Applied Clay Science 150 (2017) 23–33

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Evaluation of organic modification of montmorillonite with ionic and nonionic surfactants

Jefferson Lopes Alves[a,*], Paulo de Tarso Vieira e Rosa[b], Ana Rita Morales[a]

[a] School of Chemical Engineering, University of Campinas, Av. Albert Einstein, 500, 13083-852 Campinas, SP, Brazil
[b] Institute of Chemistry, University of Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

ARTICLE INFO

Keywords:
Montmorillonite
Organophilization
Semi-solid
Ionic surfactant
Nonionic surfactant
Statistical analysis

ABSTRACT

This work aims at evaluating the organophilization of montmorillonite with two different types of surfactants: one ionic, containing C16-C18 di(alkyl ester) dimethyl ammonium chloride (EA) and one nonionic, containing ethoxylated tallow amine (ETA). Aqueous dispersion and semi-solid routes were compared in terms of functionalization efficiency by statistical analysis, and supercritical CO_2 was performed as a complementary and comparative method. Besides, the effect of the washing process after functionalization was evaluated. X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and contact angle were used to evaluate the intercalation of surfactants into montmorillonite and process yield. The d_{001}-value was improved by both surfactants intercalation, and the conformations of the species inside the clay minerals were suggested. The final arrangement of the organic species into Mt was modified as a function of the concentration of surfactant added, and by the washing steps. Most process parameters evaluated showed significant effects on d_{001}-value and process yield. The semi-solid method was confirmed as a good alternative route due to its efficiency and it could be an environmentally friendly option to be used. ETA-modified montmorillonites showed similar d_{001}-values (around 4.0 nm) and higher thermal stability than EA-modified montmorillonite.

1. Introduction

The increasing demand for new materials, especially for polymers to replace metal and ceramic materials due to its low density, justify studies related to its mechanical improvement. In this field, clay mineral polymer nanocomposites (CPN) are highlighted and are still a matter of enormous importance in researches and in the industrial sector. Organophilic montmorillonites (OMt) have been widely used to produce CPN (Bergaya et al., 2006; Breakwell et al., 1995; Khalaf and Hegazy, 2012; Lee and Lee, 2004; Liu et al., 2014; Paiva et al., 2008). The modification of clays for CPN, i.e., purification and the functionalization process to make it organophilic/hydrophobic has been subject of many studies (Alves et al., 2016a,b; Bergaya et al., 2006; Paiva et al., 2008; Utracki, 2004).

The most used surfactants are quaternary ammonium salts, which can provide a very good intercalation between the clay layers but have low thermal stability. This fact has motivated studies with new kind of compounds to obtain functionalized clay minerals, looking for high thermal stability and better compatibility with polymers (Breakwell et al., 1995; Khalaf and Hegazy, 2012; Paiva et al., 2008; Sarkar et al., 2011; Takahashi et al., 2013; Thompson et al., 2008). Some alternative compounds are, e.g., ionic liquids based on phosphonium salts (Ha and Xanthos, 2009; Livi et al., 2011a,b; Livi et al., 2010) and imidazolium salts (Ha and Xanthos, 2009; Livi et al., 2010, 2011a,b; Takahashi et al., 2013); nonionic surfactants (Guégan, 2013; Guégan et al., 2014; Li et al., 2012; Silva et al., 2014; Zhuang et al., 2015); and anionic surfactants (Du et al., 2010; Zhuang et al., 2015).

In the past three decades, there has been a growing production of non-ionic surfactants for environmental and food applications, in particular, the derivatives of non-aromatic alcohol ethoxylate (AE), due to their low toxicity and potential biodegradability (Shen, 2001; Silva et al., 2014). These attractive characteristics in addition to their high thermal stability have raised the interest in using these kind of compound to prepare OMt for use as adsorbents of organic and inorganic waste due to their hydrophilic-hydrophobic characteristic (Guégan et al., 2014; Shen, 2001), for petroleum drilling fluids (Silva et al., 2014) and, for production of clay polymer nanocomposites (Chakraborty et al., 2013).

OMt produced with the traditional method of dispersion in solvents is not an environmentally friendly process, due to the large amounts of solvents used and effluents generated in the process (solvents and residual surfactants). Then, alternative reactional routes have been

* Corresponding author.
E-mail addresses: alvesjl.eq@gmail.com, jeffeq@feq.unicamp.br (J.L. Alves).

http://dx.doi.org/10.1016/j.clay.2017.09.001
Received 13 June 2017; Received in revised form 31 August 2017; Accepted 3 September 2017

studied, taking into account the efficiency, the environmental impacts and operational costs (Alves et al., 2016a; Livi et al., 2011a; Naveau et al., 2009; Paiva and Morales, 2012; Zhuang et al., 2015). A promising alternative is the reaction in semi-solid medium (SS) due to the low amount of solvent used (Alves et al., 2016a; Paiva and Morales, 2012). Another alternative recently used is the modification in supercritical CO_2 (SCO) because of its good solubility for many organic compounds, and low environmental impact (Alves et al., 2016a; Livi et al., 2011a; Naveau et al., 2009; Paiva and Morales, 2012; Zhuang et al., 2015). However, there are costs associated with equipment installation and operation that should be considered.

In previous work (Alves et al., 2016a), a study for montmorillonite modification was presented considering the process parameters in aqueous dispersion (AD), semi-solid and supercritical CO_2 for ammonium and phosphonium salts. SS was considered as a very good alternative for intercalation of both surfactants, whereas the SCO was only effective for the ammonium species. As a complementation of this previous work, this paper presents the study of intercalation of ionic (based on ester ammonium – EA) and non-ionic (based on ethoxylated amine – ETA) surfactants into Mt supported by the design of experiments (DOE), aiming to evaluate properties and characteristics of EA and ETA modified montmorillonite, and to confirm the alternative route as a method capable to modify clay minerals by several kinds of organic compounds.

2. Materials and methods

2.1. Materials

The bentonite used was the same used in previous works (Alves et al., 2016a,b) – purified by elutriation method - mainly composed by polycationic (with calcium and sodium cations) montmorillonite (PPMt), with a CEC of 89.3 meq/100 g, surface area = 42.8 m^2/g; micropore volume = 0.0045 cm^3/g; and micropore area = 10.3 m^2/g (Alves et al., 2016a); and by kaolinite (about (5.6 wt%) and nontronite (about 1.9 wt%).

The two organic compounds used in this work were the Armosoft DEQ, containing about 82% of a quaternary ammonium salt C16-C18 di (alkyl ester) dimethyl ammonium chloride, and 18% of ethanol as solvent, supplied by Akzo Nobel Brazil – (EA); and Ultramina TA50, a non-ionic surfactant containing ethoxylated tallow amine with 99.9% of active material, supplied by Oxiteno S/A Ind – (ETA). The structural formulas of surfactants are shown in Fig. 1.

2.2. Organophilization methods

The Mt was organically modified with both EA and ETA surfactants according to the scheme presented in Fig. 2. Experimental procedures and conditions were the same described in Alves et al. (2016a).

2.2.1. Intercalation in aqueous route

A design of experiments (DOE) was performed to evaluate some process parameters in clay mineral functionalization by water medium. Table 1 describes the parameter levels used on DOE.

Dispersion as the variable associated with the amount of water was correlated with the organophilization routes as: the lower level (− 1) was a small amount of clay – 5 wt% in water, considered as the aqueous dispersion (AD) method; the upper level (+ 1) was a large amount of clay – 85 wt% in water, considered as the semi solid (SS) method; and at center point – 45 wt% in water, was referenced as semi-aqueous (SA) method because it cannot be considered as an aqueous dispersion or a semi-solid method. The other independent variables of DOE were the surfactant amount and the use or not of washing process. OMt samples with EA were washed two times: first with 200 ml of deionized water and then with 200 ml of a solution of ethanol/water (1:1 volume). As the ETA is a nonionic surfactant, which is preferably physically adsorbed in the Mt., the ETA modified montmorillonites were washed only once with 200 ml of deionized water, since ethanol would remove the adsorbed species on the OMt external surface (Silva et al., 2014; Alves et al., 2016a). After washing, the pH of the materials was determined by pH-indicator strip. Thus, a full factorial design 2^3 with six central points was applied. The dependent variables evaluated were d_{001}-value and process yield. Statsoft Statistica, 7.0 was used to verify the significance of the effects, both main and interaction effects. A p-value lower than the level of significance ($\alpha = 0.10$) indicates a significant contribution of the factor with a 90% of confidence.

2.2.2. Intercalation in supercritical CO_2 route (SCO)

A SCO medium was applied in this work as a complementary method, aiming to verify the ability of this route to intercalate these types of compounds. For this purpose, the process parameters were used at the central point (Alves et al., 2016a).

2.2.3. Washing – a complementary study

In addition, a detailed study was performed to evaluate the effects of the washing steps on d_{001}-value and yield in function of the added surfactants by AD. The washing steps were: i) washing with only deionized water (AW1); ii) washing with a solution (1:1 by volume) of water and ethanol (AW2).

The samples were named according to the type and amount of surfactant and process as MS_am-w, where M is correlated with montmorillonite and "S" is associated with the surfactant type as MEA, which means montmorillonite modified with EA, or META with ETA surfactant, "a" is the surfactant amount based on clay CEC, "m" is related to the reaction medium – aqueous dispersion (AD), semi-solid (SS), semi-aqueous (SA), and supercritical CO_2 (SCO), and "w" means BW – before washing, AW – after washing.

2.3. Characterization

The samples were characterized by powder X-ray diffraction analyses (XRD) at room temperature to evaluate changes in d_{001}-value of the clay mineral by intercalation of each compound. The analyses were performed on Shimadzu XRD-7000 equipment, with Monochromator Shimadzu CM-3121, operating at Cu Kα radiation (λ = 1.54 Å), voltage 40 kV, current of 30 mA. Slit adjustment - divergence slit of 0.5°, scatter slit 0.5° and receiving slit 0.3 mm. The samples were scanned from 1.5° to 10° (2θ) at 1.5°/min, step size of 0.02° and preset time of 0.8 s.

Thermogravimetric analyses (TGA) were performed using a TA Instruments SDT 2960 equipment under nitrogen gas atmosphere with flow of 100 ml/min. First, approximately 10 mg of sample in alumina crucibles were stabilized at 40°C for 15 min, then it was heated at 10°C/

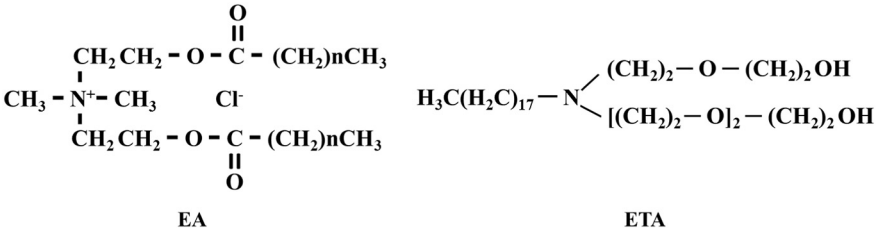

Fig. 1. Structural formulas of EA and ETA surfactants, where n = 15–17.