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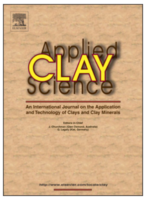

Research Paper

Investigation of the alkyl chain lengths of surfactants on their adsorption by montmorillonite (Mt) from aqueous solutions

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ABSTRACT

In this study, the behaviors of adsorption of six different quaternary ammonium salts onto montmorillonite (Mt) have been investigated. One of six cationic surfactants is branched (tetrabutylammonium bromide $(C_4)_4$ABr) and the others are linear (with five different hydrocarbon chain lengths, i.e. C_{16}TABr, C_{14}TABr, C_{12}TABr, C_{10}TABr, and C_8TABr).The organoclays were characterized by spectroscopic techniques such as XRD and FT-IR. Their surface morphologies were also determined by using the SEM images. To reveal the adsorption mechanism, the measurements of contact angle and zeta potential of the samples were carried out. When the alkyl chain length increased, the adsorption ability of the surfactant adsorbed onto Mt surface increased. The effects of temperature, surfactant initial concentration and contact time onto the adsorption were investigated. The adsorption isotherms obtained show that the experimental isotherms exhibit a good fit with the Langmuir, Freundlich and Temkin adsorption models at all the temperatures, but the fit with models decreases with the decrease of chain length. The isosteric enthalpy and entropy changes were evaluated. The adsorption of surfactants onto Mt was found to be exothermic and spontaneous at all temperatures except for C_{10}TABr adsorption. The interlayer distance and the packing density of surfactant ions in the interlayer region increased with increased chain length, as confirmed by the XRD patterns. FTIR spectrum and contact angle measurements of raw montmorillonite and organoclays indicate the incorporation of surfactants and the change in hydrophilicity of the organoclays. The values of zeta potential imply the presence of hydrophobic interactions between their hydrocarbon tails for C_{16}TABr and partly for C_{14}TABr adsorption. The negative values of zeta potential of other surfactants (C_{14}TABr, C_{12}TABr, C_{10}TABr, C_8TABr and $(C_4)_4$TABr) except for C_{16}TABr compared to the raw clay indicate that the ion exchange is more effective according to electrostatic interactions in terms of the adsorption process.

1. Introduction

Montmorillonite which is a member of the group of smectite clay, and has superior properties such as high cation exchange capacity (CEC), high surface area, low cost, high swelling and sorption capacities is commonly used in an extensive variety of applications (Dentel et al., 1995; Breen et al., 1997; Alther, 2000, 2003; He et al., 2001; He et al., 2010; Xi et al., 2010). Montmorillonite clay is composed of two tetrahedral silica layers sandwiching an aluminum octahedral layer (Frost et al., 2007; Luo et al., 2015).

The clay layers are negatively charged as a consequence of an isomorphic distribution of exchangeable counterbalanced cations such as Na^+ and Ca^{2+} in the interlayer. Because of the hydration of inorganic cations on the exchange site, the clay mineral surface is hydrophilic and thus, natural clays are ineffective sorbents for organic compounds (Prost and Yaron, 2001; Chaiko, 2002; Kim et al., 2003; Xi et al., 2010).

However, the inorganic ions of clay minerals may be replaced by organic ions and then the interlayer surface becomes hydrophobic under suitable conditions (Lee et al., 1999; Wang et al., 2004; Volzone et al., 2006; Frost et al., 2008; Zhu et al., 2009). Organically modified layered silicates can be produced by modifying clays and clay minerals with various organic compounds through intercalation process and/or surface grafting (Smith and Galan, 1995; Zhu et al., 1998; Lee et al., 1999; Yariv and Cross, 2001; Wang et al., 2004; Volzone et al., 2006; Frost et al., 2008; Zhu et al., 2011).

Adsorption of surfactants at the solid/liquid interface has been extensively studied during the last four decades (Yílmaz and Yapar, 2004; Alkan et al., 2005) and it is important for many traditional processes such as detergency, mineral flotation, corrosion inhibition, dispersion of solids, adhesion, cleaning and degreasing of metal surfaces oil recovery as well as the newer fields of templated surfaces and nanotechnology (Lee et al., 1999; Yariv and Cross, 2001; Wang et al., 2004).

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Also, there are the applications of the organoclays in different fields, such as polymer-clay nanocomposites, adsorption of organic contaminants in soil, water and air, rheological control agents, paints, cosmetics, refractory varnish and thixotropic fluids, etc. (Smith and Galan, 1995; Zhu et al., 1998; Lee et al., 1999; Wang et al., 2004; Yílmaz and Yapar, 2004; Schampera et al., 2016).

In order to prepare organoclays, various cationic (Jordan, 1963; Lagaly, 1986; Regev and Khan, 1996; Zhu and Chen, 2000; Shen, 2001; Bergaya and Lagaly, 2006; He et al., 2010; Zhang et al., 2012; Hassani et al., 2015; Ratkievicius et al., 2016), anionic (Lagaly, 1986; Amirianshoja et al., 2013), nonionic (Lagaly et al., 2006; Barati-Harooni et al., 2016) and amphoteric surfactants (Moraru, 2001; Liu et al., 2016) have been used in previous researchers. Among various surfactants, cationic surfactants have attracted the most attention for the modification of montmorillonite. Ion exchange with alkyl ammonium ions such as quaternary ammonium salts is well-known and the preferential method to prepare organoclays (Lee et al., 1999; Beall, 2003; Wang et al., 2004; Yílmaz and Yapar, 2004; Zhu et al., 2011).

Notwithstanding the wealth of information that exists on the synthesis of organoclays using quaternary ammonium salts, the studies dealing with mechanistic and structural aspects of the adsorption process depending on the chain length are not common in the literature.

For this purpose, in this study, the effect of various surfactants having different chain lengths onto the structural characteristics of organoclay was evaluated. Six cationic surfactants, one branched-molecule (tetrabutylammonium bromide $(C_4)_4$ABr), and ones with five different hydrocarbon chain lengths (C_{16}TABr, C_{14}TABr, C_{12}TABr, C_{10}TABr, and C_8TABr), were investigated comparatively. This study include; 1) the relationship between the chain length of surfactant and the organoclay structure based on XRD, FT-IR and SEM results; 2) the investigation of surfactant adsorption as a function of equilibrium concentration and temperature; 3) the supporting of the adsorption data by particle zeta potential and contact-angle measurements; 4) the compliance of the adsorption data with the isotherm models; and 5) the thermodynamic evaluation of the adsorption data. Such a study is of high importance for understanding the structure and properties of organoclays, and it will provide information for their synthesis and applications.

2. Materials and methods

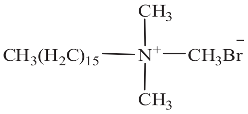
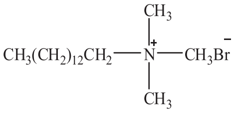
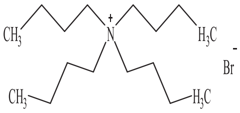
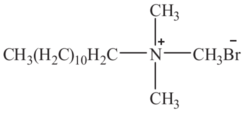
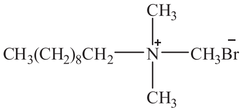
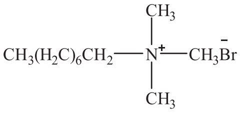
2.1. Materials

In this study, cationic surfactants of the quaternary ammonium bromide type (C_nTABr) were used: Cetyltrimethylammonium bromide (C_{16}TABr), myristyltrimethylammonium bromide (C_{14}TABr), dodecyltrimethylammonium bromide (C_{12}TABr), decyltrimethylammonium bromide (C_{10}TABr), octyltrimethylammonium bromide (C_8TABr) and also tetrabutylammonium bromide ($(C_4)_4$ABr) as a branched surfactant (see Table 1). The used surfactants and their properties are given in Table 1. The cationic surfactants were obtained from Sigma-Aldrich with a purity of 99.9%, and they were used without further purification. Also, 1,2-dichloroethane and picric acid were purchased from Sigma-Aldrich and used without any further purification. Montmorillonite, which is a commercial sample of bentonite from Çankırı deposit in Turkey, was supplied from Karakaya Mineral Co, Ankara, Turkey. The cation exchange capacity (CEC) of the Mt was 149 meq/100 g, which was determined using the methylene blue method (Brindley and Hang, 1970; Wang et al., 1996). Chemical composition of the clay was determined by X-ray fluorescence spectrometer (Table 2).

2.2. Adsorption experiments

Batch adsorption experiments were carried out in 100 mL, glass-stoppered, round-bottom flasks immersed in a thermostatic shaker bath. For this study, 0.1 g of clay was mixed with 100 mL of the aqueous solutions of various initial concentrations (50–300 mg/L) of surfactants. The flasks and their contents were shaken at the temperatures of 293, 313 and 323 K and natural pH for 30 min. Pre-experiments indicated that this time is enough to attain adsorption equilibrium. The stirring

Table 1
Characteristics of used surfactants.

Chemical name	Molecular structure	Molecular weight ($g\ mol^{-1}$)	CMC ($mol\ L^{-1}$)	CAS number
Cetyltrimethyl ammonium bromide ($C_{19}H_{42}BrN$)	 $CH_3(H_2C)_{15}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\overset{-}{Br}$	364.45	$9.01\ 10^{-4}$	57-09-0
Tetradecyltrimethyl ammonium bromide ($C_{17}H_{38}BrN$)	 $CH_3(CH_2)_{12}CH_2-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3\overset{-}{Br}$	336.39	$3.30\ 10^{-3}$	1119-97-7
Tetrabutylammonium bromide ($C_{16}H_{36}BrN$)		322.37	–	1643-19-2
Dodecyltrimethyl ammonium bromide ($C_{15}H_{34}BrN$)	 $CH_3(H_2C)_{10}H_2C-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3\overset{-}{Br}$	308.34	$15.10\ 10^{-3}$	1119-94-4
Decyltrimethyl ammonium bromide ($C_{13}H_{30}BrN$)	 $CH_3(CH_2)_8CH_2-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3\overset{-}{Br}$	280.29	$64.60\ 10^{-3}$	2082-84-0
Octyltrimethyl ammonium bromide ($C_{11}H_{26}BrN$)	 $CH_3(H_2C)_6CH_2-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3\overset{-}{Br}$	252.23	$130.00\ 10^{-3}$	2083-68-3

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