



Research paper

Thermal analysis evidence for the location of zwitterionic surfactant on clay minerals

Lingya Ma^{a,b,c}, Jianxi Zhu^{a,c}, Hongping He^{a,c,*}, Yunfei Xi^d, Runliang Zhu^{a,c}, Qi Tao^{a,c}, Dong Liu^{a,c}^a CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c Guangdong Provincial Key Laboratory of Mineral Physics and Material, Guangzhou 510640, China^d Nanotechnology and Molecular Science Discipline, Faculty of Science and Engineering, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, QLD 4000, Australia

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ABSTRACT

The exact location of surfactant molecules on clay minerals is critical for the synthesis of clay polymer nanocomposites and their applications in environmental remediation. The location and thermal characteristics of zwitterionic surfactant (Z16) composites with montmorillonite (Mt), Al₁₃-pillared montmorillonite (AIPMt), calcined AIPMt (AIPMt/500), and talc (Tlc) were investigated by using X-ray diffraction (XRD) and thermogravimetric analysis (TG). The basal spacing of Mt was markedly increased after modification with Z16, while that of Tlc, AIPMt, and AIPMt/500 was essentially unchanged. The decomposition temperature of Z16/Tlc composite (~294 °C) was similar to that of the pure surfactant. Sulfobetaine apparently failed to penetrate into the interlayer space of talc; instead it was confined to external surfaces. On the other hand, the DTG pattern of Z16-modified Mt showed two main peaks (404 and 336 °C), indicating two different intercalation mechanisms of Z16 on Mt. Sulfobetaine, loaded to AIPMt and AIPMt/500, was found to decompose at 355 and 370 °C, respectively, suggesting that Z16 occupied the interpillar space in these samples. Much more Z16 was taken up by AIPMt than by AIPMt/500, although the specific surface areas of both materials were practically identical, suggesting that the surfactant molecules in the interlayer space of AIPMt were largely adsorbed by electrostatic attraction between the negatively charged groups of Z16 and the positively charged Al₁₃ cations.

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1. Introduction

Clay minerals are important raw materials of choice for the novel materials because they are abundant, inexpensive and environmentally friendly (Bergaya and Lagaly, 2013). Being hydrophilic, however, many representative species, such as montmorillonite and saponite, as well as their inorganic pillared forms are immiscible in organic media, limiting their scope for industrial and environmental applications. Surface modification through intercalation and grafting of organic species is, therefore, an important step in processing clay minerals for industrial applications (Bergaya and Lagaly, 2001; Bergaya et al., 2011; He et al., 2013, 2014). In particular, surfactant-modified montmorillonites ('organoclay') have received a great deal of attention because of their great performance in environmental protection, remediation (Zhu and Chen, 2000; Zhu et al., 2000; Theng et al., 2008) and the synthesis of clay polymer nanocomposites (Ray and Okamoto, 2003; Theng, 2012). A recent development of great interest is the preparation of surfactant-modified pillared interlayered clays (PILC) (Tahani et al., 1999;

Annabi-Bergaya, 2008; Zhu et al., 2009a; He et al., 2014; Ma et al., 2014a, 2014b). Having both hydrophilic and hydrophobic surface properties, these inorganic–organic clays (IOC) are potentially capable of synchronically removing organic and inorganic contaminants in wastewater (Zhu and Zhu, 2007; Bouberka et al., 2009; Zhu et al., 2009b; Ouellet-Plamondon et al., 2012).

Previous studies have shown that the type of organic surfactant used can markedly influence the structural characteristics and adsorptive behavior of organoclays (OC) (Dentel et al., 1998; Shen, 2002; Heinz et al., 2007; Chitrakar et al., 2011). In this respect, zwitterionic surfactants, such as sulfobetaine, might significantly improve the adsorption capacity of OC. Besides containing both positively charged (quaternary ammonium) and negatively charged (sulfonate) functional groups, sulfobetaine is highly water-soluble, biodegradable and non-toxic (Qi et al., 2008; Zhu et al., 2011).

The location and thermal behavior of surfactant molecules on external and interlayer surfaces of clay minerals have been the subject of many investigations (Xie et al., 2002; He et al., 2005; Xi et al., 2005, 2007; Kooli, 2009; Zhu et al., 2012; Ma et al., 2014a). Cationic surfactants may associate with montmorillonite surfaces as (a), intercalated cations; (b), intercalated molecules (ion pairs); and (c), molecules filling interparticle pores (He et al., 2005; Xi et al., 2005; Zhu et al., 2012). On heating, intercalated and pore-filling surfactant molecules

* Corresponding author at: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Wushan, Guangzhou 510640, China. Tel.: +86 20 85290257; fax: +86 20 85290130.

E-mail address: hehp@gig.ac.cn (H. He).

commonly decompose at a lower temperature than that shown by their intercalated cationic counterparts (He et al., 2005; Xi et al., 2005; Zhu et al., 2012). The location of zwitterionic surfactant on clay minerals significantly affected the structure and application of obtained OMt. In previous studies (Zhu et al., 2012; Ma et al., 2014b), zwitterionic surfactants modified montmorillonites and PILC showed different structures with those modified by cationic surfactant. However, the location and behavior of zwitterionic surfactant on clay mineral surface has not yet been clarified, which is important to understand the modification mechanism.

Therefore, in this study, some evidences of the location of zwitterionic surfactant on clay mineral surfaces were tried to be found out by thermal analysis combined with X-ray diffraction (XRD), specific surface area (SSA) and pore size analysis. Zwitterionic surfactant – hexadecyldimethyl (3-sulfonatopropyl) ammonium (Z16) (Fig. 1) was selected as a surface-modifying agent for talc (Tlc), montmorillonite (Mt), Al₁₃-pillared Mt (AIPMt), and AIPMt after calcination at 500 °C (AIPMt/500). The decomposition temperature of the different samples could be directly obtained from analyzing the respective TG and derivative TG (DTG) curves (Frost et al., 2009; Liu et al., 2013). For all three Mt samples, the surfactant was capable of penetrating the interlayer space. For comparison, this study also assessed the thermal stability of Z16-modified talc where adsorption of surfactant was confined to external particle surfaces. The SSA of the clay samples was determined by adsorption of N₂ gas at –195.79 °C. The results suggest that adsorbed sulfobetaine may adopt a variety of conformations in the interlayer and external surfaces of clay minerals.

2. Materials and methods

2.1. Materials

Calcium montmorillonite (Mt), with a cation exchange capacity of 110.5 cmol₍₊₎/kg, was obtained from Inner Mongolia, China. The talc sample (Tlc) was obtained from Longsheng, Guangxi province, China. Sulfobetaine (Z16), with a chemical formula of C₂₁H₄₅NO₃S and a purity of 99%, was supplied by Nanjing Robiot Co. Ltd., China. Analytical grade AlCl₃·6H₂O and Na₂CO₃ were supplied by Guangzhou Chemical Reagent Factory, China.

2.2. Synthesis of Al-pillared montmorillonite

A hydroxyl-aluminum solution, containing Al₁₃ cations, was prepared by slowly adding a 0.5 M Na₂CO₃ solution to a 1.0 M solution of AlCl₃ at a rate of 1 mL/min with vigorous stirring in a water bath at 60 °C to give a final OH[–]/Al³⁺ ratio of 2.4. The mixture was continuously stirred for 12 h, after which it was allowed to ‘age’ for 24 h at 60 °C. Montmorillonite was then added to the mixture to give an Al/clay ratio of 10 mmol/g. The dispersion was stirred for 24 h, and then aged for 24 h at 60 °C. The resultant AIPMt was collected by centrifugation, washed 8 times with distilled water, and then freeze-dried for 48 h. Its calcined derivative (AIPMt/500) was obtained by heating AIPMt in an oven at 500 °C for 8 h.

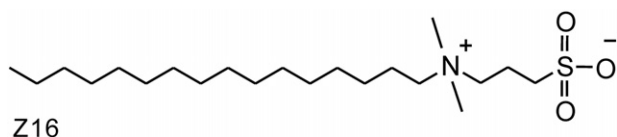


Fig. 1. Chemical structure of the zwitterionic surfactant, hexadecyldimethyl (3-sulfonatopropyl) ammonium, denoted as Z16.

2.3. Surfactant modification

Surfactant modification was carried out by adding 1 g of a given clay mineral sample to 20 mL of a 0.11 M solution of Z16 at 60 °C, and stirring for 12 h. The products were collected by centrifugation, washed 8 times with distilled water (except for the mixture of Tlc and Z16, which was washed only once) in order to remove Z16 molecules, associated with external particle surfaces, and then freeze-dried for 48 h. The various Z16-modified materials were denoted as Z16-Tlc, Z16-Mt, Z16-AIPMt, and Z16-AIPMt/500.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Ni-filtered CuK α radiation ($\lambda = 0.154$ nm, 40 kV and 40 mA) with 2.3° Soller slits, 1.0 mm divergence slit and 0.1 mm receiving slit. Patterns were collected between 1° and 80° (2 θ) at a scanning speed of 2° (2 θ) min^{–1} with a 0.01 2 θ step size and a 0.3 s counting time. Samples used for XRD were random powder.

Thermogravimetric analysis (TG) was performed on a Netzsch STA 409PC instrument. The samples were heated from 30 to 1000 °C at a rate of 10 °C/min under a flow of high-purity nitrogen (60 mL/min). The differential thermogravimetric (DTG) curves were directly derived from the corresponding TG curves.

Nitrogen adsorption–desorption isotherms were determined on samples that had been degassed under vacuum for 12 h at 120 °C, using a Micromeritics ASAP 2020M instrument. The multiple-point Brunauer–Emmett–Teller (BET) method was used to calculate the SSA value of the materials. The SSA values of the clay minerals used in this study are showed in Table 1.

3. Results and discussion

3.1. Structures characterization

The d_{001} -value of Tlc at 0.95 nm (Fig. 2a) was equal to the individual layer thickness, indicating that the interlayer space was empty. On the other hand, the d_{001} -value for Mt was 1.48 nm because of the presence of hydrated (exchangeable) calcium ions in the interlayer space (Fig. 2a). The d_{001} -value of 1.88 nm for AIPMt corresponded to an interlayer separation (distance) of 0.92 nm. This value was close to the size of the Keggin-like (Al₁₃)⁷⁺ cation (0.9 nm), indicating the successful intercalation of Al₁₃ into Mt (Plee et al., 1985). The d_{001} -value of AIPMt/500 at 1.78 nm was slightly smaller due to dehydroxylation of the cationic Al₁₃ pillars after heating at 500 °C (Klopprogge et al., 1992; Klopprogge and Frost, 1999).

The basal spacing of the Z16-modified samples clearly depended on the clay mineral species used (Fig. 2b). In the case of montmorillonite, the d_{001} -value dramatically increased from 1.48 to 4.39 nm after modification with Z16, and a second order reflection appeared. This observation indicates successful penetration of Z16 into the interlayer space where the surfactant molecules adopted a variety of conformations (Zhu et al., 2012). On the other hand, the basal spacings of Z16-modified Tlc, AIPMt, and AIPMt/500 were comparable with those of the corresponding untreated (raw) clay mineral samples. Unlike that of montmorillonite, the

Table 1
The specific surface areas of clay minerals.

Samples	Specific surface area (m ² /g)
Tlc	19.9
Mt	69.5
AIPMt	283.2
AIPMt/500	261.5
Z16-AIPMt	17.9
Z16-AIPMt/500	13.4

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