Chemical Engineering Journal 236 (2014) 306–313

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Microstructure and process of intercalation of imidazolium ionic liquids into montmorillonite

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HIGHLIGHTS

- Using green C_{16}mimCl intercalated montmorillonite and get organic composite materials.
- At high intercalation, C_{16}mimCl intercalated into the interlayer of montmorillonite.
- The main force of C_{16}mimCl intercalated montmorillonite is cation exchange.
- The process is studied by molecular dynamics simulation software.

ARTICLE INFO

Article history:
Received 18 July 2013
Received in revised form 11 September 2013
Accepted 14 September 2013
Available online 24 September 2013

Keywords:
Montmorillonite
1-Hexadecyl-3-methylimidazolium chloride monohydrate
Intercalation
Layer charge

ABSTRACT

Organically modified clays exhibit adsorption capacities for cations, anions, and nonpolar organic compounds, which make them valuable for various environmental technical applications. Research into organic molecule modified montmorillonite should place importance on studying the mechanism of the intercalation process. Herein a new kind of green and steady ionic liquid, 1-Hexadecyl-3-methylimidazolium chloride monohydrate (C_{16}mimCl) has been chosen as the intercalant agent. We have investigated the process that C_{16}mimCl is intercalated into Na-montmorillonite in aqueous solution under batch studies and molecular simulations. The C_{16}mimCl intercalation has been found relatively fast with a large rate constant. The intercalation is driven by both cations exchange and negative charge on the layer surface. The process is affected by the initial concentration and pH value of the solution; the basal spacing is increased to 2.88 nm after intercalation. Molecular dynamic simulation further reveals that the initial concentration of C_{16}mimCl can influence its configuration in the interlayer, causing the change of interlayer spacing. Apart from the electrostatic interaction, the hydrophobicity of the organic molecule also plays an important role in the intercalation process. Overall, ionic liquid intercalated montmorillonite is a promising environmental composite material with broad application potentials such as chemical fiber and aviation.

1. Introduction

Montmorillonite is a typical natural mineral with nano-stratiform structure, which can be exfoliated into nanosheet or nanotube structure in water or some other solutions. The unit layer structure of MMT is 2:1 type (TOT): one octahedral aluminate layer is sandwiched between two tetrahedral silica layers, together linked to slices in a two-dimensional space and then accumulates towards c-direction. Because of the isomorphous replacement (for example, the Al^{3+} in octahedron is replaced by Mg^{2+} or Fe^{2+}, the Si^{4+} in tetrahedron is replaced by Al^{3+}), there are some excess negative charges among the layers. This negative charge can be compensated by the absorption of cations, such as k^{+}, Na^{+}, Ca^{2+} or Mg^{2+} into the layers due to the electrostatic interaction [1,2]. The bonding force between these cations and montmorillonite layers is relatively weak; therefore, these cations can be replaced again by other cations (the organic cations and inorganic cations). In the case of being modified by organic material, the organic solvent enters the layer of montmorillonite by ion exchange or absorption. After intercalation, the interplanar spacing of montmorillonite will be changed due to the bracing effect of ion or molecule, leading to the change in its properties as a result. As such, montmorillonite with different properties can be obtained by using different intercalating modifiers.

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http://dx.doi.org/10.1016/j.cej.2013.09.063

During the preparation of organoclays, organic cations, such as quaternary alkylammonium ions, are used to replace the inorganic cations in the interlayer spaces and on the external surfaces of clay particles. The organic cations intercalate in the interlayer spaces and accumulate on the external surfaces of the clay particles. Then the organic cations can be absorbed through hydrophobic bonding, in which case an accompanying uptake of their inorganic counterions occurs. It has been suggested that the ability of organoclays to retain anionic pollutants is induced by the exchange with these previously co-absorbed counterions [3–5]. And the presence of organic cations on the external surfaces of clay particles increases the hydrophobicity of the organoclays which makes the clay capable of adsorbing nonpolar organic substances [6–8]. After the process of organoclays production, cations exchange capacity is retained to some extent since the exchange of the inorganic clay cations with organic cations is usually incomplete [5,9].

In order to gain a deeper understanding of the physicochemical process in the water–clay systems at the microscopic level molecular modeling (MD) has been widely used to study the interlayer structural characteristics of clay minerals and dry organoclays from atomic-level insights on the structural features of the system [10–14]. In addition, it can also be used to investigate sorption of contaminants on various sorbents and get information like structural, dynamic, and thermodynamic properties of the sorption process [15–18] and study the structure and physical properties of clay minerals, crystalline layers and the interlayer space and swelling behavior of smectite clays [19–25].

In the present work, 1-Hexadecyl-3-methylimidazolium chloride monohydrate (C_{16}mimCl) is used as intercalant agent for montmorillonite. The C_{16}mimCl is chemically and thermally stable, nonflammable, easy to dissolve and nonvolatile due to the absence of vapor pressure. It can also be recycled, which makes it environmentally friendly and energy saving. X-ray diffraction (XRD) technique is used to study properties of the modified montmorillonite. The cation exchange capacity of modified montmorillonite is also measured and the obtained result proves that the intercalation is successful. Based on the these experimental results, molecular dynamics simulation on intercalation process of using C_{16}mimCl as intercalant agent for montmorillonite is conducted. The simulation results further demonstrate that this kind of modified montmorillonite can be widely applied in the field of rubber filler materials and compound materials.

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 $(Ca_{0.12}\ Na_{0.32}\ K_{0.05})[Al_{3.01}\ Fe(III)_{0.41}\ Mg_{0.54}][Si_{7.98}\ Al_{0.02}]O_{20}(OH)_4$, a CEC of 85 ± 3 mmolc/100 g [26], a layer charge of 0.32 eq/mol per $(Si,Al)_4O_{10}$ [27], an external surface area (ESA) of 23 m^2/g, respectively [28], and a mean particle size of 3.2 μm with a d_{25} to d_{75} in the range of 3–10 μm.

The 1-Hexadecy1–3-methylimidazolium chloride monohydrate (CAS #: 404001-62-3), was obtained from Shanghai Darui fine chemical Co., Ltd. (Shanghai, China). It has a chemical formula of $C_{20}H_{41}ClN_2O$, molecular weight of 360.01 g/mol, and p*K*a values of 7.08 ± 0.1 due to protonation of both nitrogen atoms (Fig. 1). The p*K*a was calculated on ACD online services website. When the solutions' pH value is no more than 5.2, it exists as C_{16}mimlH$^+$; when pH value is between 5.2 to 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.

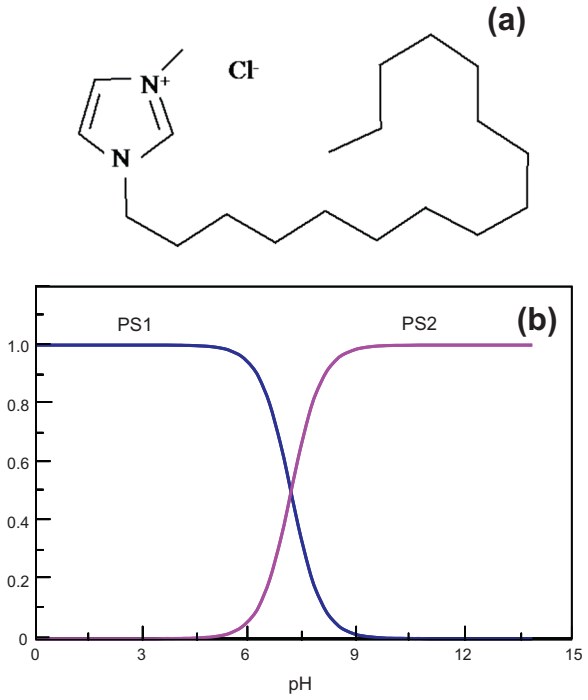

Fig. 1. Molecular structure of 1-Hexadecyl-3-methylimidazolium chloride monohydrate (a) and speciation of C_{16}mimCl (b).

2.2. Batch experiments

The initial C_{16}mimCl concentrations varied from 10 to 15,000 mg/L for the intercalation isotherm study, and 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 solution used was 10 mL for all studies except the kinetic study, for which 20 mL of solution was used. The solid and solution were combined in each 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 3, 5, 10, 20, 30, 40, 50, 60 and 120 min. After the mixtures were centrifuged at 10,000 rpm for 20 min, the supernatants were filtered through 0.22 μm syringe filters before being analyzed for equilibrium C_{16}mimCl concentrations.

2.3. Instrumental analyses

The equilibrium C_{16}mimCl concentrations were analyzed with 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 using standards of 10, 20, 30, 40, 50, and 60 mg/L with a regression coefficient of 0.9998. The amount of C_{16}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 Cu Kα radiation at 30 kV and 20 mA. Orientated samples were scanned from 3° to 70° at 8°/min with a scanning step of 0.02°.

2.4. Molecular simulation

Molecular simulation was performed under the module 'Forcite' of Materials Studio 5.0 software to investigate the sorption sites of C_{16}mimCl on SWy-2. The SWy-2 model was constructed and the atomic coordinates were derived from the space group of C2/m with