

PREPARATION AND ELECTRICAL PROPERTIES OF QUATERNARY AMMONIUM MONTMORILLONITE-POLYSTYRENE COMPLEXES

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Abstract—Intercalation compounds of styrene and quaternary ammonium montmorillonite were prepared by immersion of the clay in styrene monomer. The intercalation of stearyltrimethylammonium ($\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3^+$)-montmorillonite and styrene showed an expansion of the basal spacing to a constant value of $\sim 32 \text{ \AA}$ after immersion for 10 days. After polymerization, the amount of polystyrene in the interlayer region was determined by thermal gravimetric analysis. Styrene adsorption initially increased with increasing quaternary ammonium cation and then became approximately constant when loading of the quaternary ammonium cation exceeded 100 meq/100 g clay. The volume resistivity of the stearyltrimethylammonium-montmorillonite-polystyrene complex, which was determined with a high resistance meter, was greater than that of both the quaternary ammonium-montmorillonite and the montmorillonite, and increased in proportion to the amount of polymer adsorbed. These data indicate that polystyrene improved the insulating properties of the clay films.

Key Words—Electrical properties, Intercalation, Montmorillonite, Polystyrene, Quaternary ammonium complexes.

INTRODUCTION

The study of the electrical properties of clay minerals has dealt mainly with clay particles packed in a conductance cell (Oster and Low, 1963; Cloos and Mortland, 1965). However, self-supporting clay-mineral films are more useful than powders for the study of the structure-property relationships of clay minerals and their organic complexes. To obtain reasonable currents from insulators, samples should be thin and of high area, and the applied potential should be large (Seanor, 1965). Hence, clay films are ideally suited for this measurement. In addition, it is useful to determine the electrical properties of clay films because they have potential industrial application as insulators.

Kato *et al.* (1979) have already reported the electrical properties of various homoionic montmorillonite films and their polyacrylonitrile complexes. However, polymers with a high resistivity, such as polystyrene, should improve the insulating properties of clay films, and attempts have been made to prepare such montmorillonite-polystyrene complexes. Friedlander and Frink (1964) reported the intercalation of styrene on the basis of a slight expansion of the 001 spacing and the charring of heat-treated samples. Blumstein (1965), however, questioned styrene intercalation because no increase in the basal spacing could be detected. Pezerat and Vallet (1973) prepared a complex of acid-montmorillonite with polystyrene by swelling the montmorillonite in polar solvents which were miscible with styrene and then polymerized the styrene on the surface of the acid-

montmorillonite. Thus, it seems that the preparation of montmorillonite-polystyrene complexes is rather difficult and no standard methods of preparation have been established.

The fact that non-polar molecules such as benzene can be adsorbed by montmorillonite treated with quaternary ammonium cation was reported by McBride *et al.* (1977) and Komarov *et al.* (1976). Based on these findings, the aims of this study were to prepare quaternary ammonium montmorillonite-polystyrene complexes, to investigate the variation of the amount of polystyrene adsorbed as a function of the amount of quaternary ammonium cation, and to determine the relative contributions of the polymer and the quaternary ammonium cation to the insulating properties of the films.

EXPERIMENTAL

Materials

Montmorillonite from the Aterazawa mine, Yamagata Prefecture, Japan, was used in this study. After repeated elutriation, no crystalline impurities were detected by X-ray powder diffraction. The cation-exchange capacity (CEC) of this starting material was 102.8 meq/100 g clay, as determined by the Schollenberger and Simon (1945) method. Reagent grade methylamine hydrochloride ($\text{H}_3\text{CNH}_2\text{HCl}$), tetramethylammonium chloride ($(\text{CH}_3)_4\text{NCl}$), dodecyltrimethylammonium chloride ($\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$), and stearyl-

trimethylammonium chloride ($C_{18}H_{37}N(CH_3)_3Cl$) were used. Styrene monomer was purified by distillation under reduced pressure after the removal of *t*-butyl catechol with 10% NaOH followed by washing with water.

Preparation of organoammonium-montmorillonite and polystyrene complexes

Clay suspensions (10 g clay/500 ml water) were mixed with 2% quaternary ammonium solutions (50 or 100 meq/100 g clay) and stirred for 1 hr. The mixtures were allowed to stand for 1 day and then washed with water until free of Cl^- . After drying in vacuo ($100^\circ C$, 5 hr), the organoammonium-montmorillonites were ground to pass 100 mesh. Five-gram samples of the dried organoammonium montmorillonites were immersed in styrene monomer, stirred for 1 hr, and allowed to stand over $CaCl_2$ for as much as 25 days at room temperature in a light-screened desiccator. The samples were air-dried, ground to pass 100 mesh, dried in vacuo for 1 day, and examined by X-ray powder diffraction (XRD), using Ni-filtered $CuK\alpha$ radiation, and infrared spectroscopy (IR) using KBr discs.

For the stearyltrimethylammonium-montmorillonite, after immersion for 10 days the air-dried samples were polymerized under a stream of nitrogen at $80^\circ C$ for 5 hr using 0.5% benzoyl peroxide as the initiator. The polymerized complexes were washed with benzene in a Soxhlet extractor for 6 hr. The amount of organic materials absorbed by the montmorillonite was determined by thermal gravimetric analysis (TGA). The heating rate was $10^\circ C/min$ to $800^\circ C$; the sample weight was 100–200 mg.

Electrical measurements

Films of organoammonium montmorillonite and its polystyrene complexes were prepared by air-drying 2–3% suspensions in benzene on a mirror plate. After vacuum drying at 15 torr at $30^\circ C$ for 1 hr, the resistance of the film was measured at room temperature, using an applied potential of 250 V. The measurements were made with a Yokogawa-Hewlett-Packard 4329 A high resistance meter; surface conductivity was eliminated by the use of an apparatus described previously (Kato *et al.* 1979) which uses the guard ring technique (Seano, 1965). The volume resistivity of the sample was calculated from the following equation;

$$\rho v = (A/d) \times Rv$$

where ρv = volume resistivity of sample (Ωcm), A = effective area of the center electrode (cm^2), d = average thickness of sample (cm), and Rv = volume resistance of sample (Ω). Volume resistivities of polyethylene film, nylon film, and polystyrene film measured by this apparatus were $10^{13} \Omega cm$, $10^{14} \Omega cm$, and $10^{18} \Omega cm$, respectively, in good agreement with standard values.

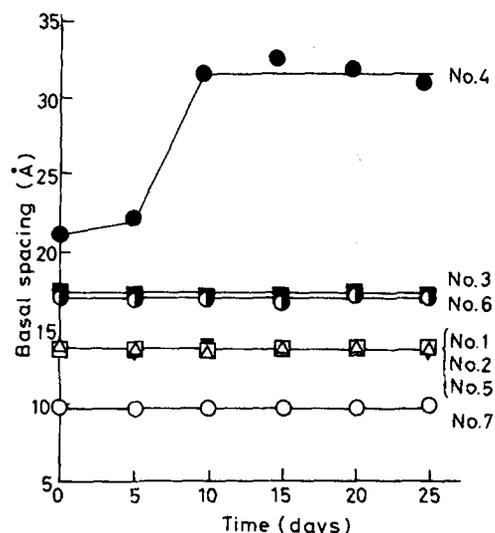


Figure 1. Basal spacings of organoammonium-montmorillonites immersed in styrene monomer (conditions of preparation are listed in Table 1).

RESULTS AND DISCUSSION

Preparation of organoammonium-montmorillonite-polystyrene complexes

Table 1 lists the organoammonium-montmorillonites which were immersed in styrene for different periods of time up to 25 days. The variation of their basal spacings is shown in Figure 1. No increase of $d(001)$ with time was observed in these ammonium montmorillonites except for sample 4. The basal spacing of sample 4 ($(C_{18}H_{37}N(CH_3)_3)$ -montmorillonite; CEC = 100 meq/100 g clay) increased with increasing immersion time and became approximately constant after 10 days.

Pronounced IR absorption bands corresponding to spontaneously polymerized styrene were found only in products prepared from sample 4. The styrene bands were very weak in products prepared from samples 3 and 6 and completely absent in the rest. The IR spectra of $C_{18}H_{37}N(CH_3)_3$ -montmorillonite (sample 4) and the polymerized sample immersed in styrene for 10 days

Table 1. Organoammonium montmorillonites used for the intercalation of styrene.

Sample	Complex	Quaternary ammonium cation added (meq/100 g clay)
1	CH_3NH_3 -montmorillonite	100
2	$(CH_3)_4N$ -montmorillonite	100
3	$C_{12}H_{25}N(CH_3)_3$ -montmorillonite	100
4	$C_{18}H_{37}N(CH_3)_3$ -montmorillonite	100
5	$C_{12}H_{25}N(CH_3)_3$ -montmorillonite	50
6	$C_{18}H_{37}N(CH_3)_3$ -montmorillonite	50
7	Original montmorillonite	—

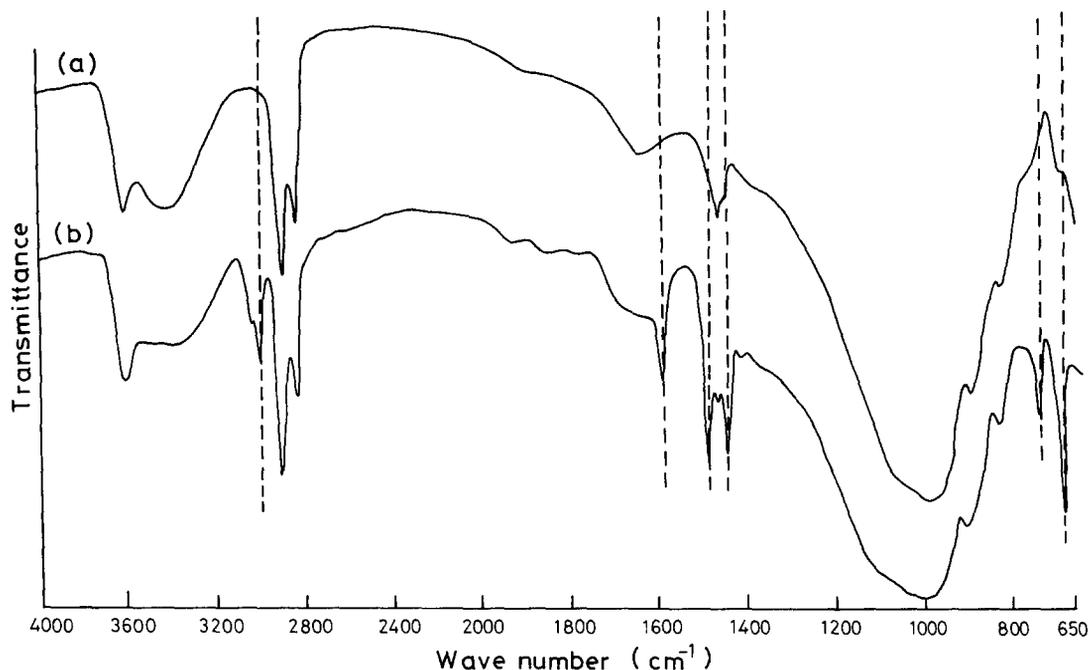


Figure 2. Infrared spectra of (a) $C_{18}H_{37}N(CH_3)_3$ -montmorillonite and (b) $C_{18}H_{37}N(CH_3)_3$ -montmorillonite-polystyrene complex.

are given in Figure 2. The spectrum of the polymerized sample, which had been washed with benzene, showed the characteristic bands due to CH-stretching ($\sim 3025\text{ cm}^{-1}$), CC-skeletal in-plane vibration (1600 cm^{-1} , 1495 cm^{-1} , 1455 cm^{-1}), and CH out-of-plane deformation (755 cm^{-1} , 690 cm^{-1}). Therefore, the $C_{18}H_{37}N(CH_3)_3$ -montmorillonite was selected for the preparation of quaternary ammonium-montmorillonite-polystyrene complexes. The high intercalation of styrene into the $C_{18}H_{37}N(CH_3)_3$ -montmorillonite may be explained by the greater hydrophobic nature of long chain alkyl groups in the interlayer space and van der Waals forces between styrene and the hydrocarbon chain.

The $C_{18}H_{37}N(CH_3)_3$ -montmorillonite-polystyrene complexes were washed with benzene in a Soxhlet extractor for 5–20 hr to remove non-intercalated polystyrene. Disorder in the XRD patterns and a decrease in strength of the characteristic bands due to polystyrene in the IR spectra of the complexes were observed after washing times greater than 6 hr. Therefore, the poly-

merized samples used for electrical measurements were washed with benzene for only 6 hr.

Electrical properties of the $C_{18}H_{37}N(CH_3)_3$ -montmorillonite-polystyrene complex

The volume resistivities of montmorillonite, $C_{18}H_{37}N(CH_3)_3$ -montmorillonite (100 meq/100 g clay), and its polystyrene complex are given in Table 2. The resistivity of the stearyltrimethylammonium-montmorillonite-polystyrene complex was higher than that of stearyltrimethylammonium-montmorillonite which was higher than that of montmorillonite. These data indicate that intercalation of organic compounds increases the

Table 2. Volume resistivity of clay films.

Sample	$\log \rho_v$ (Ωcm)
Montmorillonite	9.87
$C_{18}H_{37}N(CH_3)_3$ -montmorillonite (100 meq/100 g clay)	12.7
$C_{18}H_{37}N(CH_3)_3$ -montmorillonite (100 meq/100 g clay)-polystyrene complex	15.5

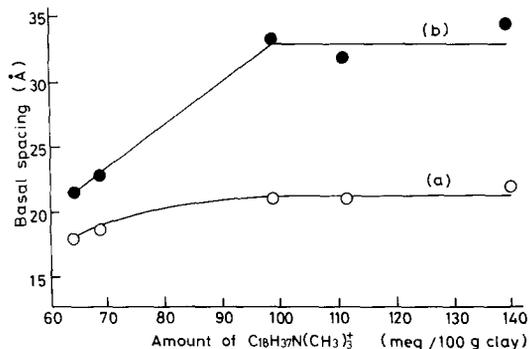


Figure 3. Basal spacings of (a) $C_{18}H_{37}N(CH_3)_3$ -montmorillonite and (b) $C_{18}H_{37}N(CH_3)_3$ -montmorillonite-polystyrene complex.

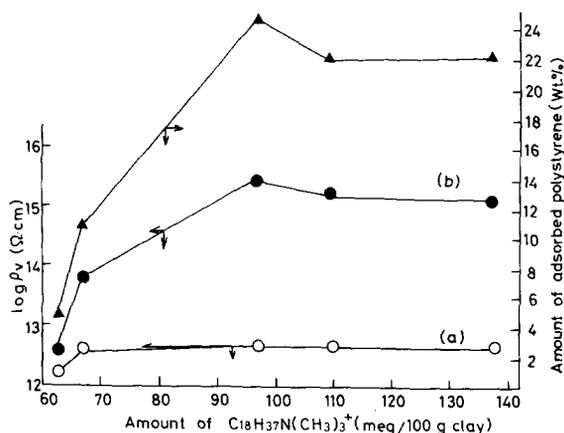


Figure 4. Volume resistivity of (a) $C_{18}H_{37}N(CH_3)_3^+$ -montmorillonite and (b) $C_{18}H_{37}N(CH_3)_3^+$ -montmorillonite-polystyrene complex and the amount of polystyrene intercalated (solid triangles) as a function of the amount of $C_{18}H_{37}N(CH_3)_3^+$ cation.

resistivity of clay films. To clarify the effect of styrene, the variation of the resistivity with extent of complexing was measured.

Figure 3 shows the variation in the basal spacings of the $C_{18}H_{37}N(CH_3)_3^+$ -montmorillonite and the polystyrene complex as a function of the amount of quaternary ammonium ion present in the montmorillonite, determined by TGA. The basal spacing of the quaternary ammonium complex was not greatly affected by the amount of quaternary ammonium ion present, but a marked dependency of the basal spacing of stearyltrimethylammonium-montmorillonite-polystyrene complex on the quaternary ammonium ion content was observed. It increased initially with increasing ammonium content and then became approximately constant at values greater than 100 meq/100 g clay.

Figure 4 shows the variation in volume resistivity of the quaternary ammonium-montmorillonite and its polystyrene complex as a function of quaternary ammonium content (curves a and b). It also shows the variation in polymer content as a function of quaternary ammonium content, determined by TGA (solid triangles). The amount of intercalated polystyrene increased initially with increasing stearyltrimethylammonium content, but became roughly constant, or decreased

slightly at levels greater than 100 meq/100 g clay. Figure 4 also indicates that the volume resistivity of the $C_{18}H_{37}N(CH_3)_3^+$ -montmorillonite-polystyrene complex varied in proportion to the amount of polystyrene complexed, and that the effect was much greater than that of quaternary ammonium ion alone. This shows that the improvement in insulating properties can be mainly attributed to the amount of intercalated polystyrene. The intercalation of polystyrene may strongly hinder electrical conduction by water, in addition to the effect of the stearyltrimethylammonium groups. The latter make the interlamellar space hydrophobic, reduce the conductivity somewhat, and allow intercalation of the polystyrene.

REFERENCES

- Blumstein, A. (1965) Polymerization of adsorbed monolayers I. Preparation of the clay-polymer complex: *J. Polym. Sci.* Pt-A3, 2653-2664.
- Cloos, P. and Mortland, M. M. (1965) Expansion and electrical conductivity of montmorillonite in ammonia atmosphere: in *Clays and Clay Minerals, Proc. 13th Natl. Conf., Madison, Wisconsin, 1964*, W. F. Bradley and S. W. Bailey, eds., Pergamon Press, New York, 231-246.
- Friedlander, H. Z. and Frink, C. R. (1964) Organized polymerization III. Monomers intercalated in montmorillonite: *J. Polym. Sci. Polym. Lett.* 2, 475-479.
- Kato, C., Kuroda, K., and Hasegawa, K. (1979) Electrical conductivity of a montmorillonite-organic complex: *Clay Miner.* 14, 13-20.
- Komarov, V. S., Barkatina, E. N., and Kozlov, N. S. (1976) Adsorption-structural and physical properties of aminated clays: *Vesti Akad. Nauk Belorusk. SSR, Ser. Khim. Nauk* (3), 41-45. (*Chem. Abst.* 85, 131015).
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M. (1977) Adsorption of aromatic molecules by clays in aqueous suspension: in *Fate of Pollutants in the Air and Water Environment, Part 1*, I. H. Suffet, ed., Wiley, New York, 145-154.
- Oster, J. D. and Low, P. F. (1963) Activation energy for ion movement in thin water films on montmorillonite: *Soil Sci. Soc. Amer. Proc.* 27, 369-373.
- Pezerat, H. and Vallet, M. (1973) Formation de polymère inséré dans les couches interlamellaires de phyllites gonflantes: in *Proc. Int. Clay Conf., Madrid, 1972*, J. M. Serretosa, ed., Div. Ciencias C.S.I.C., Madrid, 683-691.
- Schollenberger, C. J. and Simon, R. H. (1945) Determination of exchange capacity and exchangeable bases in soil: *Soil Sci.* 59, 13-24.
- Seanor, D. A. (1965) Charge transfer in polymers: *Adv. Polym. Sci.* 4, 317-352.

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Резюме—Прослойки стирена и четвертично/аммоний-монтмориллонита были приготовлены путем иммерсии глины в мономере стирена. Прослойки стеарилтриметиламмоний ($CH_3(CH_2)_{17}N(CH_3)_3^+$)-монтмориллонита и стирена после иммерсии в течение 10 дней показали расширение основных промежутков до постоянной величины $\sim 32 \text{ \AA}$. После полимеризации количество полистирена в межслойной области определялось путём термогравиметрического анализа. Сначала адсорбция стирена увеличивалась вместе с увеличивающимся количеством четвертичного катиона аммония и оставалась приблизительно неизменной, когда количество этого катиона превышало 100 экв/100 г глины. Объёмное удельное сопротивление комплекса стеарилтриметиламмоний-монтмориллонит-полистирен, определенное при помощи прибора высокого сопротивления, было больше, чем для четвертично-аммоний-монтмориллонита и монтмориллонита, и оно увеличивалось пропорционально количеству адсорбированного полимера. Эти данные указывают на то, что полистирен улучшил изоляционные свойства глинистых фильмов. [Е.С.]

Resümee—Einlagerungsverbindungen von Styrol und quarternärem Ammonium-Montmorillonit wurden mittels Immersion von Ton in monomerem Styrol hergestellt. Die Einlagerung von Styrol in Stearyltrimethylammonium ($\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3^+$)-Montmorillonit führt nach einer Immersion von 10 Tagen zu einer Aufweitung des Basisabstandes auf einen konstanten Wert von etwa 32 Å. Nach der Polymerisation wurde der Gehalt an Polystyrol in den Zwischenschichten mittels thermogravimetrischer Analyse bestimmt. Die Styrol-Adsorption nahm zu Beginn mit zunehmenden quarternären Ammonium-Kationen zu und wurde dann, wenn die Beladung mit den quarternären Kationen 100 mÄqu/100 g Ton überschritten hat, annähernd konstant. Der Gesamtwiderstand des Stearyltrimethylammonium-Montmorillonit-Polystyrol-Komplexes, der mit einem hochohmigen Meßgerät bestimmt wurde, war größer als der des quarternären Ammonium-Montmorillonit und der des Montmorillonites und nahm mit der Menge des adsorbierten Polymers zu. Diese Daten deuten darauf hin, daß das Polystyrol die Isoliereigenschaften der Tonfilme verbesserte. [U.W.]

Résumé—Les composés d'intercalation de styrène et de montmorillonite ammonium quaternaire ont été préparés par immersion de l'argile dans le monomère styrène. L'intercalation de montmorillonite stéaryltriméthylammonium ($\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_3^+$) et de styrène a montré une expansion de l'espace de base à une valeur constante de 32 Å après immersion pendant 10 jours. Après la polymérisation, la quantité de polystyrène dans la région intercouche a été déterminée par analyse gravimétrique thermique. L'adsorption de styrène a initialement augmenté proportionnellement à l'accroissement du cation ammonium, et est ensuite devenu à peu près constante lorsque le chargement du cation ammonium quaternaire excédait 100 meq/100 g d'argile. La résistivité de volume du complexe stéaryltriméthylammonium-montmorillonite-polystyrène, déterminée par un compteur à haute résistance, était plus élevée que celle de la montmorillonite-ammonium quaternaire, ainsi que de la montmorillonite, et augmentait proportionnellement à la quantité de polymère adsorbée. Ces données indiquent que la polystyrène a amélioré les propriétés isolantes des films d'argile. [D.J.]