

# Adsorbed State of Organic Compounds in Organo-Bentonite\*

## I. Infrared Study

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The structures of octadecylamine montmorillonite and stearamide-octadecylamine complex montmorillonite were studied by X-ray diffraction and infrared absorption spectrum. The relation between the amount of added organic compounds and the separation of the lattice layer of montmorillonite crystal was measured by X-ray diffraction. The basal spacing of octadecylamine montmorillonite was expanded stepwise, in increments of  $4\text{\AA}$  with the quantity of organic compound, while stearamide montmorillonite was expanded to about  $22\text{\AA}$  with the smallest amount of organic compound. These results and infrared spectra suggest that the octadecylamine montmorillonite was prepared by exchange adsorption as usually considered. On the other hand, in infrared spectra of stearamide montmorillonite, significant changes of absorption occur in the amine I and II frequencies as well as in the NH- and OH- stretching bands. These results suggest that the stearamide molecule is chemically bonded by hydrogen bond with crystal surface in the layer lattice of montmorillonite.

## INTRODUCTION

It has been well known that the organic bentonite treated with a cationic or nonionic polar organic compound swells in an organic solvent. This is due to solvation of the organic compound absorbed between the layers of sub-cells of montmorillonite crystal, and the extent of the swell is affected by the molecular size and the kind of the oleophilic groups of the organic compound. Upon such characteristics, the organic bentonite is industrially used for thickeners for paint, printing ink, lubricating grease, and so on<sup>1,2)</sup>. For the examples of such organic compound, octadecylammonium or dimethyl dioctadecylammonium are used. The former has a strong affinity to polar solvents, and the latter to nonpolar solvents. Relating to the structure of these organic bentonites, Hendricks<sup>3)</sup>, Bradley<sup>4)</sup>, Grim<sup>5)</sup>, Jordan<sup>6)</sup> and others have already carried out detailed studies mainly by means of X-ray diffraction method. However, no study has been yet carried out concerning the mechanisms of bonding between organic compounds and the crystal lattice plane, and especially concerning the reaction of nonionic organic compound with the plane. In the present work, the structures of octadecylamine bentonite and octadecylamine-stearamide complex bentonite have been studied by means of infrared absorption spectra.

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## EXPERIMENTAL

## 1. Samples

Bentonites produced in Gunma Prefecture were dispersed in water and refined by removing non-clay materials after precipitation.

Octadecylamine acetate ( $C_{18}H_{37}NH_3\text{-Ac}$ ) was used as a cationic organic compound, and stearamide as a nonionic organic compound.

As the samples, octadecylamine-montmorillonite (abbreviated as ODA-montmorillonite hereafter) prepared by adding 25~100 mg octadecylamine acetate to 100 g of montmorillonite in a suspension of the refined bentonite, namely montmorillonite, were used. Octadecylamine-stearamide complex montmorillonite (abbreviated as (ODA+SA)-montmorillonite hereafter), prepared in the similar way by adding 1:1 mole ratio octadecylamine acetate-stearamide complex which had been previously prepared, were also used. Most of the added organic compounds were adsorbed by montmorillonite and did not remain in the liquid.

## 2. Apparatus and method

The infrared absorption spectra were studied as follows: The spectra of the raw material montmorillonite was obtained with Nujol-nulls, the added organic compound and organic montmorillonite with Nujol and KBr pellet method, and the ODA-SA complex emulsion was studied in the range between 2~15  $\mu$ , in liquid cell. In addition, the change of (001) spacing of montmorillonite was measured by X-ray diffraction method.

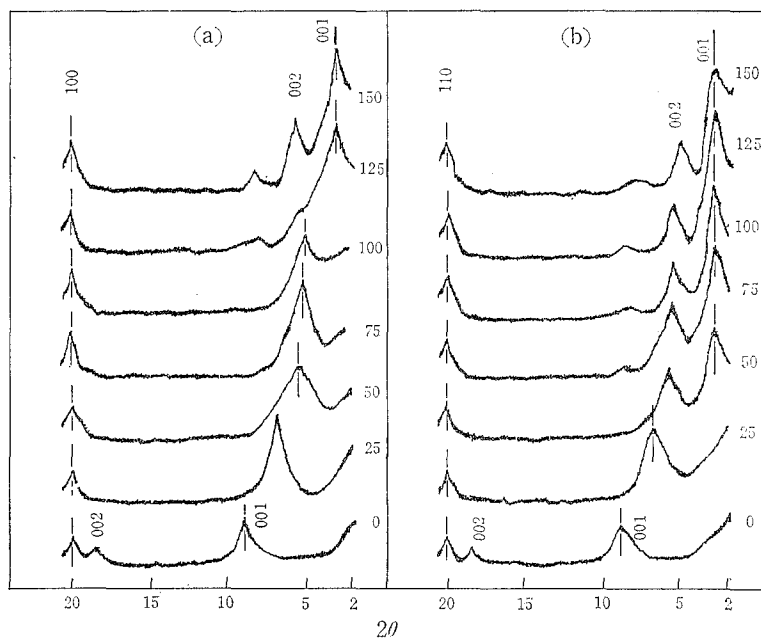


Fig. 1. Changes in X-ray diffraction of montmorillonite due to addition of organic compound.

(a) octadecylamine (b) octadecylamine-stearamide

## RESULTS

## 1. Measurements by X-ray diffraction method

Fig. 1 (a) and (b) are the X-ray diffraction diagrams illustrating the changes due to additions of ODA and (ODA+SA) to montmorillonite. As standard (001) spacing of the montmorillonite  $9.8\text{\AA}$  was used here, and the distances of the lattice layers were calculated as  $d = d - 9.8\text{\AA}$ .

The relationship between the quantity of added organic compound and the change of  $d_{(001)}$  of montmorillonite or the spacing  $d$  is shown in Fig. 2. In the case of ODA-montmorillonite,  $d$  increased stepwise as  $4\text{\AA}$ ,  $8\text{\AA}$  and  $22\text{\AA}$  with the increment of the added quantity as seen in the results reported by Jordan and others<sup>6)</sup>. As already explained, these values correspond to the state where, as shown in Fig. 3, the molecules of the hydrocarbon are adsorbed as a single layer

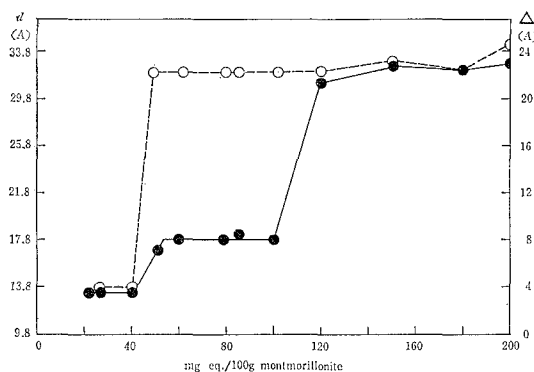


Fig. 2. Relationship between the added quantity of organic compound and the spacing of (001) planes.

● ODA-montmorillonite      ○ (ODA+SA)-montmorillonite

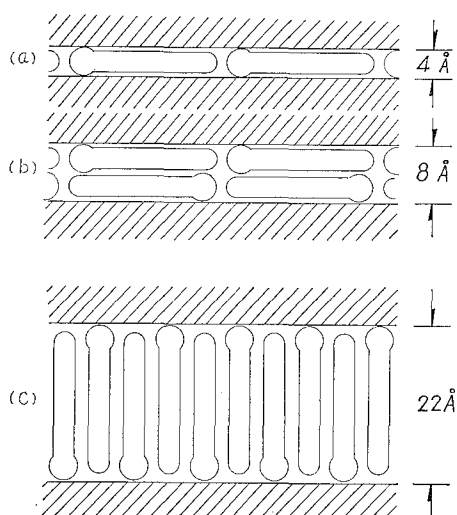


Fig. 3. States of the cationic organic compound molecules adsorbed in the crystal layers.

or as double layers parallel to the crystal plane and as a single layer perpendicular to the plane respectively.

However, in the case of (ODA+SA)-montmorillonite, the value directly increased from 4 Å to 22 Å and no region corresponding to 8 Å could be observed.

As shown in Fig. 2, in the case of ODA-montmorillonite, the (001) spacing increased stepwise with the increment of the quantity of added ODA. The specific surface area of montmorillonite calculated from the crystal structure and unit cell was about 800 m<sup>2</sup>/g<sup>7)</sup>. The specific surface area of the bentonite produced in Gunma Prefecture determined by BET method with N<sub>2</sub> gas was 827 m<sup>2</sup>/g, which agreed well with the theoretical value. The area occupied by a single molecule of octadecylamine calculated using above value, in the case of equivalent quantities

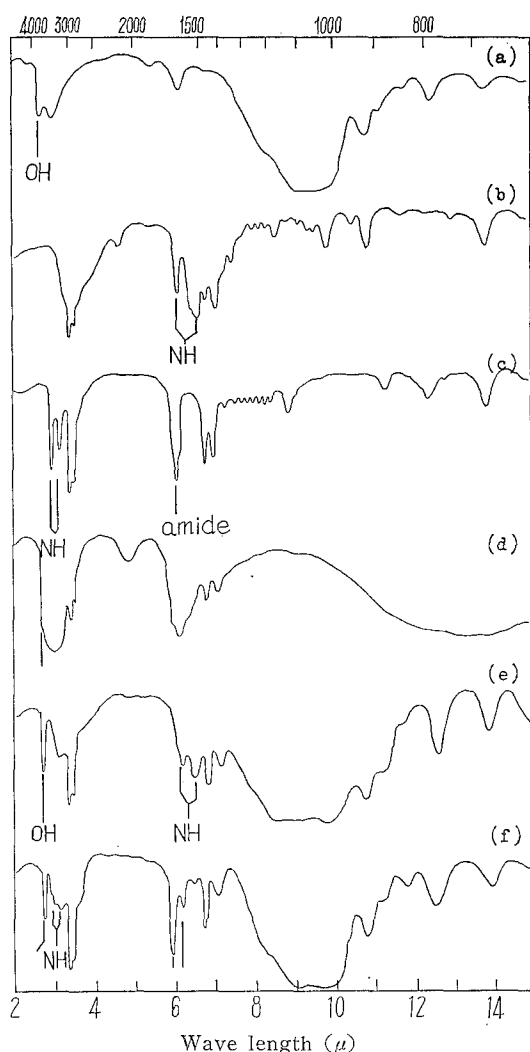


Fig. 4. Infrared absorption spectra.

- (a) Montmorillonite (b) Octadecylamine acetate (c) Stearamide
- (d) ODA+SA complex emulsion (e) ODA-montmorillonite
- (f) (ODA+SA)-montmorillonite

of 50 mg and 100 mg at which the stepwise changes occurred was  $260 \text{ \AA}^2$  and  $130 \text{ \AA}^2$ . When octadecylamine lies on the crystal plane, the area occupied by a molecule is about  $130 \text{ \AA}^2$ , therefore, the situation corresponds well to that shown in Fig. 3 (b).

However, in the case of (ODA+SA)-montmorillonite, the distances of crystal planes increased directly to  $22 \text{ \AA}$  by adding an equivalent quantity of 40 mg and no stepwise change occurred. The distance,  $22 \text{ \AA}$ , is nearly equal to the molecular length. The area occupied by a single molecule of (ODA+SA)-complex is about  $330 \text{ \AA}^2$ . Concerning this phenomenon, any conformations could not be obtained by the X-ray diffraction method.

## 2. Infrared absorption spectra

The infrared absorption spectra of each sample are shown in Fig. 4. The regions near  $3000 \text{ cm}^{-1}$  and  $1500 \sim 2000 \text{ cm}^{-1}$  regions of these spectra are illustrated in Figs. 5 and 6 where the particularly interesting changes were found.

Table 1 shows the assignments of the infrared absorption spectra of montmorillonite, octadecylamine, stearamide and the organic montmorillonites composed of

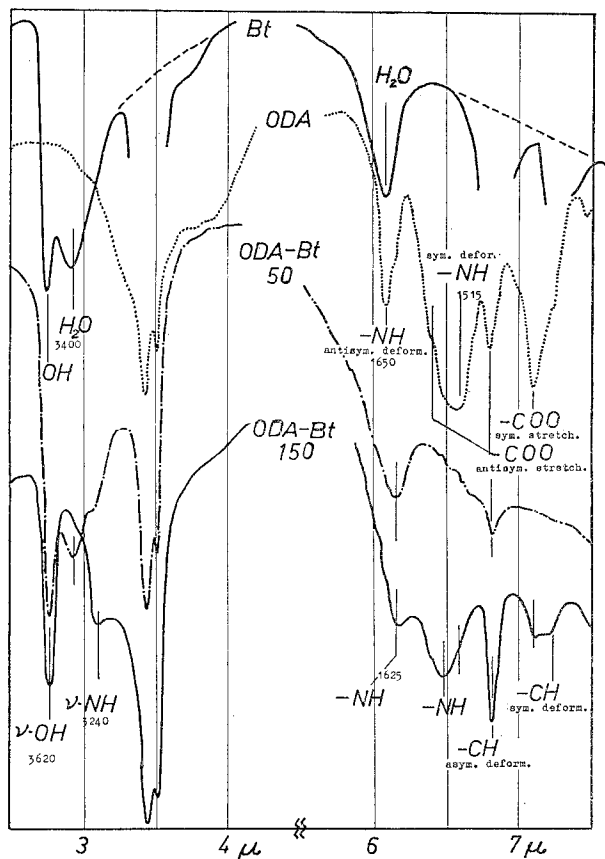


Fig. 5. Infrared absorption spectra of ODA-bentonite.

- (a) Montmorillonite (b) Octadecylamine acetate  
(c) ODA-montmorillonite (50 mg) (d) ODA-montmorillonite (150 mg)

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Table 1. The assignments for the frequencies of principal absorptions ( $\text{cm}^{-1}$ ).

Montmorillonite	ODA-Acetate	Stearamide	ODA-Mont.	ODA+SA -Mont.	assignment
3620			3620	3620	montmorillonite $\nu$ -OH
				3450	
		3400		3380	$\nu$ -NH
			3240	3250	$\nu$ -NH <sub>3</sub>
		3200		3150	$\nu$ -NH
	2920	2920	2920	2920	} $\nu$ -CH
	2855	2855	2855	2855	
		1650		1670	$\nu$ -CO amide-I
		1640		1610	$\delta$ -NH amide-II
	1650		1625		$\delta$ -NH <sub>3</sub>
	1580				$\nu$ -C $\begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix}$
	1515		1555	1555	$\delta$ -NH <sub>3</sub>
			1530		
	1475	1475	1475	1475	} $\delta$ -CH
	1465	1465	1465	1465	
		1425		1415	$\nu$ -CN
	1410		1410		$\nu$ -C $\begin{matrix} \diagup \text{O} \\ \diagdown \text{O} \end{matrix}$
	1380	1380	1380	1380	$\delta$ -CH <sub>3</sub>

them. The absorption spectra at the lower frequencies than  $1300 \text{ cm}^{-1}$  were omitted, because they were superimposed with the strong absorption due to Si-O and Al-O bonds of the clay materials.

DISCUSSION

1. ODA-montmorillonite

Fig. 5 shows the absorption spectra of montmorillonite prepared by adding 50 and 150 mg equivalent quantity of octadecylamine. The absorption at  $3400 \text{ cm}^{-1}$  due to the  $\nu$ -OH of adsorbed water was considerably strong in the case of 50 mg addition but no absorption could be observed when the added quantity was more than 100 mg (the similar absorption band at  $1620 \text{ cm}^{-1}$  due to the water was not clear because it was superimposed with that of  $\delta$ -NH of amine). It is clear that, in the case of exchange adsorption of 50 mg equivalent quantity, the adsorbed water still remained in the crystal layers because only half of the total area of crystal layer is covered as shown in Fig. 3 (a); however, no adsorbed water remains when the quantity is more than 100 mg equivalent.

The remarkable changes could be found as in Fig. 5 by comparing the absorption spectrum of octadecylamine with that of ODA-montmorillonite. That is, the absorptions in (COO<sup>-</sup>) at  $1580 \text{ cm}^{-1}$  and  $1410 \text{ cm}^{-1}$  due to acetate disappeared, and the absorption could be found at  $3240 \text{ cm}^{-1}$  in the case of montmorillonite due to  $\nu$ -NH which was assumed to be superposed in acetate salts with that at near  $3000 \text{ cm}^{-1}$  due to  $\nu$ -CH of alkyl group. In addition, the absorption at  $1625 \text{ cm}^{-1}$  was observed which seemed to be due to the symmetric deformation of NH in case of the sample containing more than 100 mg of octadecylamine, though it could

not be found in the sample containing 50 mg. ODA because of the superposition with the absorption of water (this absorption at  $1625\text{ cm.}^{-1}$  seems to be due to NH because there was no absorption at  $3400\text{ cm.}^{-1}$  due to  $\nu\text{-OH}$  of water). These results suggest that octadecylamine acetate dissociates perfectly and only the alkylamine ion is adsorbed between the crystal layers.

## 2. (ODA+SA)-montmorillonite

As seen in Fig. 6, the absorption of (ODA+SA)-montmorillonite showed remarkable changes which were different from the simple superposition of stearamide and montmorillonite. That is to say, the absorptions at  $1640\text{ cm.}^{-1}$  and  $1650\text{ cm.}^{-1}$  observed in stearamide owing to amide II ( $\delta\text{-NH}$ ) and amide I ( $\nu\text{-CO}$ ), respectively, shifted to  $1610\text{ cm.}^{-1}$  and  $1670\text{ cm.}^{-1}$  in montmorillonite. Also the absorptions at  $3400\text{ cm.}^{-1}$  and  $3200\text{ cm.}^{-1}$  due to  $\nu\text{-NH}$  changed into  $3380\text{ cm.}^{-1}$  and  $3150\text{ cm.}^{-1}$ , respectively, and a new absorption was found at  $3450\text{ cm.}^{-1}$ . Moreover, the absorption

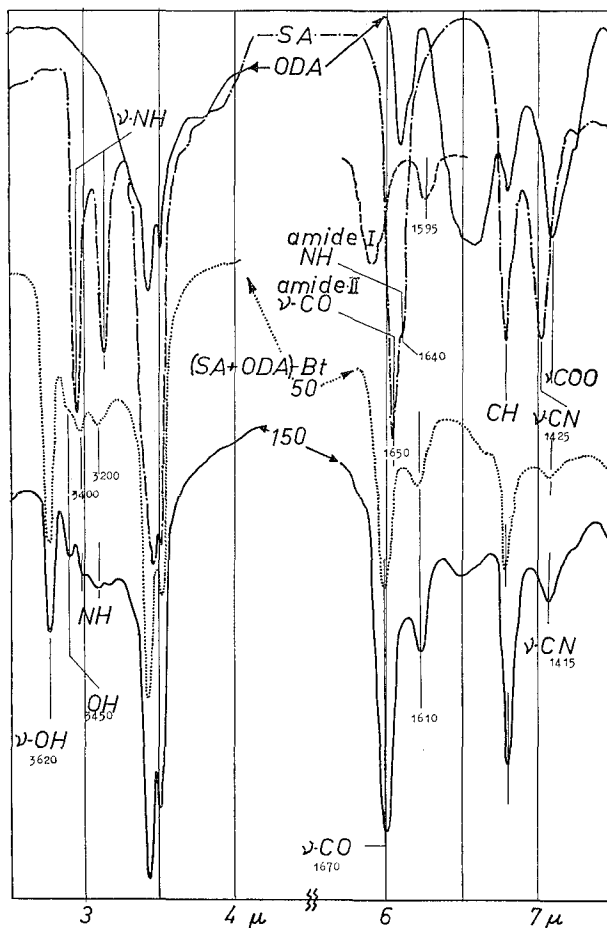


Fig. 6. Infrared absorption spectra of (ODA+SA)-bentonite.

- (a) Octadecylamine acetate
- (b) Stearamide
- (c) Stearamide (dil. soln.)
- (d) (ODA+SA)-montmorillonite (50 mg)
- (e) (ODA+SA)-montmorillonite (150 mg)

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at  $1425\text{ cm.}^{-1}$  due to  $-\text{CH}$  shifted to  $1415\text{ cm.}^{-1}$ . However, the added quantity only affected the intensity of absorption and gave no effect the wave number of the absorption band.

As to the changes of absorptions due to amide I and II, following consideration may be put forward:

The absorption spectra of stearamide shown in Fig. 6 (b) were studied with the solid sample, and spectra showed that the molecules would be associated to form the bonds like  $\text{R}-\text{C} \begin{matrix} \diagup \text{O} \cdots \cdots \text{H}_2\text{N} \\ \diagdown \text{NH}_2 \cdots \cdots \text{O} \end{matrix} \text{C}-\text{R}$ . However, if the stearamide existed as monomolecular state between the layers of montmorillonite, the absorption frequencies of amide I and II should be, of course, changed. The absorptions of amide I and II determined with dilute solution of stearamide in chloroform were  $1595\text{ cm.}^{-1}$  and  $1690\text{ cm.}^{-1}$  as shown in Fig. 6 (c). Accordingly, when the molecules were located between the layers of montmorillonite, the absorption of amide II ( $-\text{NH}$ ) would shift by  $15\text{ cm.}^{-1}$  to the higher frequency region, and the absorption of amide I ( $-\text{CO}$ ) would shift by  $20\text{ cm.}^{-1}$  to the lower frequency side. It can be said that this is due to the considerably strong bond of  $\text{CO}$  in stearamide to the plane of montmorillonite. The montmorillonite crystal has a three-layer-structure wherein tetrahedral layers of  $\text{SiO}_2$  are located on both sides of  $\text{Al-OH}$  layer; however, it has been considered that on the  $\text{Si-O}$  layer there are silanol groups, the existence of which has been already confirmed on the surface of the finely powdered silica.<sup>8,9)</sup> If it is assumed that a hydrogen bond is formed between  $\text{CO}$  of stearamide and this  $\text{Si-OH}$  group, the new absorption at  $3450\text{ cm.}^{-1}$  will be due to  $\text{OH}$  with which  $\text{CO}$  forms the hydrogen bond.

On the other hand, the absorption of octadecylamine which existed as a complex was the same as that of ODA-montmorillonite. The  $\text{CO}$  group of stearamide

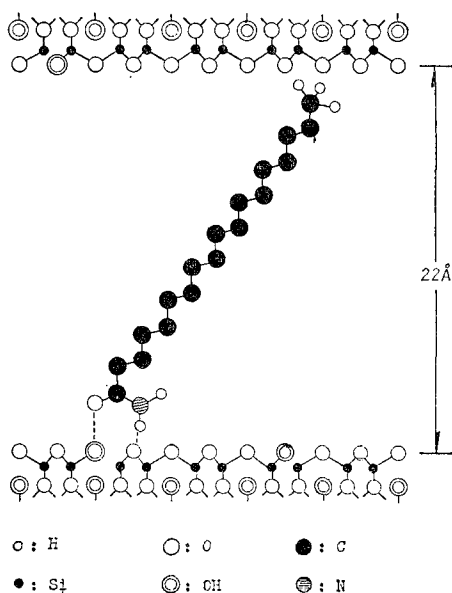


Fig. 7. State of a stearamide molecule located between the layers of montmorillonite.



can make hydrogen bonding with the OH group of the montmorillonite so that the stearamide molecule is perpendicular to the crystal plane as shown in Fig. 7. Therefore only a small amount of stearamide can cause 22 Å layer spacing.

Thus, (ODA+SA)-montmorillonite is not similar to ODA-montmorillonite prepared by means of cation exchange adsorption as has been assumed, but has strong bond among them. The more excellent effects on various phenomena due to the affinity of an organic solvent would be expected.

#### CONCLUSION

The structures of ODA-montmorillonite prepared with octadecylamine (a cationic organic compound) and the structure of (ODA+SA)-montmorillonite prepared with a complex composed of stearamide (a nonionic organic compound) and octadecylamine were studied by means of X-ray diffraction and infrared absorption method. As the result, it was confirmed that ODA-montmorillonite is dependent upon the mechanism of cation exchange adsorption which has been assumed up to the present. However, it is deduced that the mechanism of (ODA+SA)-montmorillonite is not the ion exchange adsorption but the strong bond formed between CO of stearamide and Si-OH of montmorillonite crystal.

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#### REFERENCES

- 1) H. Hasegawa and S. Kondo, *J. Chem. Soc. Japan*, (Ind. Chem. Section) **61**, 1243 (1958).
- 2) H. Hasegawa, S. Kondo and R. Tsukisaka, *Polymer Sci. Japan*, **15**, 482 (1958).
- 3) S. B. Hendricks, *J. Phys. Chem.*, **45**, 65 (1941).
- 4) E. F. Bradley, *J. Am. Chem. Soc.*, **67**, 975 (1945).
- 5) R. E. Grim, W. H. Allaway and F. L. Cuthbert, *J. Am. Ceram. Soc.*, **30**, 137 (1947).
- 6) J. W. Jordan, *J. Phys. and Colloid Chem.*, **53**, 294 (1949).
- 7) R. W. Hoffmann and C. W. Brindley, *J. Phys. Chem.*, **65**, 443 (1961).
- 8) R. S. McDonald, *J. Phys. Chem.*, **62**, 1168 (1958).
- 9) K. Naito, *Bull. Tech. Inst. Osaka.*, **9**, 147 (1958); **10**, 13, 79 (1959).