



Research paper

Microstructure of different chain length ionic liquids intercalated into montmorillonite: A molecular dynamics study



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ARTICLE INFO

Article history:

Received 6 May 2014

Received in revised form 30 June 2014

Accepted 3 July 2014

Available online 19 July 2014

Keywords:

Ionic liquid

Montmorillonite

Intercalated

Molecular dynamics study

ABSTRACT

This study employs molecular dynamics modeling to examine the interlayer microstructures of montmorillonite intercalated with different chains of $C_n\text{mimCl}$ montmorillonites with varying chain lengths, intercalation amount, arrangement and energy. $C_4\text{mim}^+$ and $C_8\text{mim}^+$ arrange themselves in monolayers, while $C_{12}\text{mim}^+$ and $C_{16}\text{mim}^+$ in parallel bilayers or tilt aligning. The basal spacing of montmorillonite and the corresponding energy increased as the chain length of organic cations is increased. It is indicated that no bond has been formed for $N^+ - O$ due to the minimum distances of no less than 3.1 Å and angles of 35°–45° between N^+ in $C_n\text{mim}^+$ and silicon–oxygen tetrahedron. These modeling results provide insights into the understanding of synthesized $C_n\text{mim}^+$ –montmorillonite microstructure and guidelines for relevant engineering applications.

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1. Introduction

Montmorillonite is one of the smectite groups, composed of silica tetrahedral sheets layered between alumina octahedral sheets. The imperfection of the crystal lattice and the isomorphous substitution induce a net negative charge that leads to the adsorption of alkaline earth metal ions in the interlayer space. Such imperfection is responsible for the activity and exchange reactions with organic compounds. Most commonly, Na-montmorillonite is used as the base mineral clay and its sodium cations can be exchanged with quaternary ammonium cations (Burns et al., 2006; Soule and Burns, 2001). QAC-coated montmorillonite exhibits higher zeta potential (Bate and Burns, 2010), enhanced strength, lower compressibility, and stronger retention of organic compounds (Lo, 2001; Redding et al., 2002) in the environment, yielding a variety of potential applications in waste containment, landfill liners, and slurry walls (Lorenzetti et al., 2005; Park and Jaffe, 1993; Sheng and Boyd, 1998; Smith and Jaffe, 1994). The structure of the surfactant (e.g., chain length, number of long chains, head group) and the intrinsic properties of the original clay material have a combined effect on the structure and properties of the resultant organoclay (Bergaya et al., 2006; Ha and Char, 2005; He et al., 2006; Osman et al., 2004; Xi et al., 2005a, 2005b).

Numerous previous studies have focused on the characterization of alkylammonium cation arrangement and conformation after intercalation in the interlayer of layered silicates (Bergaya et al., 2006; He

et al., 2006; Lagaly, 1981; Othmani-Assmann et al., 2007; Vaia et al., 1994; Xi et al., 2005a, 2005b). Depending on the packing density of the alkylammonium ions, different arrangements of organic molecules can be formed (Wen et al., 2006). The interlayer spacing of these organoclays generally increases as the surfactant loading increases and subsequently reaches a saturation limit, which is equal to or larger than the clay cation exchange capacity (CEC). Both experimental and simulation techniques have been performed, including X-ray powder diffraction (XRD) (He et al., 2006), NMR spectroscopy (Osman et al., 2004; Zhu et al., 2005), Monte Carlo simulations; Skipper et al., 1995a, 1995b), and molecular dynamics simulations (Heinz et al., 2007; Liu et al., 2009). These reported experimental and numerical simulation results have demonstrated that the organic carbon of intercalated surfactants tends to form an integral number of layers, oriented parallel to the basal surface of clay (He et al., 2005; Liu et al., 2009).

Since ionic liquids, which are a class of liquids composed solely of ions are non-volatile, non-flammable, highly conductive, and chemically and thermally stable, they can be used in technological applications such as catalysis, electrochemistry, and extraction (Dupont, 2004). The combination of ionic liquids with a solid support is believed to be a promising system for the immobilization of biological and synthetic catalysts, as well as transition metal nanostructures. This so-called supported ionic liquid phase (SILP) catalysis combines the advantages of ionic liquids with those of a heterogeneous material supported on the solid phase, resulting in low toxicity, which are environmentally benign and have a wide range of catalytic applications (Dupont et al., 2002; Lozano et al., 2007; Mehnert, 2005; Riisager et al., 2006). Ionic liquid modified mineral clay have recently drawn much attention due to their negligible vapor pressure, nonflammability and electrical

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conductivity, which are all favorable for fabricating the inorganic clay–organic intercalation compounds.

Molecular simulation is a computational technique to model behaviors of the substance at the atomic scale. The objective of the current research is to simulate the arrangement of single chain imidazolium chloride ($C_n\text{mimCl}$) surfactants of varying chain lengths, structures and quantities in the interlayer space of different montmorillonites and compare the obtained results with experimental data. Additionally, a model will be derived to predict a single chain $C_n\text{mimCl}$ in the montmorillonite interlayer for the given clay prototype and organic molecule loading. We perform molecular dynamics simulations to address the intercalated organic cation structure at the molecular level: organic cation arrangement of four single-chain $C_n\text{mimCl}$ s will be quantified for different systems, and the effects of conformation and type of intercalated organic cation will be examined.

2. Materials and methods

2.1. Materials

The montmorillonite used was SWy-2 obtained from the Clay Mineral Repositories in Purdue University (West Lafayette, IN), and was used without further purification. It has a chemical formula of $(\text{Ca}_{0.12}\text{Na}_{0.32}\text{K}_{0.05})[\text{Al}_{3.01}\text{Fe(III)}_{0.41}\text{Mg}_{0.54}][\text{Si}_{7.98}\text{Al}_{0.02}\text{O}_{20}(\text{OH})_4]$, a CEC of 85 ± 3 mmol $_c$ /100 g (Chipera and Bish, 2001), a layer charge of 0.32 eq/mol per $(\text{Si,Al})_4\text{O}_{10}$ (Borden and Giese, 2001), an external surface area (ESA) of 23 m 2 /g, respectively (Mermut and Lagaly, 2001), and a mean particle size of 3.2 μm with a d_{25} to d_{75} in the range of 3–10 μm .

These 1-butyl-3-methylimidazolium chloride monohydrate (CAS#: 79917-90-1), 1-octyl-3-methylimidazolium chloride monohydrate (CAS#: 64697-40-1), 1-dodecyl-3-methylimidazolium chloride monohydrate (CAS#: 114569-84-5), and 1-hexadecyl-3-methylimidazolium chloride monohydrate (CAS#: 404001-62-3), were obtained from Shanghai Darui Fine Chemical Co. Ltd. (Shanghai, China). They have pKa values of 7.08 ± 0.1 , calculated on ACD online services website, due to the protonation of both nitrogen atoms. When the solutions' pH value is no more than 5.2, it stabilizes as $C_n\text{mimH}^+$; when pH value is between 5.2 and 9.2, its existence will change to monovalent cation and neutral molecule, and when pH value is above 9.2, it will be of non-ion form.

2.2. Batch experiments

The initial $C_n\text{mimCl}$ concentrations were varied from 10 to 15,000 mg/L for the intercalation isotherm study, and were fixed at 1000 mg/L for the kinetic study and pH dependency study. The mass of SWy-2 used was 0.2 g while the volume of the solution used was 10 mL for all studies except the kinetic study (20 mL). The solid and solution were combined in 50 mL centrifuge tube and shaken for 60 min at 150 rpm and room temperature for all studies except the kinetic study, in which the shaking time was set to 3, 5, 10, 20, 30, 40, 50, 60 and 120 min, respectively. After the mixtures were centrifuged at 10,000 rpm for 20 min, the supernatants were filtered through 0.22 μm syringe filters before the analysis of equilibrium $C_n\text{mimCl}$ concentrations.

2.3. Instrumental analyses

The equilibrium $C_n\text{mimCl}$ concentrations were analyzed by a UV–Vis spectrophotometer (Model T6 New Century 1650, made by General Instrument, Inc. LLT, Beijing China) at the wavelength of 210 nm, corresponding to its maximal absorbance. Calibrations were made following the standards of 10, 20, 30, 40, 50, and 60 mg/L with a regression coefficient of 0.9998. The amount of $C_n\text{mimCl}$ adsorbed was calculated from the difference between the initial and final concentrations.

Powder XRD analyses were performed on a Rigaku D/max-IIIa diffractometer (Tokyo, Japan) with a Ni-filtered $\text{CuK}\alpha$ radiation at 30 kV and 20 mA. Orientated samples were scanned from 3° to 15° at 2°/min

with a scanning step of 0.01°. Powder samples were packed in horizontally held trays. The changes in the XRD peak positions reflect the intercalation of the polymer into layered silicates. The Bragg equation was applied to calculate the basal spacing of SWy-2 layers. The interlayer space sizes in intercalated hybrids were deduced from XRD peak positions of (001) of the hybrids.

Fourier Transform infrared spectroscopy (FTIR) spectra of samples were collected on a Nicolet-560 spectrometer (Thermal Nicolet Co., USA) from 400 to 4000 cm^{-1} with a nominal resolution of 4 cm^{-1} . For each spectrum 16 runs were collected and averaged. The SWy-2 specimens were prepared by adding approximately 1% of the sample powder to dry KBr powder.

2.4. Computational details

Molecular simulation was performed under the module 'CASTEP' of Materials Studio 6.0 software to investigate the sorption sites of $C_n\text{mimCl}$ on SWy-2. The primitive unit cell of SWy-2 was optimized with the generalized gradient approximation (GGA) for the exchange–correlation potential (PW91) in favor of relatively weak interactions. The resulting primitive unit cell was characterized by the parameters of $a = 15.540$ Å, $b = 17.940$ Å, $c = 12.56$ Å and $\alpha = \gamma = 90^\circ$, $\beta = 99^\circ$. Based on the primitive unit cell, a series of $(3 \times 2 \times 1)$ super cells were built with the spacing of layers set to 13.40 Å, 14.31 Å, 17.58 Å, and 20.25 Å respectively.

In order to investigate the intercalated mechanism of $C_n\text{mimCl}$ in pure SWy-2 layer, simulated annealing algorithm was used to perform canonical Monte Carlo (MC) simulation with $C_n\text{mimCl}$ simulated as adsorbate on the layer of pure SWy-2. For the grafted SWy-2, MC simulation with $C_n\text{mimCl}$ simulated as adsorbent. The number of cycle is 3 with the step of each cycle of 106, 3 cycles were determined to present a representative part of the interface devoid of any arbitrary boundary effects. Based on the structure of the preferential adsorption model of $C_n\text{mimCl}$ in the layer of SWy-2 predicted by MC calculation, GGA-PW91 was used to optimize the structure and to accurately predict the interaction energy between $C_n\text{mimCl}$ and SWy-2 layer. All of the GGA-PW91 calculations were performed using a double numerical plus polarization function (DNP) as the basis set and DFT-D correction. Herein, in all calculations the heavy atoms of SWy-2 were frozen, whereas the hydrogen of SWy-2, $C_n\text{mimCl}$ molecules was fully relaxed.

3. Results and discussion

3.1. Amount of $C_n\text{mimCl}$ intercalated into the SWy-2

Time (Fig. 1a), pH value of solution (Fig. 1b) and equilibrium concentration (Fig. 1c) of the solution are three influential factors affecting SWy-2's intercalation via four organic cations with different chain lengths. As these four organic cations with the same charged location and electricity merely differ in chain length, they are identical in influencing reacting time and pH value of the solution. It is a rapid process of intercalating organic cations into SWy-2's: half of the maximum amount of intercalation can be reached in 5 min, while the full maximum amount of intercalation will be achieved in 20 min. There have been similar reports in organic cations adsorbed or intercalated with clay minerals. Organic cations intercalating SWy-2 are mainly concerned of cation exchange in accordance with the second-order kinetic equation.

When the pH value is below 5.2, the amount of intercalation maintains at approximately 50 mg/g (Fig. 1b). As the pH value of the solution is increased to 9.2, the amount of intercalation decreases to 35 mg/g correspondingly, and when $\text{pH} > 9.2$, SWy-2 cannot attract $C_n\text{mimCl}$ due to its neutral molecule state. As seen in Fig. 1b, neutral $C_n\text{mimCl}$ can also be intercalated into the interlayer of SWy-2. Herein both cation exchange and hydrophobicity are responsible for the intercalation of organic cations. This also explains why nonionic surfactant can be intercalated into

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