

Adsorption Studies of Fatty Acids on Montmorillonite-Based Filler Clay

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ABSTRACT: Surface coating of montmorillonite-based filler clay with stearic and oleic (9-octadecenoic acid) acids was presented. Sedimentation measurements showed that the sedimentation rate and the sediment volume decreased sharply with the adsorbed amount of the acid up to a certain concentration and then became constant. The chemical analysis showed that the adsorbed amount of either acid by montmorillonite clay increased with the equilibrium concentration of the acid in the solution. The adsorption isotherm indicated the formation of a monolayer on the clay surface at a lower concentration of the acids followed by formation of

multilayers of the acids on the clay surfaces at higher concentrations. XRD analysis indicated no intercalation of either acid in the lamella of the clay. We concluded the possibility of surface coating of montmorillonite clay with a monolayer of fatty acids that render the clay organophilic. The adsorption of either acid improved the dispersibility of the clay particles in organic or polymeric media. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2574–2580, 2002

Key words: adsorption; clay; filler; colloid; coating

INTRODUCTION

The dispersion of inorganic fillers or pigments in polymeric systems has found wide application in polymer technology¹ and contributes to other applications such as waste treatment² and catalysis.³ Polymer composite materials reinforced on the molecular scale, nanocomposites, were obtained by dispersion of inorganic montmorillonite clay in a polymer matrix.^{4–11} The enhancement of barrier properties, fire retardancy,¹² and increase in mechanical properties are some of the advantages induced by this new class of materials.¹³ Generally, the efficiency of inorganic fillers to enhance the composite properties depends mainly on its dispersion in organic or polymeric systems. Clays are hydrophilic in nature; consequently, they lack the compatibility and dispersibility in organic media. Due to the hydrophilic inorganic nature of such fillers, a brittle composite would be obtained and a heterogeneous dispersion or an agglomeration of fillers that induce inorganic domains in the polymer would result. Montmorillonite clay has received great attention for its cheap, high abundance and its unique properties. Montmorillonite clay is one of the

smectic groups composed of two silica tetrahedral sheets tied up in one aluminum octahedral sheet. The isomorphous substitution that resulted from the imperfection in the crystal lattice induces a net negative charge that leads to the adsorption of some cations of earth and alkaline earth metals in the interlayer area. These silicates also contained dangling hydroxyl end groups on their surfaces.^{14,15} Studies have revealed that the mechanical and processing properties reach their maximum or limiting values at the monolayer coverage.^{16,17}

A variety of studies have been performed to characterize the adsorption and desorption of different organic compounds to montmorillonite clay such as dimethylformamide or *N*-methylformamide.¹⁸ Other scientists have developed different modifications of montmorillonite with quaternary organic compounds that react via a cation-exchange reaction with the inner cation,¹⁹ and still others have modified montmorillonite clay by an *in situ* intercalative polymerization with a functionalized polymer⁴

The aim of the present study was to prepare and characterize the organophilization of montmorillonite clay via its surface coating with stearic and oleic acids. Both acids were generally used as additives to different polymer systems to impart plasticity or as extenders. The importance of oleic acid as a flotation agent has meant the adsorption of the acid onto a variety of minerals. Different concentrations of the saturated and unsaturated fatty acids were tried. All adsorption

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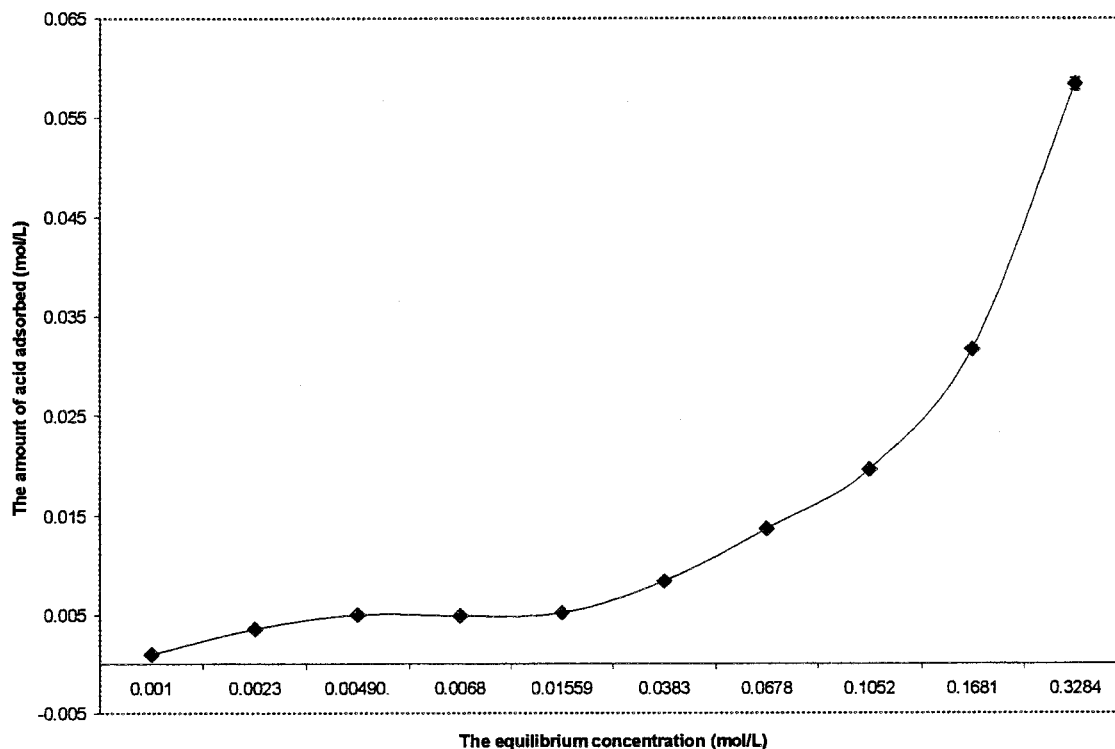


Figure 1 Adsorption isotherm of stearic acid on montmorillonite clay.

studies were carried out in nonaqueous media. The effect of such surface modification on the sedimentation properties and the intercalation behavior of both acids on the clay were also studied.

EXPERIMENTAL

The montmorillonite clay used was Wyoming bentonite clay, supplied by Southern Clay Products (TX). The stearic and oleic acids were Merck grades (Merck Sharp, Cairo, Egypt). Toluene and other solvents were pure Merck grades.

Determination of adsorption isotherm

Different concentrations of both fatty acids were prepared from 0.001 to 0.3 mol/L in toluene. The concentrations were assured by titration against an alcoholic solution of potassium hydroxide. A weighed amount of previously heated clay samples at 120°C was added to standard adsorption tubes. To each tube, 10 mL of the acid solution was added. The tubes were shaken for 1 h and left for 48 h at room temperature. The adsorbed amount of each concentration was deduced by determining the difference in the acid concentration before and after adsorption.

Test of sedimentation

After 48 h, the sediment volume was recorded. The adsorption tubes were shaken from top to bottom and the sediment volume was recorded each 30 s at the beginning of the sedimentation test and then recorded every 2 min at the final stages of the test. The sedimentation rate and the sediment volume were plotted against the amount of acid adsorbed.

Chemical analysis

The adsorbed amount of the each acid concentration was volumetrically measured by determining the difference in acid concentration before and after the adsorption for 48 h. The alcoholic KOH was standardized by titration with a standard solution of sodium carbonate using phenolphthalein as an indicator.

XRD analysis

Pure clay and dried samples of the clay modified with fatty acids were scanned by an X-ray diffractometer. Samples containing the acid solution were dried in a vacuum oven at 75°C. The scanning was performed between $2\theta = 0^\circ$ to $2\theta = 40^\circ$.

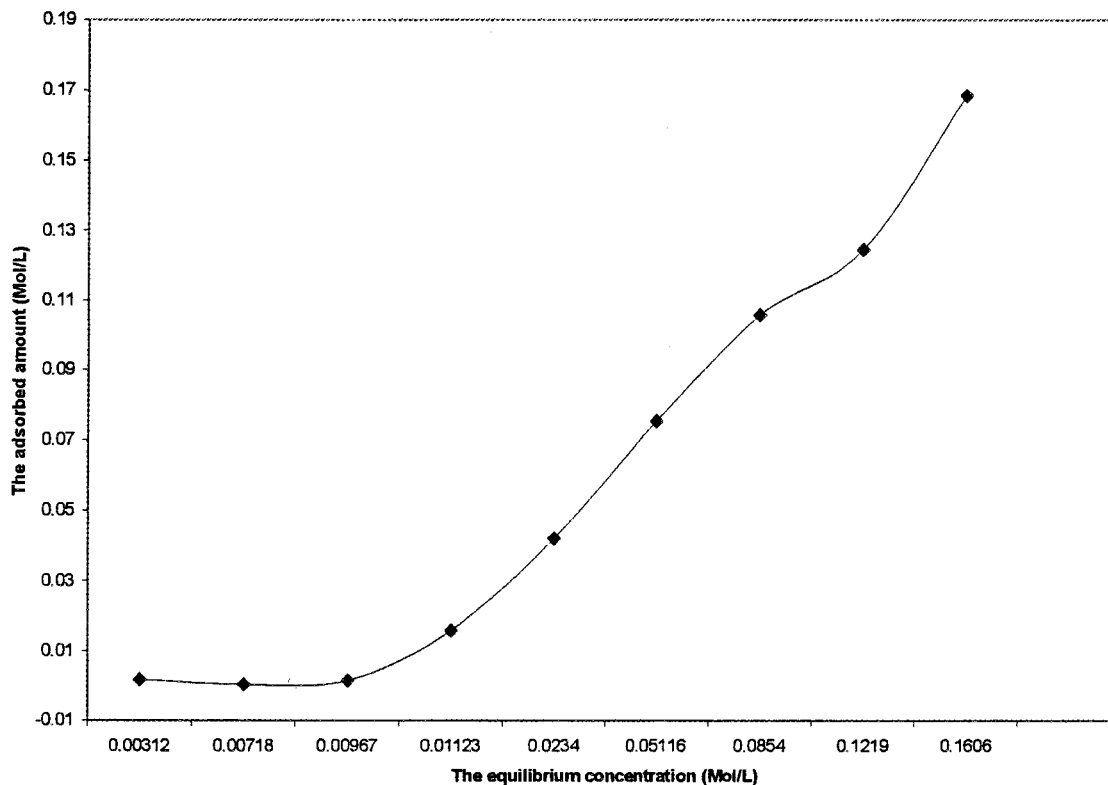


Figure 2 Adsorption isotherm of oleic acid on montmorillonite clay.

RESULTS AND DISCUSSION

The adsorption isotherms of stearic acid and oleic acid are plotted as shown in Figures 1 and 2, respectively. The adsorption behavior of both acids was studied in the acid concentration range between 0.001 to 0.3 mol/L. It was observed that, in the case of stearic acid, the amount adsorbed became almost constant from a solution concentration of 0.001 to 0.015 mol/L of stearic acid, followed by a sharp rise in the isotherm with the equilibrium concentration. The first stage in the isotherm represented the acid monolayer surface coverage on the clay, which occurred at an adsorbed amount of an average value of 0.005 mol/L. This indicated that the amount of the acid required to have monolayer coverage is 0.5 mol/m² of the clay. At a higher solution concentration, the amount adsorbed increased sharply with the equilibrium concentration. That stage was represented the formation of multilayers of the acid on the clay surface. The same type of isotherm was obtained when oleic acid was used as an adsorbent. The first stage of the adsorption isotherm, which represented the monolayer formation, occurred at an adsorbed amount of an average value of 0.0016 mol/L, indicating that the amount required to have monolayer surface coverage of oleic acid on the clay surface is 0.16 mol/m²; after that stage; the amount of the acid adsorbed increased progressively with the

equilibrium concentration. The adsorption isotherm of both stearic and oleic acids was of the type II Brunauer isotherm. These types of isotherms represent the multilayer physical adsorption of the adsorbate on non-porous solid surfaces or on microporous solids.

The effect of the quantity of stearic and oleic acids on the sedimentation properties of the clay particles in the toluene solution is shown in Figures 3 and 4, respectively. In pure toluene, the sediment of the clay was loose with a large volume, that is, the sedimentation occurred in an aggregated manner with a sharp interface. Using different adsorbed amounts of stearic acid, it was possible to determine the sedimentation rate even at higher concentrations up to 0.3 mol/L. It is clear from Figure 3 that the sedimentation rate decreased sharply with the adsorbed amount through a short range of the adsorbed amount until it leveled off. The concentration of the adsorbed acid at which the sedimentation rate started to be constant occurred at a value of 0.023 mol/L.

On the other hand, when using oleic acid as an adsorbate, the behavior was different. The sedimentation grew progressively smaller with no sharp interface. It was only possible to measure the sedimentation rate at values of adsorbed amounts up to 0.07 mol/L. At higher concentrations of oleic acid, the sedimentation was hazy, which indicated a good dis-

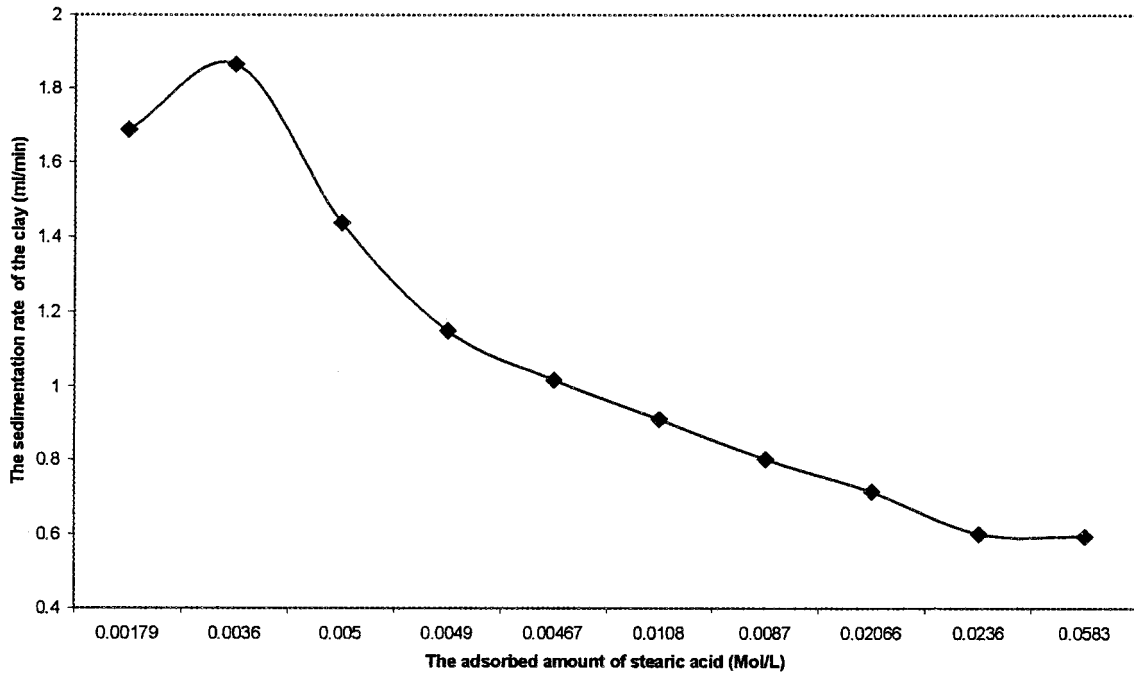


Figure 3 Effect of adsorbed amount of stearic acid on montmorillonite clay on its sedimentation rate.

persion of the clay in the medium. Through the range of measurable amounts, the change in the sedimentation rate was small with the adsorbed amount until a certain concentration value and then decreased sharply. The sedimentation rate was nearly constant

after this fast drop. The concentration at which the sedimentation rate started to be constant occurs at an adsorbed amount of approximately 0.0015 mol/L. This amount represented the monolayer coverage of oleic acid as estimated from the adsorption isotherm

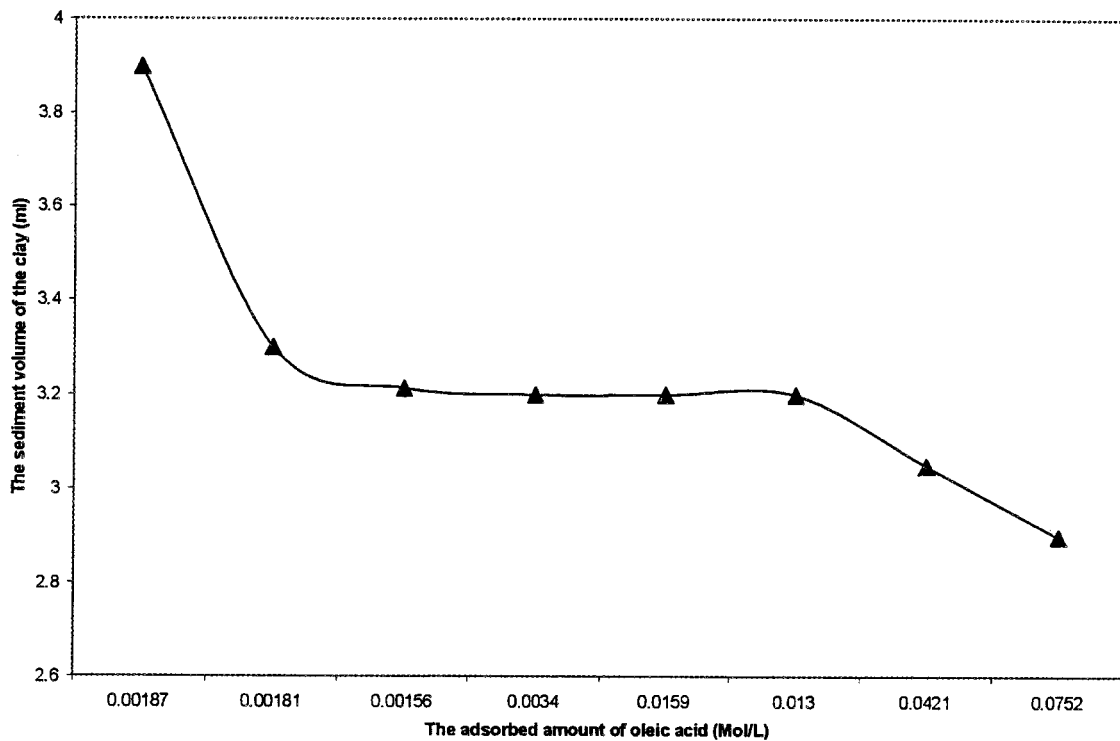


Figure 4 Effect of the adsorbed amount of oleic acid on montmorillonite clay on its sedimentation rate.

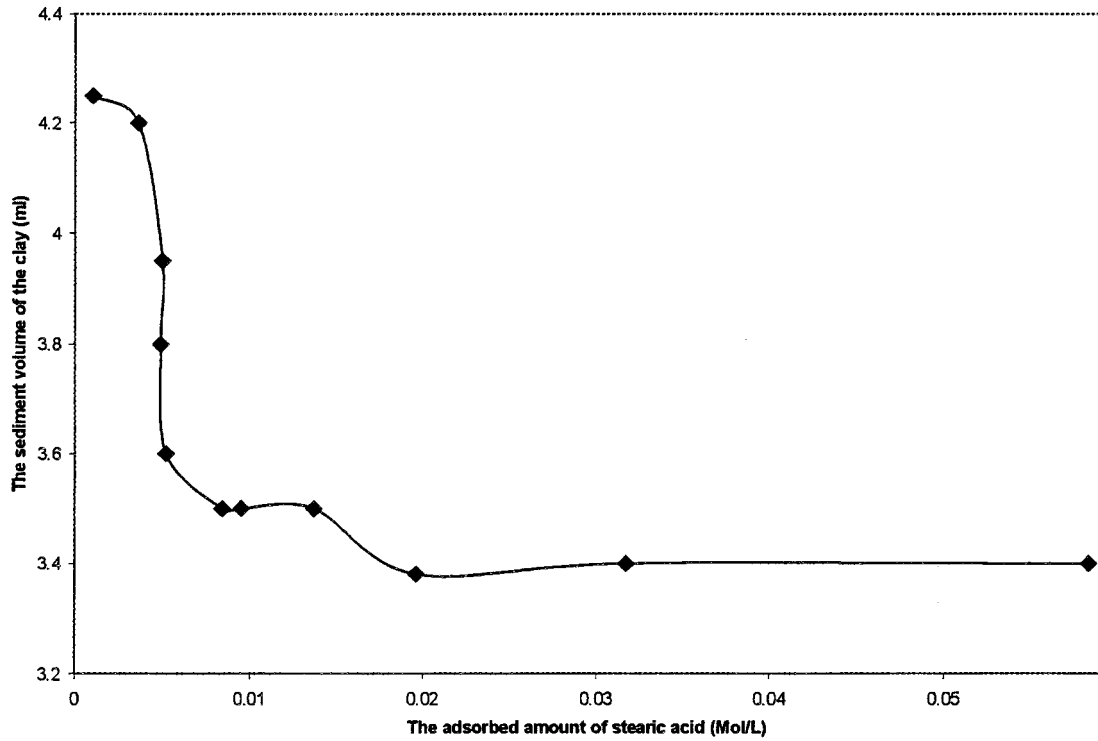


Figure 5 Effect of the adsorbed amount of stearic acid on its sediment volume on montmorillonite clay.

of the oleic acid on montmorillonite clay. It is clear that the difference in the molecular structure of the acid had a strong effect on the sedimentation behav-

ior. Since both acids have approximately the same molecular weight, then it is the presence of the unsaturated double bond in the oleic acid that has the most

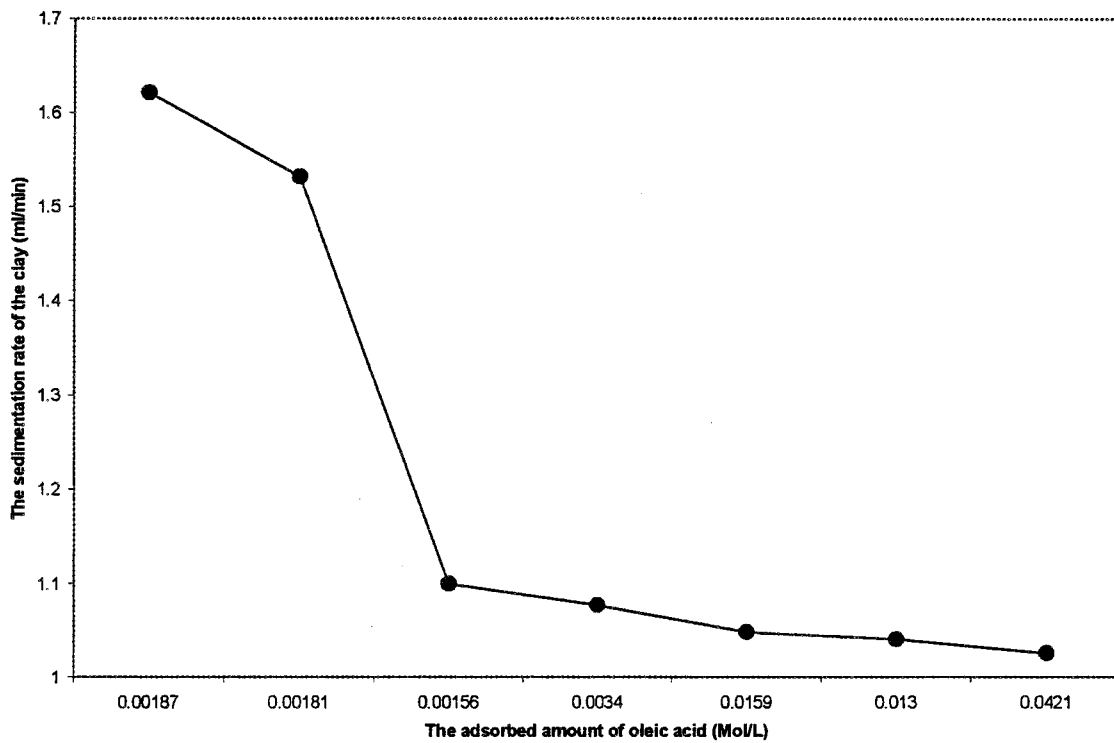


Figure 6 Effect of the adsorbed amount of oleic acid on its sediment volume of montmorillonite clay.

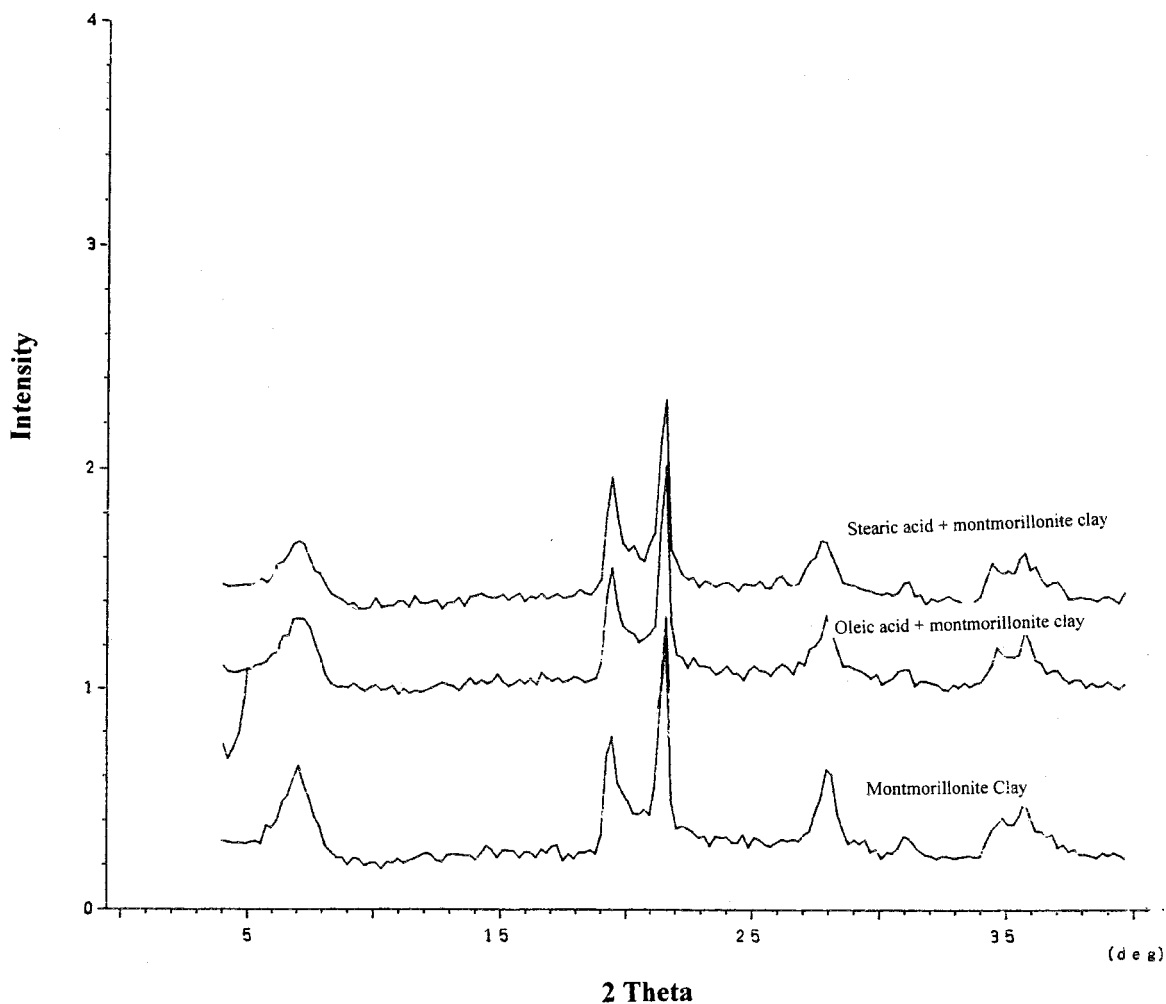


Figure 7 X-ray diffraction of pure montmorillonite clay and after coating with acids.

influencing effect since the tail of oleic acid is kinked at the double bond, which is critical to its effectiveness. The slow sedimentation of the clay in toluene at a higher concentration of the acid suggests a surface coverage of the clay with both fatty acids, which rendered the clay surface organophilic.

The effect of modification of montmorillonite clay by stearic acid and oleic acid on the sediment volume is shown in Figures 5 and 6, respectively. The effect of the adsorbed amount of stearic acid and oleic acid on the sediment volume was almost similar. Through a small range of the adsorbed amount, the sediment volume decreased sharply and then became nearly stable from an adsorbed amount of 0.0015 mol/L in case of oleic acid. Since both acids have nearly similar molecular weights, it could be suggested that the molecular weights of the adsorbate have the major role on the sediment volume rather than does the molecular structure.

The X-ray diffractometer of the modified clay with acids and unmodified clay are shown in Figure 7. In

comparing the scanning diffractometer of the clay to that of montmorillonite clay coated with both fatty acids, no changes in the basal planes of the clay were observed. Accordingly, we concluded that both acids did not penetrate the lamella of the clay lattice but were physically adsorbed at the crystal edges of the clay surface.

CONCLUSIONS

Using stearic and oleic acids can affect the surface properties of the clay particles in nonaqueous media. The adsorption of both acids was of the type II branched isotherm. A monolayer was formed at a lower concentration of the acid followed by multilayers formed at higher concentrations. In both acids, the sedimentation rate and the sediment volume decreased with the adsorbed amounts of the acid. All surface properties were measurable even at higher concentrations of the acid in the case of stearic acid but they were only measurable at lower concentrations in the case of oleic acid. The adsorption occurred at the

crystal edges of the clay particles and did not penetrate the lamella of the clay.

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