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Adsorption of poly (ethylene oxide) on smectite: effect of layer charge

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Abstract

The adsorption of polymers on clay is important in many applications. However, the mechanisms of poly (ethylene oxide) (PEO) adsorption on smectite is not well elucidated at present. The aim of this study was to investigate the effect of layer charge density on the adsorption of PEO by smectite. The results indicated that both the hydrophobic interaction (between CH₂-CH₂- groups and siloxane surface) and the hydrogen bonding (between ether oxygen of PEO and structure OH of smectite) lead to PEO preferential adsorption on the surface of low-charge smectite. In addition, the delamination of low-charge smectite in water is enhanced upon PEO adsorption presumably due to the hydrophilic ether oxygen of adsorbed PEO.

*Keywords*: Poly (ethylene oxide); Smectite; Adsorption; Layer charge; IR spectra
1. Introduction

The adsorption of polymers on clay is important in many applications such as drilling fluids, ceramics, paints, sludge dewatering, desliming, soil science and organoclay. Smectite, a 2:1 clay mineral, is characterized mainly by an Al-octahedral sheet placed between two Si-tetrahedral sheets. The isomorphous substitution of Mg$^{2+}$ for Al$^{3+}$ in the octahedral layer results in a negative surface charge on smectite. This charge imbalance is offset by the addition of cations (typically Na$^+$ and Ca$^{2+}$) in the interlayer space. The interlayer cations are situated in the hexagonal cavities outlined by two opposite tetrahedral sheets [1]. The Na$^+$ and Ca$^{2+}$ are strongly hydrated in the presence of water and result in a hydrophilic environment at the interlayer space of smectite. The interlamellar surface of smectite is composed predominately of siloxane (-Si-O-Si-) surface. The neutral siloxane surfaces found on clays with no isomorphous substitution have an overall hydrophobic character [2,3]. Poly (ethylene oxide) (PEO) is a water-soluble nonionic polymer, HO-(CH$_2$-CH$_2$-O)$_n$-H, which is available commercially in a wide range of molecular weights. The ether oxygen in the polymer chain interacts with water, causing the polymer to be water-soluble, while the CH$_2$-CH$_2$- groups are hydrophobic in nature [4,5]. Adsorption behavior of PEO for several oxides in aqueous systems has been reported [4-8]. It was found that PEO adsorbed strongly
onto silica but no PEO adsorption occurred on alumina and hematite surfaces. Hydrogen bonding between the surface silanol (SiOH) groups and the ether oxygen in the PEO was proposed to be the mechanism for PEO adsorption onto silica. Mathur and Moudgil [4] demonstrated that the ether oxygen of PEO, a Lewis base, interact favorably only with oxides such as SiO₂, MoO₂ and V₂O₅ with strong Bronsted acid sites on surface. Koksal et al. [7] postulated that no PEO adsorption occurred on alumina and hematite surfaces because that the PEO could not displace strongly adsorbed water on oxides.

In contrast to silanol (SiOH) groups on silica surface there are no electron-acceptor (Lewis acid) sites on the siloxane (-Si-O-Si-) surface of smectite available for hydrogen bonding with the ether oxygen of PEO. Our literature search for the adsorption of PEO on clays shows very limited results. Burchill et al [9] indicates that it appears that the PEO molecules adopted fully extended conformations at the surface of Na-montmorillonite. Mpofu et al [10] showed that the adsorption of PEO onto kaolinite is more favorable at elevated temperature and suggested that the adsorption process is dominated by entropic rather than enthalpic effects. They also observed that the adsorption density of PEO on kaolinite is significantly lower than those reported for SiO₂. Rossi et al [11] noted that the amount of PEO adsorbing per square meter is relatively low on montmorillonite and postulated that PEO is adsorbed
largely as trains. Yuang and Shen [5] indicated that for high molecular weight PEOs the polymer conformation adsorbed on smectite takes train segments predominantly and monolayer coverage on smectite surface was formed. Based on the results obtained by wide-angle neutron diffraction, Swenson et al [12] showed that the ethylene oxide segments displace water molecules immediately adjacent to the vermiculite surfaces and bonding directly to them by physical adsorption. The data of Parfitt and Greenland [13] for PEO adsorbing onto Ca-montmorillonite illustrated that the adsorption of uncharged polymer is largely an entropy-driven process.

To date, it appears that the mechanisms of PEO adsorption on smectite are not well elucidated. The aim of this study, therefore, is to investigate the effect of layer charge density on the adsorption of PEO by smectite. The smectite charge reduction technique proposed by Hofmann and Klemen [14] was used to prepare a series of reduced-charge smectites (RCSs) and determine the role of layer charge on PEO adsorption.

2. Materials and methods

2.1. Preparation of reduced charge smectites (RCSs)
A reference Ca-saturated smectite (SAz-1) was obtained from the Clay Source Repository. The < 2 µm fractions were obtained by wet sedimentation and subsequently Li-saturated. RCS samples were prepared by heating Li-saturated SAz-1s for 24 h at temperatures of 150 and 170 °C respectively. These samples are subsequently referred to as SAz150 and SAz170 according to heating temperature and the original unheated sample is SAz25.

2.2. PEO adsorption isotherms

PEO (MW 400,000 g/mol) were obtained from Aldrich Chemical Co. and used as received. PEO of this molecular weight was chosen to ensure the saturating loading of PEO on smectite [5]. All adsorption tests were conducted at a fixed pH to eliminate the effects of smectite’s edge charges. We have taken pH 7 as a reference since it is closest to the equilibrium value of the smectite suspensions in aqueous solutions of PEO. Adsorption was conducted in 50-ml Pyrex beakers by contacting the smectite suspension with polymer solution using magnetic stirrer at 600 rpm at room temperature. A control with no smectite addition was included. After a predetermined contact time (typically 8 hours to reach equilibrium) the sample was centrifuged at 10000 rpm for 25 minutes and the supernatant was withdrawn. Total
organic carbon analyzer (TOC 5000, Shimazdu) determined the residual PEO concentrations. The difference in the amount of PEO before and after sorption gives the amount adsorbed. All samples were run in duplicates, and the average is reported.

2.3. Characterization

The cation exchange capacity (CEC) of the prepared RCS was determined by the ammonium acetate method at pH = 7 [15]. A Siemens D5000 diffractometer, utilizing the Cu-Kα (λ=1.5406 Å) radiation, was employed to record the X-ray powder diffraction patterns over the 3~20° 2θ range. The acceleration voltage was 40 kV and a continuous scan was performed with a step scanning speed of 0.04° 2θ per second. IR spectra were obtained using a JASCO Fourier transform spectrometer (model 410) in which detection was carried out with a diffuse reflectance mode (DRIFT). Two hundreds scans in the range of 4000-400 cm\(^{-1}\) were recorded with a resolution of 8 cm\(^{-1}\). Particle size distribution (PSD) of the raw and PEO loaded RCS suspensions were measured using a centrifugal sedimentation particle size analyzer (BT-1500, Bettersize Instruments, China) which provides a size distribution based on the weight of individual particles. The suspension stability was evaluated by measuring the turbidity of the top portion of the suspension in a
sedimentation column after 24-h settling. A high turbidity indicates a well-dispersed state.

3. Results and discussion

3.1. RCS characterization

The unheated SAz25 has a CEC of 135 meq /100 g. As expected, increasing the treatment temperature caused a more extensive reduction of CEC for RCS. Upon heating at 150 °C and 170 °C for 24 h the CEC of SAz150 and SAz170 were reduced to 99 and 25 meq /100 g respectively. Higher heating temperature apparently allowed more Li⁺ ions in the gallery diffuse into the layers. Thus a series of RCS with low (CEC = 25 meq /100 g), intermediate (CEC = 99 meq /100 g) and high (CEC = 135 meq /100 g) charge density were prepared for the following experiments. Fig. 1 compares the XRD patterns of different RCSs. The d₀₀₁ spacing for the unheated SAz25 is about 1.28 nm. Taking into account the smectite layer spacing of 0.95 nm, the remaining corresponds to a monolayer of water molecules [16]. Further decrease of the layer charge (SAz150 and SAz170) causes a nonswelling phase to appear. The SAz170 contains almost only a nonswelling phase with a d₀₀₁ spacing of 0.99 nm. In
the SAz150 a mixture of expandable and collapsed layers is present.

The hydrodynamic particle size distributions of RCSs with different CEC in water were shown in Fig.2. Apparently, smectite with low CEC (SAz170) forms tactoids, groups of aligned layers, of large size \(d_{90} = 5 \mu m\) in water presumably due to the presence of non-swelling layers. Smectite with higher CEC (SAz25 and SAz150) were better delaminated in water and resulted in tactoids with smaller number of layers and smaller particle size \(d_{90} = 1 \mu m\).

Fig. 3 shows the IR spectra of RCSs assigned to stretching vibrations of structural OH groups coordinated to octahedral cations. The OH-stretching band was shift from 3619 cm\(^{-1}\) to 3637 cm\(^{-1}\) upon heating to 170 °C. In smectite the hydroxyl is tilted by 12° out of the basal plane [17]. The residual negative charge located on apical oxygens \((O_{ap})\) of the tetrahedral due to unequal isomorphic substitution in the octahedral in unheated smectites permits OH…O\(_{ap}\) interactions by hydrogen bonds which weakens the O-H bond Strength in the hydroxyl. When Li\(^+\) ions migrate into the structure upon heating to compensate for the charge deficit, a limited residual negative charge remains on \(O_{ap}\) and thus the OH…O\(_{ap}\) interactions are weaken and O-H bond strength are increased. This accounts for the observed shift of the OH-stretching band to higher wavenumbers in the heated samples.
3.2. PEO adsorption isotherms

Fig. 4 depicts the adsorption isotherms of PEO on SAz25 (CEC=135 meq/100g), SAz150 (CEC=99 meq/100g) and SAz170 (CEC=25 meq/100g). The isotherms are of the high-affinity type where the adsorbed amount rises steeply at low equilibrium concentration. A defined plateau of 450 mg/g, 373 mg/g and 245 mg/g is obtained for RCSs with a CEC of 99 meq/100g, 25 meq/100g and 135 meq/100g respectively. Our previous study [18] indicated that smectite with higher CEC was better delaminated in water and resulted in smaller tactoids with larger surface area. However, Fig.4 indicates that low-charge smectites (SAz150 and SAz170) with more non-swelling phase and less exposed surface area adsorbs more PEO (expressed in mg/g) than high-charge smectite (SAz25), hence adsorption was not singularly dependent on the available surface area in water. It is clear that PEO adsorbed preferentially on the surface of low-charge smectite. The lower PEO adsorption capacity for SAz170 comparing to SAz150 could be explained by the presence of fully collapsed interlayer in SAz170 which is inaccessible for PEO intercalation. Thus, it is reasonable to speculate that charge density on smectite surface plays an important role in PEO adsorption.
3.3. PEO loaded RCS characterization

Fig. 5 shows the XRD patterns of RCSs and their PEO loaded mixtures. The shifting of XRD peaks for all PEO loaded RCSs to lower angles indicates intercalation of polymer chains. At the fully saturated capacity loading of PEO the d spacing of all RCSs increased from 9.9 - 12.8 Å to 17.3 - 18.6 Å. Taking into account the PEO zigzag chains thickness of 3.8 Å [19], this increase of d_{001} spacing corresponds roughly to intercalation of two layers of PEO in the interlayer space. At a lower PEO loading the d spacing of all RCSs increase to about 13 Å which indicates a single layer PEO intercalated in the interlayer space of smectite. It is also interesting to note in Fig. 5(c) that the collapsed phase of SAz170 was fully reopened by PEO intercalation.

Fig. 6 clearly shows the difference in PSD of SAz170 when subject to PEO adsorption. The adsorption of PEO resulted in a decrease in d_{90} of low-charge SAz170 from 4.0 µm to 0.40 µm. Apparently PEO adsorption enhances the delamination of SAz170 and produces a suspension with a finer PSD. This result of PSD measurement is in line with the fact that PEO adsorbs preferentially on the surface of low-charge smectite and reopens the collapsed phase of SAz170 demonstrated in Fig. 4 and Fig. 5. The reopen and delamination of collapsed phase of RCS by PEO adsorption is further supported by Fig. 7 which demonstrates the
The suspension stability of RCSs before and after PEO adsorption. Clearly the suspension stability of all RCSs increased after PEO adsorption and the stability of SAz170 containing collapsed phase were dramatically improved by PEO intercalation.

The DRIFT spectra of PEO, SAz170 and PEO-adsorbed SAz170 are presented in Fig. 8. The PEO has characteristic peaks in the frequency range 2690-3000 cm$^{-1}$ which are related to methane symmetrical stretching vibration in PEO. Those characteristic peaks are exhibited by the PEO-adsorbed SAz170 that confirms the attachment of PEO on the surface of SAz170. The stretching vibrations of structural OH groups of smectite (complex absorption band near 3630 cm$^{-1}$) are very sensitive to the changes in the nearest environment of the OH groups. The OH-stretching band of SAz170 was shift from 3637 cm$^{-1}$ to 3618 cm$^{-1}$ upon PEO adsorption indicating a decrease in O-H bond strength. In addition a new component near 3676 cm$^{-1}$ appears in the spectra of PEO-adsorbed SAz170. This band, assigned to AlMgLiOH vibration, was reported as evidence of local trioctahedral domains [20,21] and it confirms the presence of fixed Li$^+$ in the formerly vacant octahedral sites in SAz170. We believe that this already existing band was brought out upon PEO adsorption due to the right-shift of the major component of 3637 cm$^{-1}$. 
3.4. Discussion

In this study we found that the charge density of smectite has a pronounced effect on the adsorption of PEO. That is, PEO adsorbed preferentially on the surface of low-charge smectite. In addition the delamination of low-charge Li-smectite in water was enhanced upon PEO adsorption. As the structure of the PEO has shown, PEO contain hydrophilic ether oxygen and hydrophobic CH$_2$-CH$_2$-groups [1]. On the other hand, it has been demonstrated in literatures [22-25] that the siloxane surface of smectite is hydrophobic in nature except those regions close to exchangeable cations usually reside at the hexagonal cavity of siloxane surface [1]. Thus, it appears reasonable to conclude that the hydrophobic interaction between CH$_2$-CH$_2$-groups and siloxane surface is a source of driven force for PEO adsorption on smectite [26]. In addition, the fact that the stretching vibration band of structural OH groups of SAz170 was shifted from 3637 cm$^{-1}$ to 3618 cm$^{-1}$ (Fig. 8) indicates a decrease in O-H bond strength upon PEO adsorption onto siloxane surface. One plausible cause is that the structure OH was perturbed by the presence of ether oxygen of PEO sitting closely above them at hexagonal cavity (Fig. 9). Thus weak OH…O bonds (hydrogen bonds) were developed and consequently weakened the O-H bond strength. Based on the discussion above we may propose that both the hydrophobic interaction (between
CH$_2$-CH$_2$-groups and siloxane surface) and the hydrogen bonding (between ether oxygen of PEO and structure OH of smectite) are responsible for the adsorption of PEO on smectite. This proposed mechanism perfectly explains the observed preferential adsorption of PEO on low-charge smectite and enhanced delamination of smectite upon PEO adsorption. Firstly, reducing the number of exchangeable hydrated cations frees up more hexagonal cavities and hydrophobic area of siloxane surface, allowing more ether oxygen of PEO to interact with structure OH and more CH$_2$-CH$_2$-groups to interact hydrophobically with free siloxane surface. In contrast, in high-charge smectite large amount of hydrated cations residing at the hexagonal cavity hinders the hydrogen bonding between ether oxygen and structure OH. Also the exchangeable hydrated cations occupying the majority of the siloxane surface are strongly hydrophilic sites and hence, hinder the hydrophobic interaction with PEO. In this way that PEO adsorbed preferentially on the surface of low-charge smectite can be explained. Secondly, when the hydrophobic siloxane surface in the low-charge smectite is covered by PEO molecules, the hydrophilic ether oxygen of adsorbed ethylene oxide allows a more effective interaction between smectite and water, leading to an increase of hydrophilicity and delamination of smectite in water.

4. Summary
The results of this study confirmed the hydrophobic nature of siloxane surface of smectite and concluded that both the hydrophobic interaction (between CH$_2$ – CH$_2$ – groups and siloxane surface) and the hydrogen bonding (between ether oxygen of PEO and structure OH of smectite) are the major driven forces for PEO adsorption on smectite. In this context, high-charge smectite with a large portion of the siloxane surface covered by exchangeable cations demonstrated a diminution of PEO adsorption capacity. In contrast, PEO adsorbed preferentially on the surface of low-charge smectite and the delamination of low-charge smectite in water was enhanced due to PEO adsorption presumably due to the hydrophilic ether oxygen of adsorbed PEO.

References


Figures

Fig. 1. X-ray diffraction patterns of different RCSs.

Fig. 2. The hydrodynamic particle size distributions for different RCS.

Fig. 3. The IR spectra of structural OH stretching in RCSs.

Fig. 4. The adsorption isotherms of PEO on different RCSs.

Fig. 5. X-ray diffraction patterns of RCSs and their PEO loaded mixtures: (a) SAz170; (b) SAz150; (c) SAz170.

Fig. 6. Particle size distributions of SAz170 before and after PEO adsorption.

Fig. 7. The suspension stability of RCSs before and after PEO adsorption.

Fig. 8. The IR spectra of PEO and structural OH stretching in SAz170, and PEO-adsorbed SAz170.

Fig. 9. Model of the hydrogen bonding between structure OH of smectite and ether
oxygen of PEO.
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