregation after drying: (I) Saponite dispersed in water to form (II) Saponite dispersion and (III) Saponite hydrogel; (V) interaction of the saponite hydrogel with polarized PA to form (VI) Saponite NaPA dispersion; (IV) Saponite-control and (VII) Saponite-NaPA reaggregated from Saponite hydrogel and Saponite-NaPA dispersion, respectively; (b) Illustrations of the interactions between saponite particles and NaPA: (I) Chemical formula of NaPA and schematic structure of NaPA; (II) interaction between aggregated saponite particle and NaPA. Reprinted with permission from (Li et al., 2019a). Copyright 2019 American Chemical Society.

Hectorite, in particular the synthetic one, has been widely used in hydrogels (Du et al., 2016). In recent years, hydrogels with mechanical toughness have important application prospects in the fields of tissue engineering, health care, electronic skin, and soft robots, which have attracted great attention from researchers (Takeno and Nakamura, 2013; Takeno and Kimura, 2016; Takeno and Nakamura, 2019). Takeno and Kimura (2016) found that hydrogels prepared by simply blending an anionic NaPA with synthetic hectorite including a dispersant, tetrasodium pyrophosphate (TSPP), significantly improve the mechanical toughness of the resultant synthetic

hectorite/NaPA/TSPP gel. Due to the addition of TSPP, synthetic hectorite particles were homogeneously dispersed in the gel, since TSPP prevented formation of house-of-cards structure by adsorption of pyrophosphate anions onto the positively charged edge of hectorite particles (**Fig. 9a**). Thus, the structural homogeneity in the hydrogel causes a significant increase of mechanical properties. In the case of anionic NaPA, carboxylate anion is also adsorbed on positively charged edge of synthetic hectorite particle (Takeno and Nakamura, 2013).

Molecular weight of NaPA in the synthetic hectorite/NaPA/TSPP gel system affects the tensile properties (Takeno and Kimura, 2016). Adding high molecular weight NaPA polyelectrolyte will improve the mechanical properties of hectorite / NaPA / TSPP gel system because the electrostatic interaction of high molecular weight NaPA with hectorite particles was stronger than for low molecular weight. In the case of the gel with high molecular weight NaPA, NaPA chains were capable of bridging adjacent synthetic hectorite particles. The long chain can keep cross-linking adjacent synthetic hectorite particles even under high elongation (**Fig.9b**). However, in the case of the gel with low molecular weight NaPA, when the gel was stretched, the short chains were not capable of bridging adjacent synthetic hectorite particles. Therefore, gel with low molecular weight NaPA has poor mechanical properties (**Fig.9c**). Hence, the use of high molecular weight polyelectrolytes is essential for producing blended hydrogels with mechanical toughness.

Fig.9 (a) A schematic representation of synthetic hectorite /NaPA/TSPP gel; and hydrogels composed of synthetic hectorite and NaPA with (b) high molecular weight ($3.50 \times 10^6 \leq Mw \leq 2.11 \times 10^7$) and (c) with low

molecular weight ($2.25 \times 10^5 \leq M_w \leq 1.55 \times 10^6$) before and after stretching. Reprinted from (Takeno and Kimura, 2016). Copyright (2016), with permission from Elsevier.

Synthetic hectorite is a multifunctional cross-linker helping polyelectrolyte form networks. (Ehsan et al., 2017) prepared weak sulfonated polyacrylamide (SPA) nanocomposite hydrogels using synthetic hectorite nanoparticles and/or Cr^{3+} as crosslinker in saline solution. The interaction between the SPA and synthetic hectorite was a combination of hydrogen bonding and ionic interaction. The interactions between SPA and synthetic hectorite as well as the formation of SPA/synthetic hectorite systems and SPA/ Cr^{3+} /synthetic hectorite systems are shown in **Figure 10**. The oxygen atoms on the synthetic hectorite surface with the amide proton of SPA may form hydrogen bonds, and the metal atoms on the synthetic hectorite surface may form a complex with the carboxylate oxygen of SPA (Li et al., 2008). Adsorption properties of SPA/ Cr^{3+} /synthetic hectorite systems increased when synthetic hectorite concentration was increased. This phenomenon may be due to the increased hydrogen bonding interaction of the amide group of the SPA with Si-OH and Si-O-Si groups, or ionic interaction of the synthetic hectorite surface (Abdurrahmanoglu and Okay, 2010). Both SPA/ Cr^{3+} /synthetic hectorite systems and SPA/synthetic hectorite systems interactions increased the storage modulus. The SPA crosslinked with Cr^{3+} and synthetic hectorite nanocomposite hydrogel exhibited better viscoelastic behavior than SPA polyelectrolyte or SPA/ Cr^{3+} hydrogels. Therefore, SPA/ Cr^{3+} /synthetic hectorite systems may be a potential option for field applications in hostile conditions due to better viscoelasticity and adsorption.

Fig.10 Schematic drawings of the formation of SPA/hectorite and SPA/ Cr^{3+} /hectorite hydrogels. Reprinted by permission from Springer Nature: Springer (Ehsan et al., 2017). Copyright 2017.

4. Amphoteric polyelectrolytes

4.1 Montmorillonite

An amphoteric polyelectrolyte has both cationic and anionic groups distributed along the carbon chain. The solubility of amphoteric polyelectrolytes in water depends on the charge density, charge balance, asymmetry, and the chemical nature of the ionizable groups (Rabiee et al., 2014). The polymer bridging, charge neutralization, and polymer adsorption (Song et al., 2010) between the smectite and amphoteric polyelectrolytes promote flocculation in aqueous smectite-amphoteric polyelectrolytes dispersion, so amphoteric polyelectrolyte has been used in water treatment (Wang et al., 2019), and drilling fluid (Bai et al., 2015; Chu et al., 2013) (**Table 3**).

Gelatin, a natural amphoteric polyelectrolyte, due to biocompatibility, biodegradable properties, and no toxicity and availability, can potentially be a suitable substitute for the existing flocculants (Karimi et al., 2013). Gelatin can be effectively adsorbed on montmorillonite surfaces thereby changing the electrochemical nature of montmorillonite particle surface changes (Nazarzadeh et al., 2017). The adsorbed gelatin chains introduce bridging forces and steric forces in addition to electrostatic repulsion and Van der Waals attraction. In addition, the range of montmorillonite particle-particle interactions will also change with the thickness of the adsorbed layer, especially tail length of gelatin chains in the aqueous montmorillonite dispersion. Nevertheless, gelatin chains including cationic, anionic and uncharged monomer residues, the adsorption depends on the Coulomb interaction between the net charge on the carbon chain and the charged surface of montmorillonite (Kudaibergenov and Ciferri, 2007). If the excess charge on the gelatin chain is same as the charges of the montmorillonite surface, the Coulomb repulsion may inhibit adsorption. If the excess charges on the gelatin chain are opposite to those of the charges of the montmorillonite surface, the Coulomb interaction may promote adsorption.

Because amphoteric polyelectrolyte has both cationic and anionic groups distributed along the carbon chain, the content of anions and cations are needed to achieve specific purpose can be adjusted. For example, based on the ratio of cationic and anionic groups on the chains, amphoteric polyacrylamides exhibited variable flocculation efficiencies (Shaikh et al., 2017b) (**Fig.11a**). Polyacrylamides with a high ratio of cationic groups/anionic groups clearly displayed cationic behavior with high removal efficiency, while poor flocculation capabilities were observed with a low ratio of cationic-groups/anionic-groups. Hydrolyzed poly(acrylamide/dimethyl diallyl ammonium chloride) (HPAD), a polyampholyte containing quaternary ammonium groups, carboxylic acids, and amides has high ratio of cationic quaternary ammonium groups and specific carboxylic acids, and amides (Lin and Luo, 2018) (**Fig.11b**). The addition of HPAD amphoteric polyelectrolyte to the aqueous montmorillonite dispersion results in a strong electrostatic interaction between the charged chemical groups (quaternary ammonium groups, carboxylic acids, and amides) and montmorillonite particles, thus causing the formation of HPAD polymer bridges between adjacent montmorillonite particles and enlarges the charge imbalance of montmorillonite

(Liu et al., 2016). Therefore, by introducing electrostatic repulsion, the HPAD helped montmorillonite maintain a broad particle size distribution. In return, broad particle size distribution contributed to the adsorption of HPAD on montmorillonite. Optimization of the composition of amphoteric polyelectrolyte could be useful for the future design and synthesis of filtration reducers in the oil and gas field.

Fig.11. Chemical structures of the non-ionic polyelectrolytes

4.2 Saponite and hectorite

The amphoteric polyelectrolyte can interact with saponite. In saponite–cationic PAM–anionic PAM–water mixtures, the cationic PAM was first adsorbed on the saponite particles by electrostatic and hydrogen bonding (Zhang et al., 2005). Then, the anionic PAM was adsorbed on the saponite particles by electrostatic or Van der Waals forces. The PAM molecule crosslinks with the cationic PAM adsorbed on the saponite particles in saponite aqueous solution to form a spatial network. The viscosity of the saponite–cationic PAM–anionic PAM–water mixtures was increased due to the interaction between anionic PAM and cationic PAM. Under the shear force, the spatial network was gradually destroyed. The structure can be reformed again when rested for a while due to thixotropy. This system can be used as an excellent water blocking agent for oil layers with large pores and high permeability.

Interaction between hectorite and amphoteric polyelectrolytes can improve the thermal stability of the drilling fluid. Huang et al. (2019) studied the interaction between hectorite and a terpolymer (AAD) by synthesizing through radical polymerization of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and diallyldimethylammonium chloride monomers. The disk-shaped synthetic hectorite nanoparticles was well dispersed in aqueous terpolymer AAD dispersion, and the hectorite nanoparticles were establishing strong interactions between terpolymer AAD. The interactions included (Fig. 12): 1) electrostatic attractions between negatively charged synthetic hectorite surfaces and quaternary ammonium cationic groups of terpolymer AAD; 2) electrostatic attractions between positively charged synthetic hectorite edges and negatively charged sulfate groups of terpolymer AAD; and 3) possible hydrogen bonding between hydroxyl groups of synthetic hectorite and amide groups of terpolymer AAD. The interactions reduced the mobility of terpolymer AAD chains and also slowed down the degradation. This hectorite-terpolymer AAD system can increase the viscosity of drilling fluids. Synthetic hectorite could substantially improve the thermal stability of drilling fluid by protecting

terpolymer AAD. This interactions between synthetic hectorite nanoparticles and amphoteric polyelectrolytes provided a novel strategy to develop high temperature-resistant drilling fluids for deep reservoir excavation (Akhtarmanesh et al., 2013; Li et al., 2015).

Fig.12 The proposed mechanism of the interactions between synthetic hectorite nanoparticles and terpolymer ADD. Reprinted from (Huang et al., 2019). Copyright 2019, with permission from Elsevier.

Table 3

Recent typical studies on the interaction between smectite and amphoteric polyelectrolytes.

Amphoteric polyelectrolytes.	Type of smectite	Conditions	Interaction	References
HPAD	Montmorillonite	HPAD:0.5-2 wt%; Montmorillonite: 5wt%; Na ₂ SO ₃ :0.25 wt%; pH 8.	Adsorption; Introducing electrostatic repulsion and entropic repulsion.	(Lin and Luo, 2018)
PAM	Montmorillonite	PAM: 2.0% v/v; Montmorillonite: 100 ml; The system: pH 9.	Lower adsorption capacities due to steric hindrance.	(Shaikh et al., 2017b)
PECT/CS	Montmorillonite	PECT/CS ratios: 1:1, 1:2 and 2:1; Montmorillonite concentration: 0.5 and 2% wt.	Novel nanocomposite hydrogels were produced; Increased the degree of swelling and the mechanical resistance.	(da Costa et al., 2016)
ADD	Synthetic hectorite	AAD: 1-2 g; Synthetic hectorite:2 wt%; pH 7.	Electrostatic attractions; Hydrogen bonding; Rheological.	(Huang et al., 2019)

ADD: acrylamide, 2- acrylamido-2-methylpropane sulfonic acid, and diallyldimethylammonium chloride monomers

HPAD: Hydrolyzed poly(acrylamide/dimethyl diallyl ammonium chloride)

PAM: Polyacrylamide

PECT/CS: pectin/chitosan

Generally, for cationic polyelectrolytes, they are adsorbed onto the smectite surface through hydrogen bonding interactions between the Si-OH and Al-OH groups and functional group of polyelectrolyte's (Nasser et al., 2013). Cationic polyelectrolytes can also interact with the smectite through ion exchange by the electrostatic attraction between the positively charged cationic polyelectrolytes and the negatively charged smectite. By contrast, electrostatic repulsion occurs between anionic polyelectrolytes and smectite surfaces because both carry the negative charge. The electrostatic repulsion weakens the adsorption of smectite by anionic polyelectrolytes, thereby reducing the adsorption capacity. It also interacts with the smectite through van der Waals and possibly by H-bonding. Amphoteric polyelectrolytes exhibit both cationic polyelectrolytes and anionic polyelectrolytes behavior and their adsorption capacities are in between the cationic and anionic polyelectrolytes. Under the same conditions, for the same polyelectrolyte with different surface charge types, the adsorption affinity of smectite surface are easier and stronger for polyelectrolytes in the order: cationic polyelectrolytes > amphoteric polyelectrolytes > anionic polyelectrolytes (Shaikh et al., 2017).

5. Concluding remarks and future work

Recent studies have significantly deepened the understanding of the interactions between smectites and polyelectrolytes. The polyelectrolytes contribute to the adsorption, flocculation and rheological behavior of aqueous smectite dispersion. It is expected that the use of such polyelectrolytes with smectites will enhance the smectite processing, separations and waste water treatment and oil well drilling fluid.

It is now known that different types of polyelectrolytes and type of smectite along with polyelectrolyte molecular weight, charge type and charge density affect the interactions between smectite and polyelectrolyte. Although great progress has been made but scientific knowledge of the role of interactions between smectite and polyelectrolyte is still in its infancy. Most of the current research on smectite and polyelectrolyte interactions has so far been concerned with montmorillonite and fewer studies exist on the interaction between polyelectrolytes and saponite or hectorite. In addition, the species of polyelectrolytes are numerous but only a few types have been investigated for their interactions with smectites. The accurate experimental evidence on the hydrogen bonding, hydrophobic interaction, ion binding, electrostatic interaction, and van der Waals forces are limited. In particular, no quantitative data and reliable equations have been established. Hence, the detailed models and mechanisms at the molecular or atomic level remain unclear.

Moreover, it needs to be mentioned that interactions between smectite and polyelectrolyte in wastewater treatment was mostly conducted at laboratory scale. Wastewater treatment by

adsorption, flocculation and separation on an industrial scale is still a challenge. Desirable polyelectrolytes as flocculants and smectite should be economically able to provide enough removal efficiency for pollutants in wastewaters under a wide range of conditions. Meanwhile, the polyelectrolyte and the process should be environmentally friendly, cost-effective and easily reproducible.

The interaction between smectites and polyelectrolytes get conventionally involved in using smectite-polyelectrolyte system as adsorbent, flocculant, rheological additives. Some studies have demonstrated new applications in biomaterial, three-dimensional (3D) printable ink materials and sensor devices by taking advantage of the interaction of smectites with polyelectrolytes. The smectite-based nanocomposites and hierarchical materials can be fabricated by the surface engineering and tactic assembly of smectites. Interactions between smectites and polyelectrolytes can result in the formation of nanohybrids as biosensors, catalysts and drug carriers. In-depth understanding of the interaction between polyelectrolytes and smectites also helps expanding the integration and functionality and inherent mechanism of advanced smectite-polyelectrolyte materials.

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