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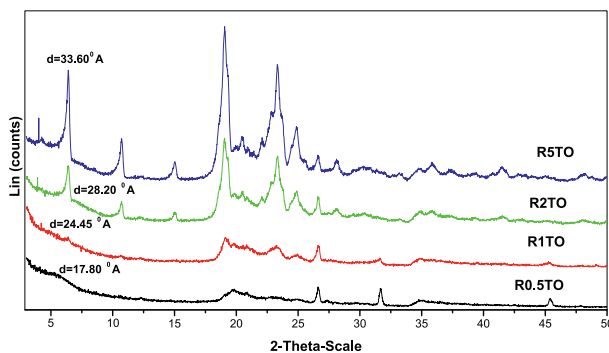
Effect of surfactant types and their concentration on the structural characteristics of nanoclay

M.F. Zawrah^{a,*}, R.M. Khattab^a, E.M. Saad^b, R.A. Gado^a^a National Research Center, Ceramics Department-Center of Excellence for Advanced Sciences, 12622-Dokki, Cairo, Egypt^b Ain Shams University, Faculty of Science, Chemistry Department, Cairo, Egypt

HIGHLIGHTS

- Organo-modified nanoclays were synthesized using surfactants having different alkyl chain lengths and concentrations.
- Surfactant concentration and alkyl chain length greatly influence the structural characteristics.
- The basal *d*-spacing of organo-modified clay were proportional to the surfactant concentration and the alkyl chain length.
- The maximum *d*-spacing of the organo-clay synthesized with TO was 33.6 Å.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of organo-modified nanoclays was synthesized using three different surfactants having different alkyl chain lengths and concentrations [0.5–5.0 cation exchange capacity (CEC)]. These surfactants were Ethanolamine (EA), Cetyltrimethylammoniumbromide (CTAB) and Tetraoctadecylammoniumbromide (TO). The obtained modified nanoclays were characterized by X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) and compared with unmodified nanoclay. The results of XRD analysis indicated that the basal *d*-spacing has increased with increasing alkyl chain length and surfactant concentration. From the obtained microstructures of these organo-modified nanoclays, the mechanism of surfactant adsorption was proposed. At relatively low loading of surfactant, most of surfactant entered the spacing by an ion-exchange mechanism and is adsorbed onto the interlayer cation sites. When the concentration of the surfactant exceeds the CEC of clay, the surfactant molecules then adhere to the surface adsorbed surfactant. Some surfactants entered the interlayers, whereas the others were attached to the clay surface. When the concentration of surfactant increased further beyond 2.0 CEC, the surfactants might occupy the inter-particle space within the house-of-cards aggregate structure.

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Introduction

The layered expandable clay minerals (e.g., smectite, hydrotalcite) always possess charges on their layer sheet; these charges compensated by counter inorganic ions. Because of the strong

hydration capability of these inorganic ions, the interlayer spaces of the clay minerals are hydrophilic in nature. As a result, the natural clay minerals show rather weak affinity to most of the hydrophobic organic compounds (HOCs), and they are seldom used as sorbents for HOCs [1]. Under suitable conditions, the inorganic ions on clay minerals can be replaced by organic ions, and then the interlayer spaces become hydrophobic. As a result, the sorption

* Corresponding author. Tel.: +20 1222437949; fax: +20 233370931.
 E-mail address: mzawrah@hotmail.com (M.F. Zawrah).

capacity of the modified clay minerals (i.e., organoclays) towards HOCs can be significantly improved [2–5].

In the past two decades, cation surfactant-modified montmorillonite has been the most widely studied organoclays. Montmorillonite is a swelling-clay mineral that has exchangeable cations in the interlayer spaces. These cations counterbalance the permanent negative charge on the montmorillonite surfaces caused by isomorphous substitution in the crystal lattice. The interlayer exchangeable cations can be substituted easily with some organic cations, such as cationic surfactants and dyes. The substitution of inorganic exchangeable cations by organic cations in the interlayer of clay is irreversible, resulting in expansion of the interlayer spacing thereby leading to an increase in the basal spacing. These organic cations render the clay mineral hydrophobic at the surface while also increasing its wettability and thermodynamically [6].

Different surfactants have been used to prepare organoclays. These include single and dual cationic surfactants [7–9], anionic-cationic surfactants [10,11] and nonionic surfactants [12]. It is well known that the chemical composition of montmorillonites varies from one deposit to another. This variation is reflected by the magnitude of the cation exchange capacity (CEC), arising from isomorphous substitution (e.g., Mg^{2+} for Al^{3+} in the octahedral sheet and/or Al^{3+} for Si^{4+} in the tetrahedral sheet) in the montmorillonite layer. The resultant deficiency in positive layer charge is compensated by the adsorption of Na^+ or Ca^{2+} ions in the interlayer space. These inorganic cations can be exchanged with, or replaced by, other cations, including cationic surfactant [13].

Either unmodified or modified clays have been mostly chemically modified for various industrial applications such as rheological additives, as thickeners in coating products, glues, platisols, drilling fluids, cosmetics [14–19] and for wastewater treatment [20,21]. The new pesticide formulation using clay minerals can be used for potential applications such as removal of toxic compounds from environment and to reduce dispersion of pollutants in soil, air and water [22–26]. Also, organoclays are used as thickeners in paints, greases, oil-base drilling muds and for the purpose of gelling various organic liquids [27–31]. Ca- and Na-montmorillonite are used as carriers for agricultural insecticides to increase production of grains used for food supply [32]. Clay minerals also find applications in various paints and varnishes where they act as a filler, stable against weathering, to provide and improve abrasion and scratch resistance, for the flattening effect and for adhesion in thixotropic suspensions. Paints and varnishes filled with clay minerals also provide protection against corrosion and erosion [32].

In this paper, effect of surfactants type (i.e. having different chain lengths) and concentration on the structural characteristics of nanoclay is addressed. Three different aliphatic ammonium compounds, namely Ethanolamine (EA), Cetyltrimethylammoniumbromide (CTAB) and Tetraoctadecylammoniumbromide (TO) were used as a comparison study. These organonano-clays can be used in various research and industrial applications.

Materials and methods

Materials

The raw clay sample was supplied by Egypt Bentonite & Derivatives Company, Alexandria, Egypt. The chemical composition of the clay powder sample has been estimated through the quantitative determination of its constitution oxides using X-ray fluorescence (XRF) technique [33]. XRF analysis of raw clay sample is illustrated in Table 1. It is observed that the major constituents in the raw clay are SiO_2 , Al_2O_3 and Fe_2O_3 in a descending order. The higher SiO_2 and lower Al_2O_3 content are mainly due to the pre-

dominance of montmorillonite clay mineral as well as the presence of considerable amounts of quartz (SiO_2) and feldspar (alkali aluminosilicates) as non clay minerals [33–36].

Ethanolamine (EA), Cetyltrimethylammoniumbromide (CTAB) and Tetraoctadecylammoniumbromide (TO) are chemically pure surfactants purchased from Carl Roth GmbH Co., Bio Basic Inc and Aldrich Co., respectively, and used to modify the under investigated clay.

Preparation of organo-modified nanoclays

The Cation Exchange Capacity (CEC) was determined for the raw clay sample by saturation with 1 N solution of sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) for long time at pH 8.2, then washing for several times by ethanol 95% to get rid the excess sodium ion. The reacted sodium (Na^+) with the clay sample was extracted by reaction with 1 N ammonium acetate solution followed by sodium determination using flame photometer in the extracted solution [37–39]. CEC could be calculated from the following equation:

$$CEC(\text{meq}/100\text{g}) = \text{meq}/L \text{ Na} \times A/Wt \times 100/1000$$

where A is the total volume of extract (ml) and Wt is the weight of air dry sample (g).

5 g of clay was dispersed in 300 ml of distilled water for 24 h at room temperature using a magnetic stirrer and then a desired amount of surfactant (EA, CTAB and TO) was slowly added. The concentration of surfactant varied from 0.5 to 5.0 according to the CEC of clay. The reaction mixtures were stirred for 5 h at 80 °C. Consequently, the cation exchange reaction occurs rapidly. The resulting organoclay suspension was mixed further for 12 h. All products were washed until free from bromide anions and dried at 90 °C. Finally, the resulting material was ground using SFM-1 Desk Top Planetary Ball Miller (MTI) for 3 h, in order to obtain a nanoscale powder. The organo nanoclay product was stored in bottle [40–43]. The batches of organo modified clay were designed according to the concentration and symbol of relevant surfactant as illustrated in Table 2.

The phase composition and d -spacing of the raw clay and organo-modified nanoclay were identified by X-ray using a Philips 1730 diffractometer with Ni filter, Cu K α radiation at a scan speed of 0.5° min⁻¹ [33–35]. Microstructure of clay and organo-modified clay with different surfactants were examined using scanning electron microscope (Philips XL 30) after coating with gold thin films [44]. Fourier transform infrared spectroscopy (FTIR) was used for further investigation of the modified and unmodified nanoclay. FTIR spectra were recorded using a JASCO FT/IR-6100 in the range of frequency 400–4000 cm⁻¹ at 25 °C. For each spectrum, 128 consecutive scans with 4 cm⁻¹ resolution were averaged [45,46].

Results and discussion

Structural characterization and cation exchange capacity of starting raw clay

XRD of raw clay powder is shown in Fig. 1. It is evident that quartz, montmorillonite, kaolinite are the major phases in the pattern. The strongest d -spacings of the essential clay minerals in the pattern are $d = 12.6 \text{ \AA}$, 4.50 \AA and 3.02 \AA for montmorillonite; $d = 7.14 \text{ \AA}$, 4.22 \AA and 3.57 \AA for Kaolinite; and $d = 3.34 \text{ \AA}$ and 4.25 \AA for quartz [47,48].

The cation exchange capacity (CEC) for clay determined by replacement of sodium was found to be 101 mEq/100 g. Since the mEq equal to mg \times valence of surfactant divided by its molecular weight, the amount of CEC will be changeable according to the molecular weight of each surfactant.

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