

INTRODUCTION

Surface modifications of clay minerals have received an intensive attention because it allows the creation of new materials and new applications [1-3]. Ion exchange with alkyl ammonium ions such as quaternary ammonium salts is well-known and the preferential method to prepare organoclays [5-7]. Notwithstanding the wealth of information that exists on the synthesis of organo clays using quaternary ammonium salts, the studies investigating from mechanistic and structural aspects of the adsorption process depending on the chain length is not common in the literature. For this purpose, in this study, effect of surfactants type, i.e. having different chain lengths on the structural characteristics of nanoclay is evaluated. Six different aliphatic ammonium compounds which one of them has a branched structure (tetrabutyl ammonium bromide (C_{16} ABr)) and others are with five different hydrocarbon chain lengths, i.e. C_{16} TABr, C_{14} TABr, C_{12} TABr, C_{10} TABr, and C_8 TABr, were used as a comparison study. Such a study is of high importance for understanding the structure, properties of organoclays, and it will be guide to the future their synthesis and applications.

MATERIAL AND METHODS

The inorganic clay, used in this study, montmorillonite, which is a commercial sample of bentonite from Çankırı deposit in Turkey, was obtained from Karakaya Mineral Co., Ankara, Turkey. The cation exchange capacity (CEC) of the clay sample was determined by the methylene blue method [8]. (CEC: 149,7 meq/100 g). The chemical composition (wt%) of the montmorillonite was determined by Rigaku RIX-3000 X-ray fluorescence spectrometry (Rigaku Corporation, Tokyo, Japan) and it was SiO_2 :59.3, Al_2O_3 : 17.2, Fe_2O_3 :5.9, MgO : 3.6, CaO :2.2, Na_2O : 1.7, K_2O :0.1, TiO_2 , SO_3 :0.5 and others. The above mentioned cationic surfactants were obtained from Sigma Aldrich with a purity of 99.9 %, and they were used without further purification. Adsorption experiments were carried out for the various initial surfactant concentrations (50-300 mg/L) and at three temperatures (293, 313 and 323 K). The concentration of surfactant in the supernatant was determined by spectrophotometric method [9]. The organo clay samples characterized by using XRD, FT-IR and SEM methods and their zeta potentials and contact angles were measured.

RESULTS AND DISCUSSION

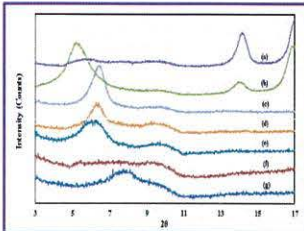


Fig.1. XRD patterns of the pristine montmorillonite and surfactant modified montmorillonite samples. (a) C_{16} ABr/MMT (b) C_{14} TABr/MMT (c) C_{12} TABr/MMT (d) C_{10} TABr/MMT (e) C_8 TABr/M (f) C_{16} TABr/MMT (g) MMT

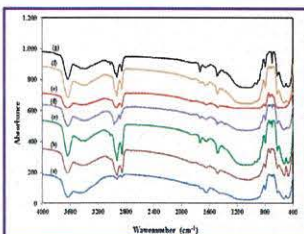


Fig.2. FT-IR spectra of the pristine montmorillonite and surfactant modified montmorillonite samples (a) MMT (b) C_{16} TABr/MMT (c) C_{14} TABr/MMT (d) C_{12} ABr/MMT (e) C_{10} TABr/MMT (f) C_8 TABr/MMT (g) C_8 TABr/MMT

The organoclay samples prepared by using 300mg/L of initial surfactant concentration and 0.1 g of clay characterised with the techniques of XRD and FT-IR. The results are given in Figs.1 and 2. It is observed from the XRD diffractograms that the d-spacing of the organo-modified nanoclay has increased with alkyl chain length of the surfactant as compared with pristine montmorillonite. For montmorillonite, there is a peak at $2\theta = 7.19^\circ$ corresponding to a d spacing of 1.23 nm. This peak represents d_{001} plane, analogous to the interlayer spacing and it indicates clay sample used as adsorbent in this study is Na-montmorillonite [10].

After addition of C_{16} TABr, d_{001} diffraction peak of montmorillonite are vanished by reducing its intensity, a weak peak at 1.76 nm and wide and flat peak occurred, suggesting that both predominantly microcomposite structures (a phase separated composite) due to poor interaction between the C_{16} TABr and the clay and intercalated structures (1.76 nm corresponds to the lateral bilayer arrangement) formed as a result of incorporation of C_{16} TABr. After addition of C_{14} TABr, (C_{14})ABr (branched), C_{12} TABr, C_{10} TABr and C_8 TABr surfactants, a relative decrease expansion in the interlayer space is obtained i.e. the peaks occurred at 1.68, 1.60, 1.46, 1.42 and 1.40 nm, respectively, compared with the addition of C_{16} TABr indicating the lateral monolayer arrangements with the various angle from the clay surface [11].

FT-IR results showed the intercalation of all surfactants in the interlayer galleries of montmorillonite. It was understood from the FT-IR results, the intensity of interactions increased with alkyl chain length. From the SEM imagings of the organo clay samples, it was seen that the more compact structures occurred for C_{16} TABr/MMT and C_{14} TABr/MMT due to cohesive interactions between their tails and hydrophobic interactions disappeared almost as decreased the chain length (Fig 5).

Isotherm studies was carried out for three temperatures (293 and 313 and 323 K) and all of surfactants and the equilibrium adsorption isotherm drawn for 293 K was given in Fig.3. As seen from this figure, both adsorption efficiency and effectiveness increased with increasing of alkyl chain length due to the more amount of surfactant adsorption with longer chain length and their largesize.

The value of zeta potential of the pristine montmorillonite and organoclay samples show that ion exchange is more dominant than electrostatic interactions in the adsorption process of C_{14} TABr, C_{12} TABr, C_{10} TABr, C_8 TABr and (C_{16})ABr, because their zeta potential values more negative than that of C_{16} TABr. And also, it can be said that the presence of mutual interactions between the tails of C_{16} TABr and partly C_{14} TABr. According to the raw clay, the higher values of contact angles of C_{16} TABr/MMT and C_{14} TABr/MMT organoclay samples supported this result (Fig.4). The temperature had no effect on the isotherms indicating thermal motion not changed orientations of surfactant molecules in the interlayer galleries

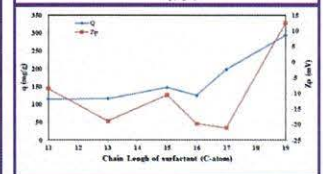
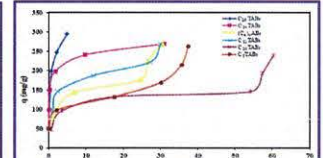


Fig.3. Adsorption isotherms of surfactant modified montmorillonite samples. The variation of adsorption capacity and zeta potential values with surfactant chain length

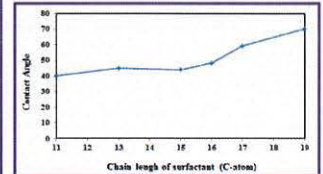


Fig.4. The variation of contact angle of surfactant modified clay samples with surfactant chain length



Fig.5. The SEM images of the pristine montmorillonite and surfactant modified montmorillonite samples A) MMT B) C_{16} TABr/MMT C) C_{14} TABr/MMT D) (C_{16})ABr/MMT E) C_{12} TABr/MMT F) C_{10} TABr/MMT G) C_8 TABr/MMT

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