

# A Study on the Synthesis of Organophilic [TEACOOH]-Montmorillonite Intercalations Complex and its Swelling Properties

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## ABSTRACT

In this research an organic cation, [TEACOOH] Br, with a long alkyl chain was synthesized which will replace the metal ion between the layers of Na-Montmorillonite and an organophilic [TEACOOH]-Montmorillonite intercalations complex was formed by the cation exchange reaction between the Na-Montmorillonite and the synthesized [TEACOOH] Br. After drying of this intercalations complex in high vacuum we have tried to experiment on the probability whether it will form complexes with various swelling solutions such as dist. water, methano, ethanol, toluene, acetonitrile and propionitrile and the corresponding basal spacings measured were 17.41 Å, 31.90 Å, 34.42 Å, 30.52 Å and 32.36 Å, respectively.

**Key words :** Na-Montmorillonite, Organic cation, Intercalations complex, Cation exchange reaction, Swelling solutions

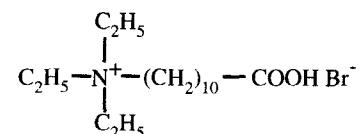
## 1. Introduction

Montmorillonite which belongs to the smectite group<sup>1,2)</sup> is a layer silicate of mica type<sup>3,4)</sup> and used very widely in forming intercalations complexes of clay as well as in industry because of the increasing ability of its own volume by one-dimensional innercrystalline swelling.<sup>5,6)</sup> Especially there exists a exchangeable metal cation in the interlayer space of montmorillonite, therefore if this metal ion would be replaced with an organic cation which has at least one long chain by a cation exchange reaction, organophilic montmorillonite intercalations complexes which have different material properties could be formed. This kind of organophilic montmorillonite can be used not only as a filler for lacquer, greese, cosmetics, paint, etc,<sup>3)</sup> but also in refining a factory waste water which is contaminated by organic compounds,<sup>7,8)</sup> It will also be used as a model system with which its behavior under various different conditions could be proved.<sup>9-11)</sup>

If the organic cation has a long chain with an organic functional group and organic monomer polymerizes with this functional group after it is additionally intercalated between the silicate layers, a composite in which inorganic and organic polymer are chemically bonded, i.e. a clay-polymer nanocomposite can be synthesized by the chemical linking of the organic cation as a counter ion for the clay layers which have an anionic electrical charge with the organic polymer,<sup>12-16)</sup> In this kind of composite the organic polymer won't be separated from the clay under any solvent in which it is soluble except acid. Otherwise, i.e. in case that clay (inorganic polymer) and the organic polymer ain't be chemi-

cally bonded, the organic polymer will be separated from the clay under the solvent in which it is soluble and then the resultant clay-polymer nanocomposites can't play role as a composite any more. These nanocomposites can be used, for example, as an automobile bumper and it will have an excellent stability because of the absorbing effect of the impact, a good economical efficiency because of the long durability and take part of the protection of environment because of the reduction of the waste plastics.

Therefore in this research taking this kind of view into consideration we have synthesized a following organic cation which has a long alkyl chain with an organic functional group (COOH-group), formed organophilic montmorillonite intercalations complexes by a cation exchange reaction between Na-Montmorillonite and the synthesized organic cation and studied their swelling properties under various different swelling conditions:



(will be abbreviated as [TEACOOH] Br after now)

## 2. Experimental Method

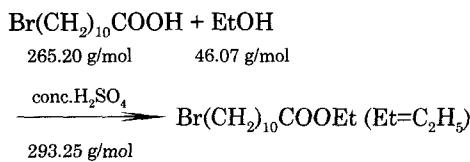
### 2.1. Synthesis of 10-Carboxy-n-decyltriethylammonium Bromide ([TEACOOH] Br)

The organic cation, [TEACOOH] Br, used in this research was not commercially obtainable and synthesized directly in this research in the following three steps: In first step 11-Bromoundecanoic acid ethylester was synthesized by the esterification reaction of 11-Bromoundecanoic acid with ethyl alcohol.

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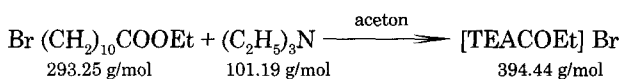
Secondly a quaternary ammonium acid ester was formed by the reaction of this synthesized 11-Bromoundecanoic acid ethylester with triethylamine. Finally the desired end product, [TEACOOH] Br, was synthesized by the acidic saponification reaction of the quaternary ammonium acid ester.

### 2.1.1. Synthesis of 11-Bromoundecanoic Acid Ethylester ( $\text{Br}(\text{CH}_2)_{10}\text{COOEt}$ )<sup>17)</sup>



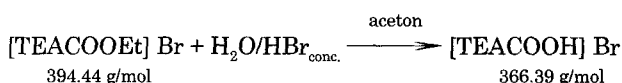
3 g ( $\approx 11.31$  mmol) of 11-Bromoundecanoic acid was mixed with 25 mL of ethanol and 0.22 g ( $\triangleq 0.12$  mL  $\triangleq 2.26$  mmol) of conc.  $\text{H}_2\text{SO}_4$  in 100 mL round flask and this mixture was heated under reflux for about 35 h. After cooling of the reaction mixture the rest of ethanol was removed by distillation using rotavapor. The residue from the removal of the rest of ethanol was mixed with ice water of about 5 times more amounts than the residue and then with 50 mL ether. The ether phase was isolated from the water phase using separating funnel. The water phase was then extracted three times with 20 mL ether respectively. The all ether phases which involved still a few amounts of  $\text{H}_2\text{SO}_4$  were then put together and this mixture of ether phases was made free from acid with the saturated  $\text{Na}_2\text{CO}_3$ -solution as long as the pH value of the sodium carbonate solution was not changed any more. The ether phases was then washed with dist. water to the neutral pH-value, dried with  $\text{CaCl}_2$  and filtered to separate this drying agent. Subsequently the solvent was removed from the ether phases which involves the product by distillation using rotavapor.

### 2.1.2. Synthesis of 10-Carboxylic Acid Ethylester-*n*-decyl-triethyl-ammonium Bromide ([TEACOOH] Br)



3.00 g ( $\approx 10.23$  mmol) of  $\text{Br}(\text{CH}_2)_{10}\text{COOH}$ , acetone 30 mL and 2.07 g ( $\triangleq 2.85$  mL  $\triangleq 20.46$  mmol) of triethylamine were put into the 100 mL round flask one after another. This reaction mixture was then heated under reflux for about 40 h. After cooling of the reaction flask the mixture was brought into the crystallization by the addition of ether in excess. The white precipitate was then separated using suction flask and buchner funnel, washed with ether several times and dried in high vacuum at 50 for 10 h. This dried sample was then recrystallized from isopropyl alcohol for refining.

### 2.1.3. Synthesis of 10-Carboxy-*n*-decyltriethylammonium Bromide ([TEACOOH] Br)



3.00 g ( $\triangleq 7.6$  mmol) [TEACOOEt] Br were solved in 100 mL acetone and 0.53 mL 48%  $\text{H}_2\text{O}/\text{HBr}_{\text{conc.}}$  were added into the solution. This reaction flask with the mixture was then covered up with aluminium foil to protect the decomposition of HBr into  $\text{Br}_2$  under light, whereafter the reaction mixture was heated under reflux for ca. 48 h.

After cooling of the reaction flask the reaction mixture was brought into the crystallization by the addition of ether in excess. The precipitate was filtered with suction, washed out with a mixture solution from ether/acetone(1:1) at first and then with ether in continuance. The so obtained white solid substance was dried in high vacuum ( $10^{-3}$  torr) at  $65^\circ\text{C}$  for 10 h and recrystallized from ethyl alcohol for refining.

## 2.2. Formation of the Organophilic [TEACOOH]-Montmorillonite Intercalations Complex

A suspension from 6 g Na-Montmorillonite which was obtained by refining Ca-beatonite<sup>18)</sup> and 82 mL dist. water were prepared and a water solution from 3.74 g ( $\triangleq 10.3$  mmol) [TEACOOH] Br and 20 mL water were added to the suspension under stirring. The whole mixture was then left at  $65^\circ\text{C}$  for 48 h under occasional stirring and thereafter centrifuged so that the swelling solution can be isolated from the product, [TEACOOH]-Montmorillonite intercalations complex. This [TEACOOH]-Montmorillonite was dried at  $100^\circ\text{C}$  in oven at first and continuously at  $65^\circ\text{C}$  in high vacuum of  $10^{-3}$  torr for 24 h.

## 3. Results and Discussion

### 3.1. Analysis Results of the Synthesized [TEACOOH]Br

The IR-spectrums for the products obtained in each step to synthesize [TEACOOH] Br are demonstrated in Fig. 1 and the interpretations of the results are as follows:

#### 3.1.1. IR-Spectrum of $\text{Br}(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$

$\text{Br}(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$  compound was synthesized by the substitution of OH-group with  $\text{OC}_2\text{H}_5$ -group by the esterification reaction of  $\text{Br}(\text{CH}_2)_{10}\text{COOH}$  and therefore it can be proved by the following check points whether the new product has been successfully formed;

① A broad peak which typically appears between 2500 and  $3000 \text{ cm}^{-1}$  for the carboxylic acid compound, i.e. COOH-group, should have disappeared in the new synthesized ester compound and this could be proved from the Fig. 1(C).

② In the case of the new compound the typical peak for the stretching vibration of the functional group  $\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-O-C}$  appears at ca.  $1030 \text{ cm}^{-1}$  and that for  $\text{OC}_2\text{H}_5$ -group at  $855 \text{ cm}^{-1}$ <sup>19)</sup> and this was also proved from Fig. 1(C).

③ In ester compound the typical aliphatic C-halogen peak, i.e. C-Br peak should appear between 564 and  $645 \text{ cm}^{-1}$  and this could be observed from the Fig. 1(C).<sup>20)</sup>

④ In the case of carboxylic acid the typical peak for the carbonyl group (C=O) between 1700 and  $1725 \text{ cm}^{-1}$  should appear between 1735 and  $1750 \text{ cm}^{-1}$  in ester compound and

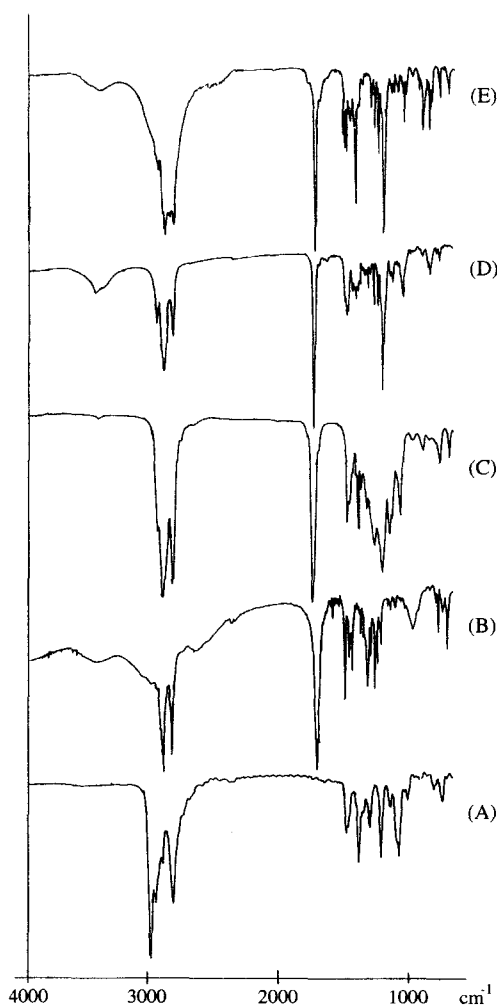


Fig. 1. IR-spectra for  
(A) triethyl amine (B)  $\text{Br}(\text{CH}_2)_{10}\text{COOH}$   
(C)  $\text{Br}(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$  (D)  $[\text{TEACOOEt}] \text{Br}$   
(E)  $[\text{TEACOOH}] \text{Br}$ .

this could be confirmed from Fig. 1(C).<sup>20)</sup>

### 3.1.2. IR-Spectrum of [TEACOOH] Br

[TEACOOH] Br is a quaternary ammonium salt which is a kind of salt compound and therefore it could be confirmed by the following check points:

① The aliphatic C-Br peak between  $564$  and  $645 \text{ cm}^{-1}$  should disappear in the new compound and this can be proved from Fig. 1(D).

② In case of all ammonium salts a broad peak should appear between  $2200$  and  $3300 \text{ cm}^{-1}$  because of the combination peak of the  $\text{NR}_4^+$ -group<sup>21)</sup> and this could be confirmed from Fig. 1(D).

③ The N- $\text{CH}_2$  peak which appears at  $2780 \text{ cm}^{-1}$  typically for the tertiary amine<sup>20)</sup> should not appear in the new synthesized quaternary ammonium compound any more and this could also be proved from Fig. 1(D).

### 3.1.3. IR-spectrum of [TEACOOH] Br

This compound was synthesized by the replacement of ethoxy group of  $[\text{TEACOOOC}_2\text{H}_5] \text{Br}$  with OH-group by the

hydrolysis under acid catalysis and therefore it could be confirmed by the following check points if the new compound has been successfully formed;

① In ester compound the typical peak for the carbonyl group ( $\text{C}=\text{O}$ ) appears between  $1735$  and  $1750 \text{ cm}^{-1}$ , but this should appear between  $1700$  and  $1725 \text{ cm}^{-1}$  in the new synthesized carboxylic acid compound and this could be observed Fig. 1(E).

② In the new product the typical broad peak for the COOH-group of carboxylic acid should appear between  $2500$  and  $3000 \text{ cm}^{-1}$  and this could also be confirmed from Fig. 1(E).

③ The typical peaks for the functional group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}$  at ca.  $1030 \text{ cm}^{-1}$  and for the ethoxy group ( $\text{OC}_2\text{H}_5$ ) at about  $855 \text{ cm}^{-1}$  should disappear in the new carboxylic acid compound and this could be observed from Fig. 1(E).

### 3.2. Results of the Synthesized Organophilic [TEACOOH]-Montmorillonite

The organophilic [TEACOOH]-Montmorillonite intercalations complex obtained from the reaction of Na-Montmorillonite with [TEACOOH] Br by the method described in chapter 2.2 was characterized with X-ray diffractometer (Philips Novelco) using  $\text{Cu K}_\alpha$ -radiation ( $\lambda=1.541 \text{ \AA}$ ) with a

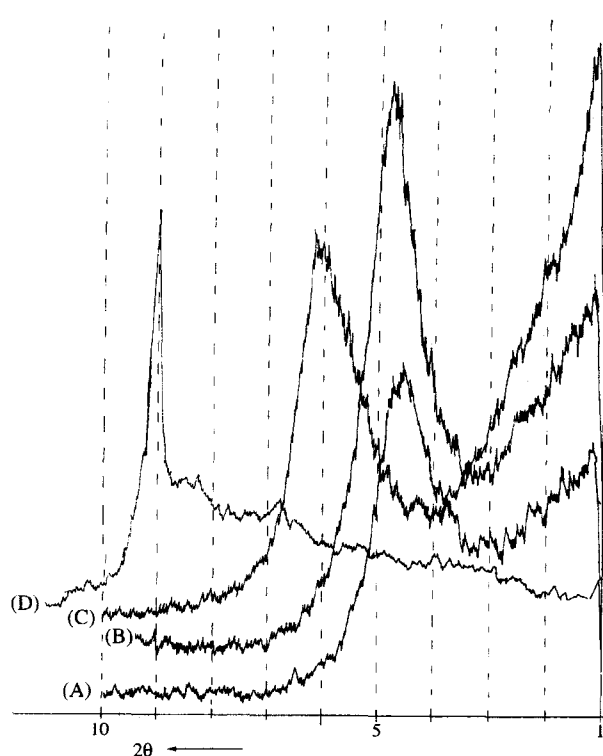


Fig. 2. X-ray diffraction patterns of [TEACOOH]-Montmorillonite.

(A) after 48 h exchange-time, under exchange solution  
(B) after eight times washing, under water

(C) after 24 h drying in high vacuum at  $65^\circ\text{C}$

(D) Na-Montmorillonite dried in high vacuum at  $65^\circ\text{C}$  24 h.

**Table 1.** Basal Spacings( $\text{\AA}$ ) Measured after Cation Exchange Reaction

Sample treatment	Basal Spacings ( $\text{\AA}$ ) of	
	Reaction product	Na-Montmorillonite
after more than 48 h exchange time, measured under exchange solution	19.60	
after eight times washing with dist. water, measured under water	18.52	toward infinitely
after drying in high vacuum at 65°C for 24 h	14.52	9.8–10.1

scan speed of 1.00 deg/min under the following conditions:

① The equilibrium solution after cation exchange reaction was centrifuged;

The solid residue was analyzed with X-ray diffractometer under still wet condition with the adherent equilibrium solution(Fig. 2(A)).

② Thereafter the centrifuged solid sample was washed eight times with dist. water until it was free from halide and characterized with X-ray diffractometer under still wet condition with water(Fig. 2(B)).

③ The washed sample was dried at 65°C for 24 h in high vacuum( $10^{-3}$  torr) and analyzed with X-ray diffractometer under the dried condition in high vacuum(Fig. 2(C)).

The results measured with X-ray diffractometer are summarized in Table 1 which shows us that the basal spacing values between the reaction products, [TEACOOH]-Montmorillonite and the starting material, Na-Montmorillonite, are quite different.

The Na-Montmorillonite used as a starting material swells toward infinitely under dist. water, i.e. the layer of the crystals separate to the individual layers and these swim each other under water solution. The attractive interactions between the adjacent layers reduce on the order of a few  $k \cdot T$ . After drying it in high vacuum we can see from the Table 1 that its basal spacing fell to 9.8~10.1  $\text{\AA}$ .

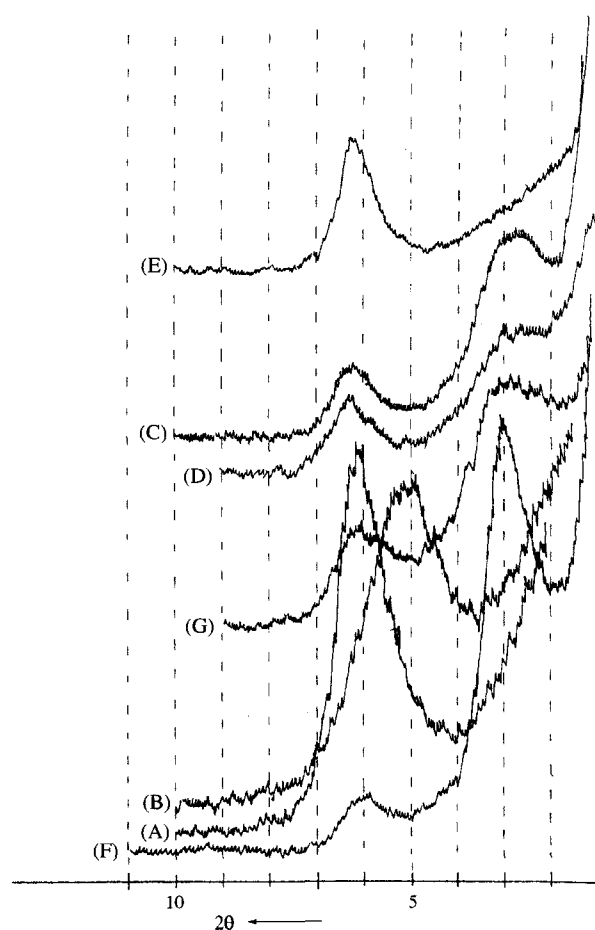
In case of [TEACOOH]-Montmorillonite the basal spacing of 19.60  $\text{\AA}$  is obtained under the exchange solution, but it lies on 18.52  $\text{\AA}$  with the reduction of 1.08  $\text{\AA}$  after washing eight times with water until it was free from halide. under this condition it is obvious that the sample has still much water between the layers of the intercalations complex. Therefore the sample was dried at 65°C in high vacuum ( $10^{-3}$  torr) for 24 h, whereafter a closed packing was obtained and the basal spacing also decreased upto 14.52  $\text{\AA}$  with the reduction of 4  $\text{\AA}$ . It is comprehensible value, because the density of charge of montmorillonite used in this research is very small. Under such density of charge the alkyl ammonium ions with upto at least 12 C-atom numbers form a flat lying monolayer, as we know from many other researches.

### 3.3. Results of the swelling tests of [TEACOOH]-Montmorillonite

In order to know if the [TEACOOH]-Montmorillonite obtained by the method of chapter 2.2 and dried in high vacuum( $10^{-3}$  torr) can form an intercalations complex also under swelling solution. The each sample of the dried [TEACOOH]-Montmorillonite was mixed with various different

**Table 2.** Basal Spacings( $\text{\AA}$ ) Obtained after Swelling of Dried Organophilic [TEACOOH]-Montmorillonite

after swelling in	Basal Spacings ( $\text{\AA}$ ) of [TEACOOH]-Montmorillonite
dist. water	17.41
methanol	31.90
ethanol	34.42
toluene	14.20
acetonitrile	30.52
propionitrile	32.36

**Fig. 3.** X-ray diffraction patterns after swelling of [TEACOOH]-Montmorillonite.

- (A) [TEACOOH]-Montmorillonite as a starting material dried in high vacuum.  
 (B) sample (A) with dist. water  
 (C) sample (A) with methanol  
 (D) sample (A) with ethanol  
 (E) sample (A) with toluene  
 (F) sample (A) with acetonitrile  
 (G) sample (A) with propionitrile

solvents such as dist. water, methanol, ethanol, toluene, acetonitrile and propioutile and the each mixture was left at room temperature for 2 days with the occasional shaking, whereafter the each sample was studied with X-ray diffractometer. The results are summarized in Table 2.

As a result of swelling reaction of the dried [TEACOOH]-Montmorillonite with dist. water we have become a basal spacing of 17.41 Å and this is the increased based spacing value of 2.87 Å more than that of 14.54 Å for the dried [TEACOOH]-Montmorillonite. This extension value of the basal spacing is less than the diameter of water molecule and this is the result caused by a few additional enlargement of the basal spacing because the water molecules entered into the hole spaces which exist in the interlayers. In every reaction of [TEACOOH]-Montmorillonite with all other swelling liquids than that with toluene in which no practical extension of the basal spacing occurred. We have become an intensive enlargement of the basal spacing with the values of between 30.52 Å and 34.42 Å. Under these basal spacings the reorientation of the organic cations between the layers of the [TEACOOH]-Montmorillonite would occur intensively. If it won't be reoriented this kind of large extension of the basal spacing will bring the instability.

The X-ray diffraction patterns for the each swelling test result summarized in Table 2 are showed in Fig. 3. From the X-ray diffraction patterns in Fig. 3 we can observe that the (001)-interferences obtained by the reaction with all other swelling solvents except acetonitrile are not sharp, but widely spreaded. In this case it will occur much errors of the basal spacing, so we have to take it into consideration if we discuss on the extension of the basal spacing.

#### 4. Conclusion

The analysis results for the organophilic [TEACOOH]-Montmorillonite which has been obtained by the cation exchange reaction between [TEACOOH] Br and Na-Montmorillonite are as follows:

① As a result of X-ray diffraction analysis under wet condition for the [TEACOOH]-Montmorillonite after the cation exchange reaction the basal spacing of 19.60 Å has been obtained.

② The basal spacing obtained after eight times washing with dist. water until it was free from halide was 18.52 Å.

③ The basal spacing measured after drying in high vacuum at 65°C for 24 h was 14.52 Å.

The results of the swelling reaction of the [TEACOOH]-Montmorillonite dried in high vacuum with various swelling solutions are as follows:

④ There has been no practical enlargement of the basal spacing under the swelling solution with toluene.

⑤ The basal spacing obtained by the swelling reaction with dist. water was 17.41 Å with the basal spacing extension of 2.87 Å.

⑥ In case of the swelling reaction with every other swell-

ing solvents the extensive enlargements of the basal spacing have been obtained and the basal spacings lie between 30.52 Å and 34.42 Å.

From the results of these swelling tests we could observe the fact that the organophilic [TEACOOH]-Montmorillonite formed the additional intercalations complexes under various swelling liquids.

#### Acknowledgement

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