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ORIGINAL CONTRIBUTION

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Bonding mechanisms and conformation of poly(ethylene oxide)-based surfactants in interlayer of smectite

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Abstract A better understanding of the interactions between poly(ethylene oxide) (PEO)-based nonionic surfactants and smectite is important to fully comprehend the transport and the fate of nonionic surfactants in the environment and to design novel organo-clay composites. We studied the bonding between the surfactants and smectite and the molecular conformations of the surfactants in the interlayer of smectite. A reference polymer PEG and three nonionic surfactants—Brij 56, Brij 700, and PE-PEG—were intercalated into a smectite. The polymers and the composites were characterized with X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The XRD and FT-IR results indicate that the bulk surfactants existed as crystalline materials at room temperature, and surfactant molecules had both helical/extended diblock and planar zigzag conformations. The surfactants intercalated smectite and expanded the d(001) spacing of smectite to nearly 1.8 nm. The shapes and positions of the IR bands of interlayer surfactants were similar to those of the melted (amorphous) bulk polymers: the wagging vibrations of the CH_2 merged to a single band at 1,350 cm^{-1}, the twisting bands of CH_2 had 9 cm^{-1} or more blue shifts. These changes imply that the PEO segments of the surfactants existed with a distorted and extended conformation in the interlayer of smectite, and this extended conformation was an intermediate form of the helical and planar zigzag conformations. The molecular conformation of the interlayer surfactant was not affected by the seven types of exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, and H^+) tested. There were 20 cm^{-1} or more red shifts from the C–O–C stretching bands when the surfactants were adsorbed. The red shifts suggest that surfactants were bonded to smectite mainly through (1) H-bonding between oxygen atoms of the PEO segments and water molecules in hydration shells of the exchangeable cations, and (2) direct coordination or ion–dipole interaction between the oxygen atoms of the PEO segments and the exchangeable cations. With the extended conformation, the oxygen atoms of the PEO segments have maximum exposure to the bonding water molecules and exchangeable cations.

Keywords Bonding · Conformation · Poly(ethylene oxide) · Nonionic surfactant · Smectite

Introduction

Poly(ethylene oxide) (PEO)-based surfactants are the most common nonionic surfactants used in industry, agriculture, and domestic applications [1]. Most commercial nonionic surfactants are composed of nonionic PEO segments combined with aliphatic or aromatic hydrocarbon chains. Nonionic surfactants are introduced into the soil systems through agrochemical formulations, detergents, and additives. Interactions between the surfactants and soil components are important to understand their fate and transport in soils. In addition, the interactions induce surface modifications on original soil minerals and therefore, change in the sorption and transport of other organic and inorganic compounds in soil. Understanding the interactions is also essential for designing novel organo-clay composites for environmental and industrial applications. One promising benefit of using nonionic-surfactant modified clays is their dual ability to remove both heavy metal ions and aromatic organic compounds [2].

Bonding mechanisms

Bonding mechanisms and molecular conformations of nonionic surfactants on expandable minerals are less understood compared with those on nonswelling minerals such as silica [3–5] and kaolinite [6, 7]. On silica surfaces, adsorption of the PEO-based surfactants is dominated by hydrogen bonds between the oxygen atoms of the PEO segments and surface silanol groups of the silica [3, 6]. The first layer of adsorbed surfactants can attract more surfactants to the solid surface by lateral interactions between hydrophobic segments of the surfactants [8]. Aggregation of surfactants on mineral surfaces has the common features of bulk micellization [7].

For the adsorption of nonionic surfactants on expandable minerals such as smectite, different adsorption mechanisms are anticipated. The PEO-based surfactants may have similar adsorption characteristics as uncharged organic species such as pure PEO polymers. Ion–dipole interactions between the exchangeable cations of smectite and the polar functional groups are the dominant bonding for a series of nonionic organic compounds such as amides, alcohols amines, and ethers [9–11]. We expect that the same bonding exist between the PEO-based surfactants and smectite. The H-bonding, van der Waals force, and entropy effect can contribute to the adsorption of polymeric surfactants [12].

Molecular conformations

According to the rules summarized by Matsuura and coworkers [13–15], the PEO-based nonionic surfactants with long-aliphatic chains (e.g., contained 16 or more carbon) and a greater number (e.g., eight or more) of repeating ethylene oxide (EO) units would exist with a helical-extended diblock conformation (Fig. 1a). The PEO segment has the same conformation as a pure PEO polymer in a crystalline state, that is, it forms a 7/2 helix structure wherein seven repeating EO units comprise two turns around an axis [16]. The helix structure of the PEO chain is the result of a conformational arrangement of trans (C–C–O–C), trans (C–O–C–C), and gauche (O–C–C–O). The aliphatic hydrocarbon chain has the most stable zigzag conformation. In addition to the favored helical/extended diblock conformation, the surfactant may convert to a more extended form. A fully extended planar zigzag conformation is shown in Fig. 1b, yet this extended conformation has not been confirmed experimentally.

A pure PEO polymer changed its conformation from helical to disordered and more extended when the polymer was melted [17, 18] or was dissolved in a solvent [19]. It has also been reported that the PEO chain took preferentially a planar zigzag conformation when it was blended with poly(methyl methacrylate) [20]. Takahashi

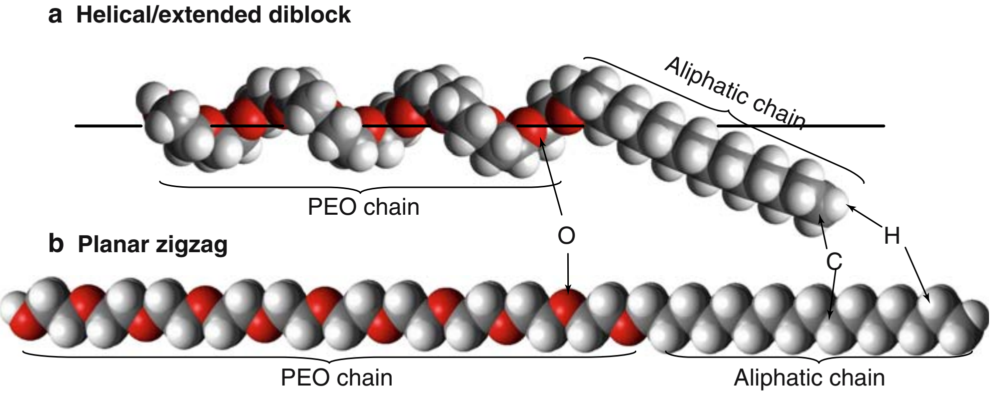

Fig. 1 Two possible molecular conformations of PEO-based surfactants in a crystalline state: **a** a favored helical/extended diblock conformation and **b** a fully extended planar zigzag conformation. Intermediate forms between these two conformations exist in an amorphous state

et al. [21] have observed that a PEO chain converted to a planar zigzag conformation when the polymer was under tension caused by stretching. The energy difference between the helical and the extended conformations is only about 0.1 kcal mol^{-1} per EO unit [22], suggesting the PEO chain is flexible. The observed conformational changes on pure PEO chains under various conditions and the small energy difference between the two conformations suggest that it is possible for the PEO-based surfactants to convert to a more extended form. Intermediate forms between the helical/extended diblock (Fig. 1a) and the planar zigzag (Fig. 1b) conformations may exist.

There is little information available about the molecular conformations of the PEO-based surfactants after adsorbing on smectite. The PEO segments of the adsorbed surfactants may have similar conformations as adsorbed pure PEO polymers. Unfortunately, the conformation of adsorbed PEO polymers in smectite is still a subject in debate. For example, Aranda and Ruiz-Hitzky [23, 24] postulated that the PEO polymer preserved the helical conformation in the interlayer of Na^{+}-saturated montmorillonite and hectorite; they rejected the possibility that the polymer existed in the planar zigzag form based on IR, ^{13}C NMR, and X-ray diffraction studies. They also reported that the conformation of the PEO polymer changed from helical to planar zigzag when the minerals were saturated with NH_4^+. They attributed the conformation change to the strong H-bonding between the oxygen atom of the PEO polymer and the exchangeable NH_4^+, and suggested that that the PEO chain would change back to the helical structure if the NH_4^+ cations were replaced by Na^{+}. On the contrary, computer simulation indicates that the helical conformation was highly distorted and the extended conformation was energetically more stable when PEO entered the interlayer of a Li^{+}-saturated smectite [25, 26]. The reported multiple conformations of pure PEO polymer in the interlayer of smectite imply that the PEO-based surfactants may also have different conformations in the interlayer of smectite, and exchangeable cations may alter the conformations.

The objectives of this study were to investigate (1) the conformations of the nonionic surfactants in the interlayer of smectite; (2) the effect of exchangeable cations on the conformation of the adsorbed surfactants; and (3) the bonding mechanisms between the surfactants and smectite.

Materials and methods

PEO-based nonionic surfactants, poly(ethylene glycol), and smectite clay

A pure poly(ethylene glycol) (PEG), which has an identical chemical structure as PEO, was employed as a reference compound. Three PEO-based nonionic surfactants, Brij 56, Brij 700, and PE-PEG, were used in the study (Table 1). The surfactants and PEG were obtained from Aldrich Chemical Company. All of them are wax-like white materials at room temperature. The <2 μm fraction separated from a bentonite (Gonzales, TX, USA) was saturated with Ca^{2+} and freeze dried. This clay was denoted as Ca–Sm. Smectite was the only mineral detected in this clay by X-ray diffraction (XRD) and infrared analyses. This clay has a cation exchange capacity (CEC) of 81.2 cmol(c) kg^{-1} and a surface area of 787 m^{2} g^{-1} (Ethylene glycol monoethyl ether method) [2]. Synthesis of the Brij 56-smectite composite was described in an earlier paper [2]. Other surfactant- and PEG-smectite composites were synthesized similarly. In brief, one gram Ca–Sm was mixed with 25 mL 1 g L^{-1} surfactant or PEG solution in a 40 mL centrifuge tube. The tube was shaken overnight and centrifuged, the supernate was replaced with fresh surfactant or PEG solution. The surfactant and PEG treatments were repeated three times. Excess surfactants and PEG in the tubes were removed by washing with distilled water. The resulting surfactant- and PEG-smectite composites were freeze dried. Surfactants and PEG loading in the composites were quantified with Walkley–Black method [27], but this method may underestimate the loading in smectite because the interlayer organics cannot be oxidized completely (Table 1).

Table 1 Properties of the PEO-based nonionic surfactants and PEG, and their loading on Ca–Sm

	Chemical name	Chemical formula	Molecular weight	Melting point (°C)	Loading (mg g^{-1})
PEG	Poly(ethylene glycol)	$H(OCH_2CH_2)_nOH$, n~76	3,400	55	137
Brij 700	Polyoxyethylene(100) stearyl ether	$C_{18}H_{37}(OCH_2CH_2)_nOH$, n~100	4,670	51–54	169
PE-PEG	Polyethylene-block-poly(ethylene glycol)	$CH_3CH_2(CH_2CH_2)_m(OCH_2CH_2)_nOH$ (80 wt% ethylene oxide, m~15, n~40)	2,250	89	177
Brij 56	Polyoxyethylene(10) cetyl ether	$C_{16}H_{33}(OCH_2CH_2)_nOH$, n~10	683	32–34	235

Different cation saturated Brij56-smectite composites

To investigate the effect of cation on surfactant conformation, we further saturated Brij56-smectite composite with additional six types of cations. Due to the similar properties of surfactant-smectite composites, other composites were not used in this experiment. For Na^+, K^+, and Mg^{2+} saturations, the surfactant-smectite composites were washed three times with 0.5 M NaCl, KCl, or 0.25 M $MgCl_2$. Each washing included adding 25 mL solution to 0.2 g composite in a 40-mL Nalgene centrifuge tube, shaking for 2 h, centrifuging, and replacing supernate with fresh electrolyte solutions. For Cu^{2+} and Ni^{2+} saturations, the surfactant-smectite composites were acidified with pH 4 HCl solution and then treated three times with pH 4 solutions of 0.016 M $CuCl_2$ or $NiCl_2$. Hydrogen-composite was synthesized by washing the composite with pH 4 HCl solution four times. Excess electrolytes in the above treatments were removed by water washing. Most surfactants remained in the composites after the electrolyte treatments [2]. The Ca–Sm was also similarly saturated with the six types of cations.

FT-IR analyses

Two methods were used in IR sample preparations. For most smectite and composite samples, self-supporting films were prepared according to White et al. [28]: about 1.5 mL of 2% (w/w) smectite or surfactant-smectite composite suspension was pipetted onto a Mylar plastic sheet (Spex CertiPrep Inc.) and air dried. The clay film was carefully separated from the supporting plastic sheet. For samples used to study the IR bands of the adsorbed surfactants in the range 900–1,200 cm^{-1}, less clay and composites were deposited and air dried on ZnS windows. For pure surfactants and PEG, the organics were heated to slightly above their melting points (Table 1) and then were smeared on warm ZnS windows. The IR spectra of pure surfactants and PEG were recorded in both liquid state (above melting point) and solid state (22°C).

The IR spectra were recorded with a resolution of 1 cm^{-1} on a Perkin Elmer System 2000 FT-IR. A deuterated triglycine sulfate (TGS) detector was selected in the study. Sixty-four coadded scans were collected for each spectrum. The optic bench of the instrument and sample chamber were purged with dry and low-CO_2 air from a Balston 75-52 FT-IR purge gas generator. The spectra were processed with software SPECTRUM (Perkin-Elmer). To reveal the IR bands of the adsorbed surfactants in the range 900–1,200 cm^{-1}, the spectra of different cation-saturated smectites were subtracted from the spectra of surfactant-smectite composites saturated with same cations. Spectrum subtraction was conducted in the absorbance mode.

Results and discussion

Molecular conformations of pure surfactants in solid state

XRD patterns of pure surfactants and PEG

The three PEO-based surfactants, Brij 56, Brij 700, and PE-PEO copolymer, are crystalline materials at room temperature. They had brilliant birefringence colors when examined with cross-polarized lights (images not shown), and had intense XRD peaks (Fig. 2). Moreover, the XRD patterns of the surfactants were similar or nearly identical to the pure PEG polymer: all of the polymers showed two strongest diffractions peaks near 0.46 and 0.38 nm; other weak peaks of the surfactants also closely match those of the pure PEG polymer. In terms of position, intensity, and resolution of the XRD peaks, the similarity to PEG decreased with the order Brij 700 > PE-PEG > Brij 56. This order is correlated to the numbers of repeating EO units in the surfactants, that is, when the numbers of the repeating EO units increased, the XRD pattern of the surfactant becomes more similar to that of pure PEG polymer. The similar or nearly identical XRD patterns suggested that, in crystalline state, the PEO segments of the surfactants had the same or similar conformation as the pure PEG polymer. Because PEG molecules preferentially exist with the 7/2 helical conformation in the crystalline state, it is reasonable to claim that at least part of the PEO segments in surfactants Brij 56, Brij 700, and PE-PEG copolymer would preferentially took the helical conformation. The surfactant molecules could exist with the conformation as shown in Fig. 1a.

FT-IR spectra of the pure surfactants and PEG

In the solid (crystalline) state, each spectrum of the pure surfactant and PEG (top patterns in Fig. 3) showed two well-resolved bands at 1,358 and 1,344 cm^{-1} that arise mainly from the wagging vibrations of the CH_2 groups of the PEO segments. The twisting vibration of the CH_2 group occurred at 1,280 cm^{-1} in all of the surfactants and PEG. As will be shown in Fig. 6, the C–O–C stretching vibrations of the surfactants and the PEG were well resolved to at least three bands at 1,146, 1,113, and 1,061 cm^{-1}. The CH_2 rocking band of crystalline surfactants occurred at 964 cm^{-1}. According to Marcos et al. [29], the 1,358, 1,280, and 1,061 cm^{-1} bands arise from the helical PEO chain, and the 1344, 1241, and 962 cm^{-1} bands from the planar zigzag chain (Table 2). The occurrence of these bands in the surfactant and PEG suggests that both the helical-extended diblock

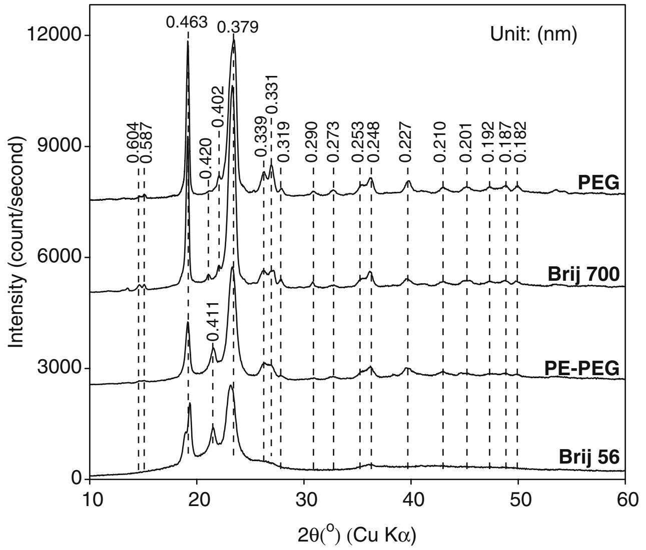

Fig. 2 The XRD patterns of PEG and the three PEO-based surfactants

(Fig. 1a) and the planar zigzag (Fig. 1b) conformations occurred in the bulk surfactants.

When PEG and the surfactants were melted, the IR bands became broader and weaker, and some bands shifted or merged (middle patterns in Fig. 3). Only one new band appeared at 1,349 cm^{-1} (the wagging vibration of CH_2). The twisting bands of CH_2 occurred at 1,297 cm^{-1} and 1,250 cm^{-1}, that is, had 18 and 9 cm^{-1} blue shifts compared with the bands in the crystalline surfactants. The merging and the shifts of IR bands of heated surfactants were nearly identical to those of heated pure PEG, indicating that the PEO segments of surfactants had similar conformation changes as PEG after melting. Because the melted PEG chains lost their helical conformation [17, 30], and they do not have the IR characteristics of the planar zigzag conformation, the melted surfactants should similarly change to a distorted and extended conformation between the helical-extended diblock (Fig. 1a) and the planar zigzag (Fig. 1b) conformations.

Intercalation of smectite by PEG and the nonionic surfactants

The surfactants and PEG expanded the d(001) spacing of smectite to 1.6–1.8 nm at room temperature (Fig. 4a), indicating intercalation occurred in the composites. No free surfactants or PEG were detected because the major surfactant peak at 0.38 nm was absent on the XRD patterns [2]. The d(001) spacing of different cation treated Brij56-smectite composites were in the range of 1.5–1.8 nm (Fig. 4b), and were consistently higher than those of Ca–Sm saturated with the same cations, indicating at least part of the surfactants remained in the interlayer of smectite after the cation treatment.

Table 2 Infrared bands (cm^{-1}) of PEG and surfactants in crystalline state, amorphous state, and after adsorbing on smectite[a]

Crystalline		Amorphous		Adsorbed		Assignments[b]	Conformation of PEO chain[c]
PEG	Brij56	PEG	Brij56	PEG	Brij56		
	1472	1485	1485			$\delta(CH_2)_s(93)$	
1467	1466		1466	1471	1467	$\delta(CH_2)_a(68)-\delta(CH_2)_a(24)$	
1412	1410					$\omega(CH_2)_a(80)$	
1359	1359					$\omega(CH_2)_s(62)+v(CC)(19)$	Helix
		1349	1349	1350	1350	$\omega(CH_2)_a(87)$	
1344	1345					$\omega(CH_2)_a(87)$	Zigzag
1324	1322	1324	1323				
		1298	1297	1304	1304	$t(CH_2)_a(52)+t(CH_2)_s(42)$	
1280	1279					$t(CH_2)_a(52)+t(CH_2)_s(42)$	Helix
		1250	1250			$t(CH_2)_a(95)$	
1242	1241					$t(CH_2)_a(95)$	Zigzag
1234	1234					$t(CH_2)_a(95)$	Helix
1149	1146	1142			1118	$v(CC)(49)-v(COC)_{fa}(15)$	
1115	1113	1111	1117		1076	$v(COC)(52)$	
1061	1061				1044	$v(COC)(61)+\gamma(CH_2)_s(18)$	Helix
	1037	1039			1017		
964	964					$\gamma(CH_2)_s(52)-v(COC)_a(17)$	Zigzag
946	944	948	946			$\gamma(CH_2)_s(52)-v(COC)_a(17)$	Helix
842	842	852	864			$\gamma(CH_2)_a(72)$	Helix

[a] Surfactants Brij 700 and PE-PEG had similar band positions as those of Brij 56

[b] Assignment followed Yoshihara et al. [17] and Kimura et al. [30]

[c] According to Marcos et al. [29]

Symbols: δ bending; ω wagging; v stretching; γ rocking; t twisting; a antisymmetric; and s symmetric

Numbers in parentheses are potential energy distribution (in %) among coordinates

Signs + and − denote phase relations of coupled coordinates

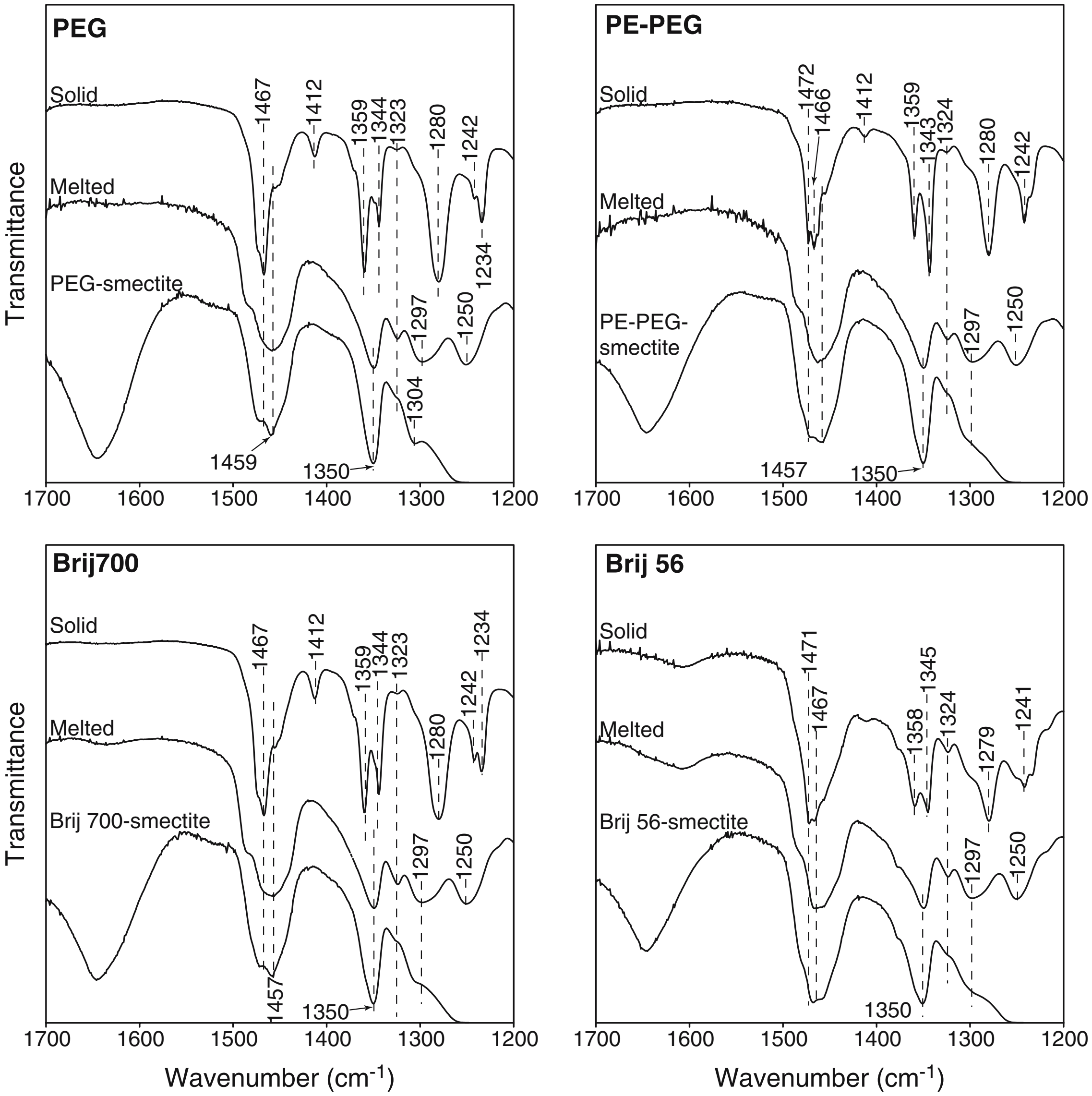

Fig. 3 Infrared spectra of PEG and the PEO-based surfactants in solid (crystalline) and melted (amorphous) states, and their smectite composites

Conformation of adsorbed surfactants on smectite

When PEG and the surfactants were adsorbed on smectite, the IR bands of smectite did not show distinct changes in terms of band position and therefore, are not shown or discussed here. Even though the IR spectra of the polymer-smectite composites were recorded at room temperature, the IR spectra of adsorbed polymers (bottom patterns in Fig. 3) were similar to those of melted bulk polymers. For example, the wagging vibrations of the CH_2 groups appeared only at 1,350 cm^{-1} as a single band. When the IR spectrum of the smectite was subtracted from the IR spectrum of Brij56-smectite composite, the resulting spectrum of Brij 56 showed broad bands at 1,296 and 1,250 cm^{-1} (data not shown). The IR spectra suggest that the adsorbed surfactants had the same molecular conformations as the melted (amorphous) polymers, namely the adsorbed surfactants had a more extended conformation in the interlayer of smectite.

Conformation of adsorbed surfactants with different exchangeable cations

When Brij 56-smectite composites were saturated with different cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, and H^+), the positions and shapes of the IR bands of the composites were very similar or nearly identical to each other (Fig. 5). The IR bands showed the characteristics

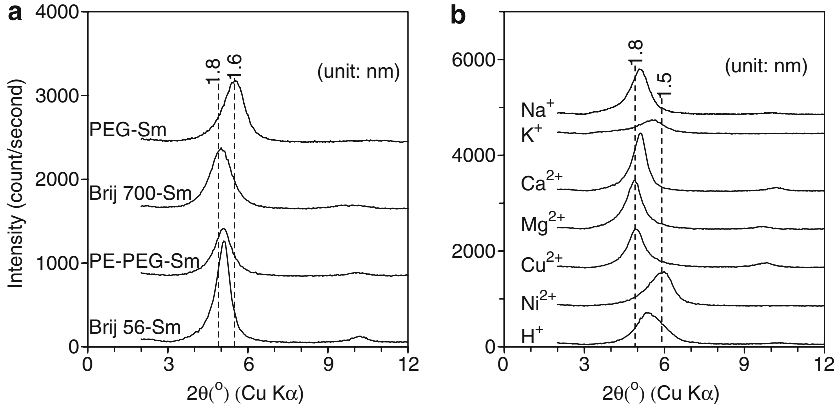

Fig. 4 XRD patterns of **a** PEG- and surfactant-smectite composites and **b** Brij 56-smectite composites saturated with seven different cations. Patterns were recorded at room temperature

of melted surfactant as described earlier: the CH_2 wagging vibrations occurred as a single band at 1350 cm^{-1}, the CH_2 bending vibrations occurred as a broad band at 1,467 cm^{-1}. The similarity among the seven different cation saturated Brij 56-smectite composites suggests that the conformation of the adsorbed surfactants was well preserved during the ion exchange reactions.

Bonding mechanisms revealed by IR bands of C–O–C vibrations

The surfactants and PEG had similar IR bands in the range 900–1,200 cm^{-1}, and they showed similar responses when the the PEO chains changed from the helical conformation to the extended form after melting: the well resolved three bands at 1,146, 1,113 and 1,061 cm^{-1} merged to one band centered at around 1,118 cm^{-1} (e.g., Fig. 6a). When the polymers adsorbed on smectite, the C–O–C stretching vibrations would change their positions if the oxygen atoms of the EO units were involved in the bonding. The infrared spectra indicate that, after adsorbing on smectite, the C–O–C stretching vibration at 1,118 cm^{-1} remained, yet additional bands appeared at lower frequencies: 1,076, 1,044 and 1,017 cm^{-1} (Table 2, Fig. 6b). All of the four bands persisted when the composite was saturated with the seven different cations mentioned above. It appears that the 1,017 cm^{-1} band became more intense in Cu^{2+}-, Ni^{2+}-, or H^{+}-saturated composites.

The IR bands at 1,118, 1,076, 1,044 and 1,017 cm^{-1} may have two sources, one is from the surfactants and the other one is from the band shifts of smectite. The Si–O stretching vibration of smectite occurred at around 1,045 cm^{-1}, and it can be affected by water and the polymers adsorbed on the mineral. Water molecules have been partially expelled by the surfactants in the composites as indicated by the weakened water bands around 1,645 cm^{-1} in the IR spectra (e.g., Fig. 5) and at around 3,400 cm^{-1} (spectra not shown). The reduced water environments may cause the Si–O stretching bands to shift. However, several authors have found that, when moisture content decreased in Li^{+}- and Na^{+}-saturated montmorillonites, the 1,045 cm^{-1} band became weaker [31, 32]. The 1,044 cm^{-1} bands of the surfactant-smectite composites studied here were enhanced but not weakened. The difference suggests that at least part of the 1,044 cm^{-1} band intensity enhancement was due to the adsorbed surfactant. In other words, the C–O–C stretching vibrations shifted to this frequency. Similarly, the enhanced bands at 1,118, 1,076, 1,017 cm^{-1} can also be attributed to the surfactants. Compared to the IR bands of the pure surfactants, the

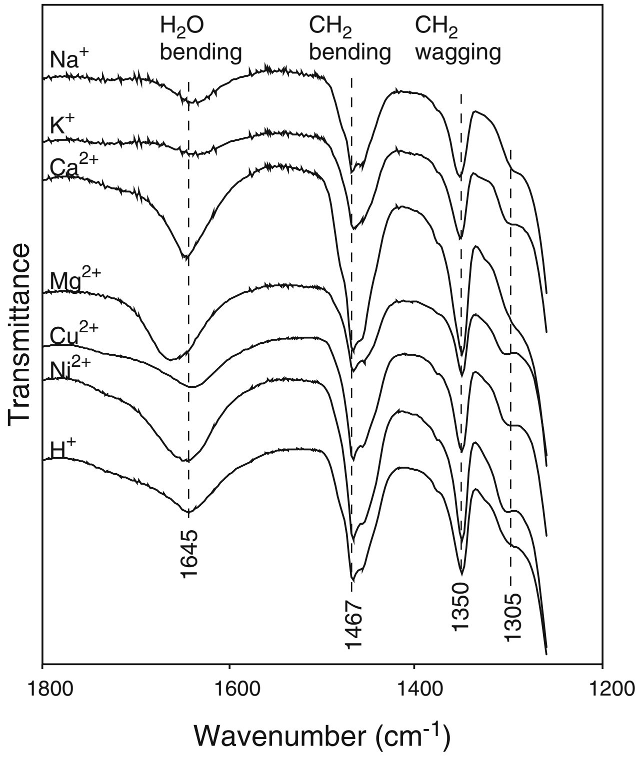

Fig. 5 Infrared spectra (1,200–1,800 cm^{-1}) of Brij 56-smectite composites saturated with different cations

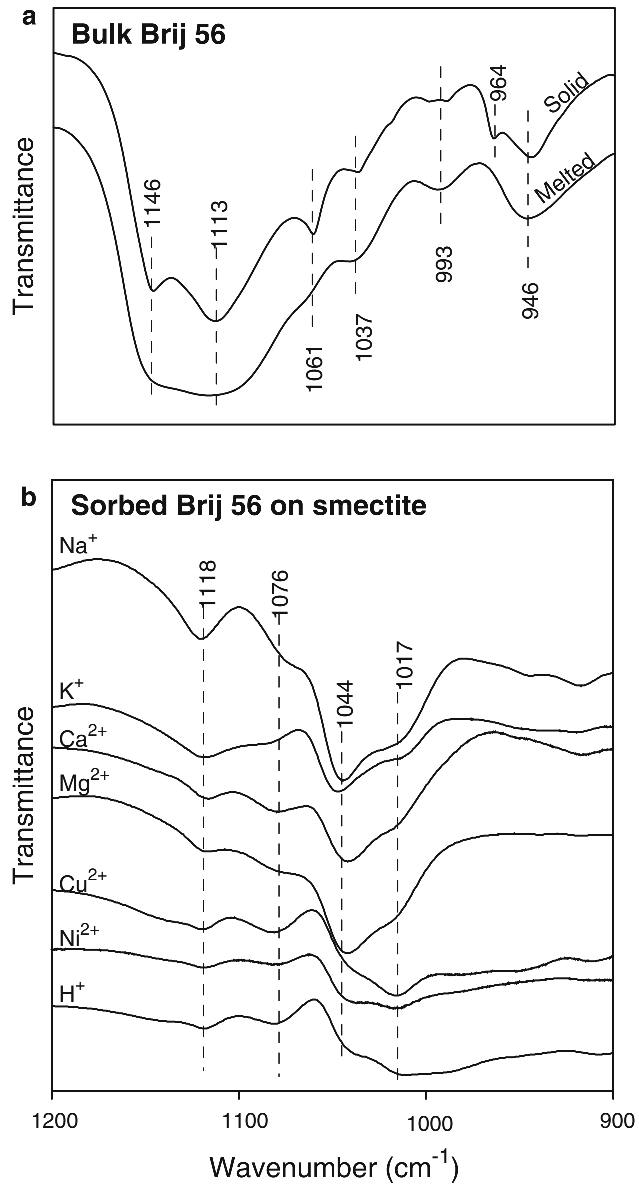

Fig. 6 Infrared spectra (900–1,200 cm^{-1}) of Brij 56. **a** Free bulk Brij 56 in solid and melted states and **b** adsorbed Brij 56 on smectite saturated with different cations

IR bands of the adsorbed surfactants had 20 cm^{-1} or more red shifts, implying that the C–O bonds of the surfactants were weakened when the surfactants were adsorbed on smectite.

The weakening of the C–O bonds of surfactants is likely caused by two kinds of interactions between the PEO segments of the surfactants and the exchangeable cations: (1) surfactants form H-bond with water molecules in the hydration shell of exchangeable cations (Fig. 7a), and (2) the PEO segments directly bond to the exchangeable cations through ion–dipole interactions or coordination (Fig. 7b). The bonding through water molecules is likely the dominant force between the surfactant and the exchangeable cations when the cations are still hydrated such as when the samples are only air dried. The enhanced 1,017 and 1,044 cm^{-1} bands in Cu^{2+}- and Ni^{2+}-treated composites also suggested there were stronger ion–dipole interaction or coordination between the exchangeable transition heavy metal cations and the PEO segments than those between alkali or alkaline earth cations and the PEO segments. These two bonding mechanisms were supported by observations that the Ca^{2+}-saturated surfactant-smectite complexes were more thermally stable than the Na^{+}-saturated surfactant-smectite composites [1, 2]. The divalent cations would have stronger ion–dipole interactions with the PEO segments than the monovalent cations would. The ion–dipole interactions or coordination between exchangeable cation were also proposed as the main bonding forces between pure PEO polymer and smectite by Aranda et al. [33, 34]. It was also postulated that PEO was adsorbed onto the exchange cations of smectite via a water bridge, and the CH_2 group of PEO was directly adsorbed onto the surface of smectite by van der Waals interaction [35, 36]. The H-bonding between water molecules in the hydration sphere of exchangeable cations on montmorillonite and the oxygens of the PEO polymer has also been suggested [25, 37, 38,]. In addition to the H-bonding, interlamellar water can control polymer adsorption from aqueous solution due to large entropy gains when large numbers of water molecules are replaced by the polymers [10, 11].

The proposed bonding mechanisms explain the conformations of the adsorbed surfactants. The PEO segments in the interlayer of smectite existed with the distorted and more extended conformation. With this conformation, the oxygen atoms of the PEO chains have maximum exposure to its surrounding molecules and therefore, have the strongest interactions with water molecules or the exchangeable cations. If the PEO segment kept the helical conformation, the oxygen atoms of the PEO chains face the center axis of the helix (Fig. 1a),

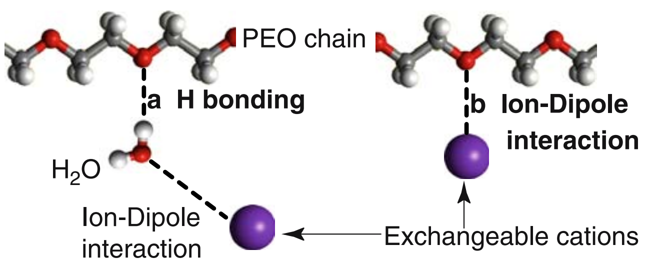

Fig. 7 Two possible major bonding mechanisms between the PEO segments of the surfactants and exchangeable cations of smectite. **a** Water bridging: oxygen atoms of the PEO segment form H-bonding with water in the hydration shells of exchangeable cations; and **b** direct ion–dipole interactions or coordination between the oxygen atoms of the PEO segments and the exchangeable cations

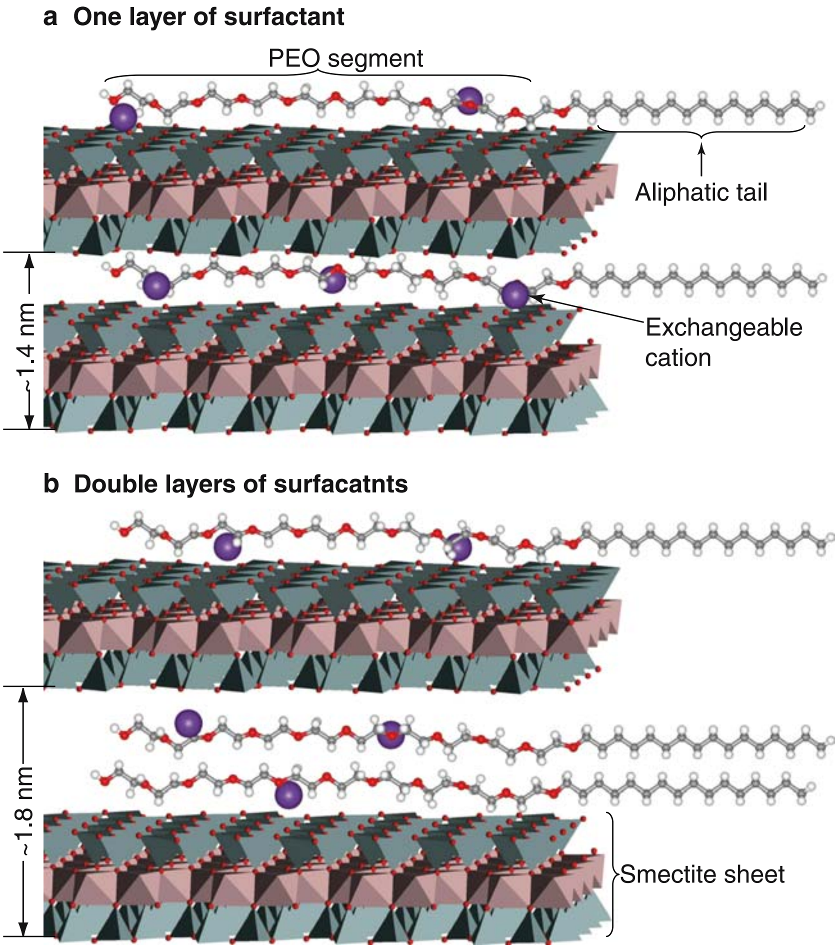

Fig. 8 Schematic models of PEO-based surfactant-smectite composites: **a** one layer and **b** double layers of surfactants in the interlayer of smectite. The PEO segment of a surfactant molecule lost its favored helical conformation and became disordered and more extended. The exchangeable cations can be hydrolyzed. Water molecules are not shown in the models

which are shielded from exchangeable cations and water molecules, and thus less likely to form strong bonding with smectite. This may be energetically unfavorable for the surfactants in the interlayer of smectite.

Models for surfactant-smectite composites

The composites used in this study had high-surfactant loading (Table 1). The d(001) spacing of smectite was expanded to nearly 1.8 nm by the surfactants and did not collapse by electrolyte washing except by K^+ (Fig. 4). In an early paper, we reported that the d(001) spacing of the surfactant-smectite varied from 1.4 to 1.8 nm, depending on the loading of the urfactants [45]. We postulate that smectite adsorbs one or two layers, but not more, of the surfactants in its interlayer space. At low surfactant loading, one layer of the surfactant coordinates with the exchangeable cations and expands the smectite to about 1.4 nm. The oxygen atoms and the exchangeable cations are probably located at the center distance from the neighboring oxygen basal surfaces of the silicate (Fig. 8a). When more surfactant molecules enter the interlayer, two layers of surfactants form in the interlayer and expand the smectite to about 1.8 nm (Fig. 8b).

Conclusions

The shapes and positions of the IR bands of adsorbed surfactants in the interlayer of smectite resemble the melted (amorphous) PEO. The PEO segments of surfactants were arranged in a distorted and more extended form in the interlayer of smectite, instead of its favored helical conformation as in the crystalline state. The conformation change was due to maximum exposure of oxygen atoms of the PEO chain for bonding water molecules or exchangeable cations in the interlayer of smectite. The type of exchangeable cations in the interlayer of smectite did not affect the conformation of the adsorbed surfactants. The red shifts of the C–O–C stretching bands of the sorbed surfactant were caused by the H-bonding of the oxygen atom with water in the hydration shell of the exchangeable cations, or direct coordination or ion–dipole interaction between the exchangeable cations and the oxygen atoms of the PEO segments.

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