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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 CH_2–CH_2– 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.

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 SiO_2, MoO_2 and V_2O_5 with strong Brønsted 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 SiO_2. 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.

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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 h to reach equilibrium) the sample was centrifuged at 10,000 rpm for 25 min and the supernatant was withdrawn. Total organic carbon analyzer (TOC 5000, Shimadzu) 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-$K\alpha$ ($\lambda = 1.5406$ 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 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 d_{001} 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 d_{001} spacing of 0.99 nm. In the SAz150 a mixture of expandable and collapsed layers is present.

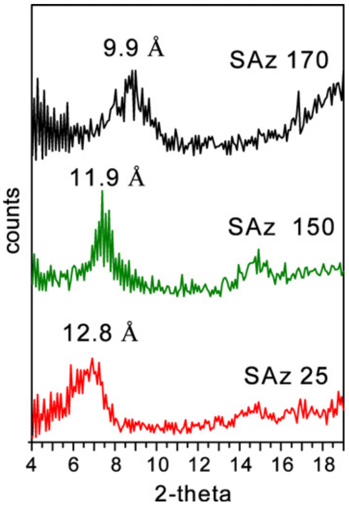

Fig. 1. X-ray diffraction patterns of different RCSs.

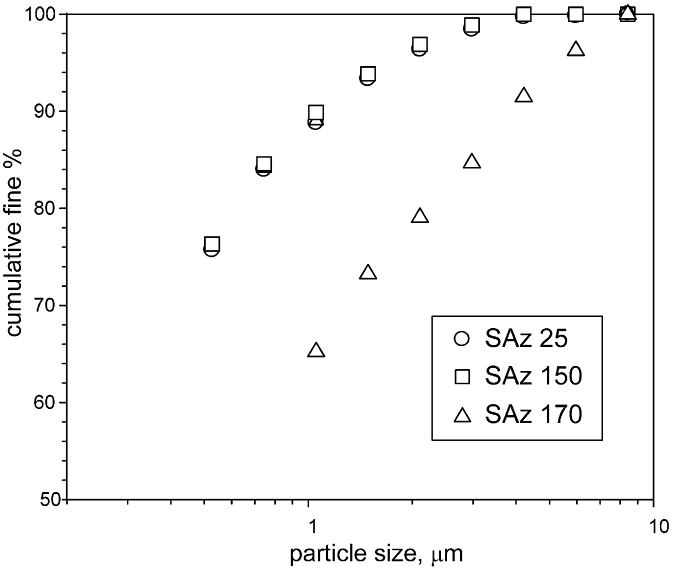

Fig. 2. The hydrodynamic particle size distributions for different RCSs.

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 ($d_{90} = 5$ μm) in water presumably due to the presence of nonswelling 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 ($d_{90} = 1$ μm).