

INTERCALATION OF SALTS OF FATTY ACIDS INTO KAOLINITE

P. SIDHESWARAN, A. N. BHAT, AND P. GANGULI

Hindustan Lever Research Centre, Andheri (East), Bombay 400 099, India

Abstract—Intercalation of sodium and potassium salts of lauric, myristic, palmitic, elaidic, oleic, 12-hydroxystearic, and a blend of C₈–C₁₀ acids in kaolinite has been followed by X-ray powder diffraction, nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy, and thermal studies. The 7-Å 'c' axis spacing in kaolinite expands to 11 Å as a result of intercalation; this expansion is independent of the alkyl chain length of the fatty acid. The orientation of the organic molecules in the kaolinite interlayer is nearly flat, and ¹H NMR indicates an enhanced ordering in the potassium laurate intercalate. The reversal or equalization of the relative intensities of hydroxyl bands at 3696 and 3619 cm⁻¹ of kaolinite are related to the phenomenon of intercalation. The decomposition temperature of these salts decreases when they are intercalated in kaolinite.

Key Words—Fatty acid, Fourier-transform infrared spectroscopy, Intercalate, Kaolinite, Nuclear magnetic resonance, Orientation, X-ray powder diffraction.

INTRODUCTION

Among various clay-organic interactions, the phenomenon of intercalation has received considerable attention. Intercalation has led to the development of clay products that exhibit novel rheological, surface, and structural properties that have found useful applications in the paper industry, in polymer composites, as matrices for slow release of trapped molecules, and as soil conditioners (Lagaly, 1984; Theng, 1974, 1982). The use of kaolinite in soap and detergent formulations is also fairly common in the patent literature (Kanfer *et al.*, 1987; Ridley, 1987; James, 1953; Chadbourne, 1921, 1922). Investigations involving montmorillonite have been relatively more extensive than those involving kaolinite or other clay minerals, probably due to the ease of intercalation in smectite structures.

Detailed investigations on the intercalation of kaolinite and highly polar organic molecules, such as amides and sulfoxides were reported by Breen *et al.* (1988), Raupach *et al.* (1987), Thompson and Cuff, (1985), and Lipsicas *et al.* (1986). Solid-state nuclear magnetic resonance (NMR), attenuated total reflection (ATR), and X-ray powder diffraction (XRD) have been used to map the molecular orientations in the kaolinite interlayers. Fatty acids in clay interlayers have also been studied because of their importance in the generation of petroleum hydrocarbons in soil (Brindley and Moll, 1965; Jung and Eisma, 1964; Shimoyama and Johns, 1971).

In recent studies in this laboratory, the mechanism of intercalation of potassium salts of short-chain carboxylic acids has been investigated (Sidheswaran *et al.*, 1987, 1988). The present study was undertaken to examine this phenomenon (intercalation) using sodium and potassium salts of long-chain fatty acids.

MATERIALS AND METHODS

Preparation of sodium and potassium salts of fatty acids

Sodium and potassium salts of fatty acids (lauric, myristic, palmitic, elaidic, oleic, 12-hydroxy stearic, and a blend of C₈–C₁₀ acids) were prepared by mixing the fatty acids with calculated quantities of aqueous alkalis in stoichiometric molar proportions. The final pH of the resulting solutions was adjusted to 8.7 ± 0.1. Water was removed by heating at 110°C. Kaolinite from English India China Clay Company, having a chemical analysis of SiO₂, 44.3%; Al₂O₃, 42.3%; Fe₂O₃, 0.37%; and H₂O, 13.5%, was used.

Intercalation

The kaolinite and fatty acid salts (FAS) were mixed in the ratio of 4.9:1. The kaolinite was slowly added with vigorous stirring at about 20°C to a mixture containing FAS (17 g) and hydrazine-hydrate (40–60 ml). XRD patterns of the resulting materials were recorded every day until the material became dry and the patterns remained unchanged.

Instrumental techniques

XRD patterns were recorded on a Siemens D-500 Kristalloflex diffractometer using Ni-filtered CuK α radiation. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the samples were made on a Du Pont 990 Thermal Analyzer. Fourier-transform infrared (FTIR) spectra (300–4000 cm⁻¹) were obtained using a Nicolet SXB 20 instrument. Wide-line NMR spectra were obtained using a Bruker Minispec PC20 apparatus.

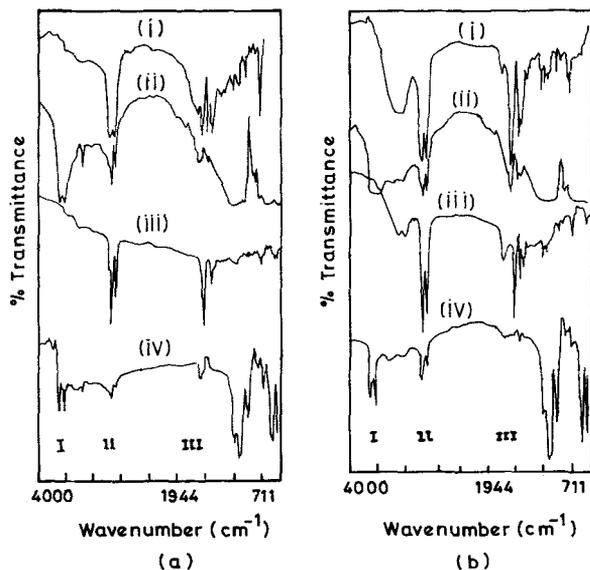


Figure 1. Fourier-transform infrared spectra of palmitate (a) and hydroxy stearates (b) before and after intercalation. Region I, kaolinite hydroxyls ($3600\text{--}3700\text{ cm}^{-1}$); Region II, alkyl groups ($2850\text{--}2930\text{ cm}^{-1}$); Region III, carboxyl stretchings ($1470\text{--}1640\text{ cm}^{-1}$). a. (i), K-palmitate; (ii), Intercalated K-palmitate; (iii), Na-palmitate; (iv), Intercalated Na-palmitate. b. (i), Na-hydroxy stearate; (ii), Intercalated hydroxy stearate; (iii), K-hydroxy stearate; (iv), Intercalated K-hydroxy stearate.

RESULTS AND DISCUSSION

Characterization of the kaolinite

The kaolinite sample used in this study had a c -value of 7.08 \AA . The kaolinite was also characterized by OH-stretching bands at 3696 (s) , 3619 (s) , 3670 (w) , and $3653\text{ (w)}\text{ cm}^{-1}$ (by FTIR); a weight loss of 13.9% (by TGA) due to dehydroxylation; and endothermic dehydroxylation at 525°C (by DSC and TGA).

Fatty acid salt-kaolinite interaction

The surface hydroxyl groups on the kaolinite can form hydrogen bonds with fatty acid salts. The IR spectra of the potassium and sodium salts of palmitic acid and hydroxystearic acid and the corresponding intercalates are given in Figure 1. The spectra of the intercalated kaolinite showed no change (shift) in the bands corresponding to the hydroxyl group. The relative intensities of the 3696- and 3619-cm^{-1} bands were reversed in the case of the intercalates of the Na salts of oleic and stearic, and the potassium salts of elaidic, oleic, stearic, and hydroxystearic acids. For intercalates of the sodium salts of lauric, palmitic, and $\text{C}_8\text{--C}_{10}$ acid blends, the intensities of the two bands were comparable. For the untreated kaolinite, the band at 3696 cm^{-1} had a higher intensity than the band at 3619 cm^{-1} . Only for the intercalates of the sodium salt of 12-hydroxystearic acid was the hydroxyl region (3625

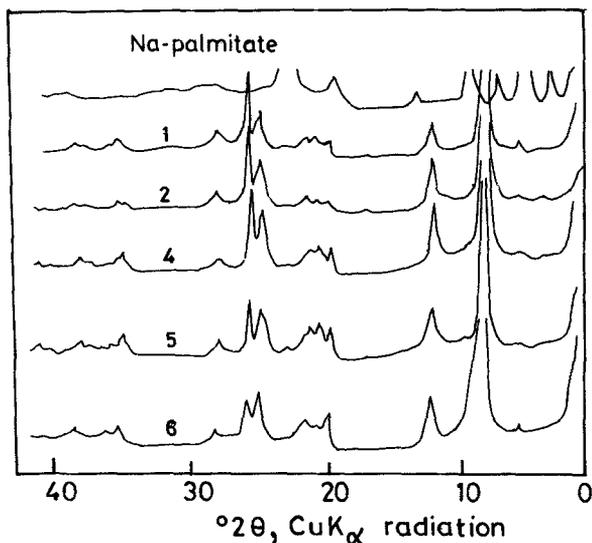


Figure 2. X-ray powder diffraction patterns of kaolinite at various stages of intercalation with Na-palmitate. Numbers refer to the age of the intercalate in days.

cm^{-1}) of kaolinite broad. No such changes were observed for the corresponding potassium salt of 12-hydroxy stearic acid.

XRD patterns (Figure 2) of the kaolinite-FAS systems were made as a function of time. The intensity of the peak at $12.5^\circ 2\theta$ (7.08 \AA) of kaolinite decreased to about 10% of its original value after one day of the reaction. An intercalation by the entrainer, hydrazine hydrate, possibly together with the FAS into the kaolinite layer, is suggested by the strong peak at $8^\circ 2\theta$ (11 \AA). With time the peak at 12.5° grew and the peak at $\sim 8^\circ 2\theta$ decreased in intensity. The appearance of additional peaks at $7.0^\circ 2\theta$ also suggests intercalation of FAS with different orientations. For potassium laurate, the peak due to entrainer intercalation disappeared completely after 7 days, and the peak at 11.5 \AA increased in intensity, broadened, and developed a shoulder suggesting partial intercalation by FAS.

Sidheswaran *et al.* (1987) reported that the peak at $25^\circ 2\theta$ splits after intercalation. They noted that the doublet persisted even after 7 days in all the intercalated samples. If the intercalation was marginal, the doublet at 25° was not as well resolved as that of the potassium laurate intercalate.

To confirm that the observed intercalation was due to FAS and not due to residual hydrazine hydrate entrainer, the intercalate was dried thoroughly in vacuum at 45°C for 6 hr, because under such conditions, kaolinite-hydrazine complexes have been shown to be unstable, the interlayer spacing collapsing to 7.1 \AA (Sidheswaran *et al.*, 1987). In the present system, the peak at $8^\circ 2\theta$ did not change, suggesting intercalation to be due to FAS only. Chemical analysis of the intercalates

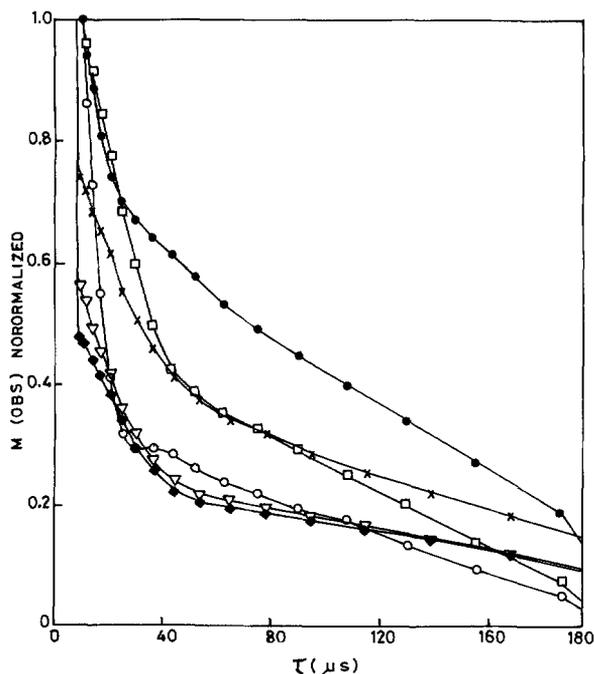


Figure 3. Free-induction decay curves for soaps and the intercalation compounds. \circ = Na-stearate; ∇ = Na-stearate (intercalated); \blacklozenge = kaolinite; \square = hydrazine hydrate treated kaolinite; \bullet = K-laurate; \times = K-laurate (intercalated, after 7 days).

for nitrogen by Kjeldahl method also showed low levels of nitrogen (<0.1%).

Orientation of fatty acid salts in the intercalates

X-ray powder diffraction. Although extensive literature is available on the orientation of fatty acids in montmorillonites (Lagaly, 1984; Brindley and Moll, 1965; Theng, 1974; Sieskind and Ourisson, 1971), the nature of the packing of such molecules in kaolinite is only poorly understood. Complexes of synthetic fluoromontmorillonite and natural montmorillonite, both in their calcium form, show a close packing of fatty acid molecules in pairs, with a head-to-tail arrangement in the interlayer. A fairly strong correlation exists between the stepwise expansion of the 'c' axis and the number of carbon atoms in the fatty acid chain (Brindley and Moll, 1965). In the fatty acid-kaolinite complexes, the c spacing value was constant (~ 11 Å) and fairly independent of the nature of the alkyl groups in the fatty acid molecule. For vertical stacking of the molecules the interlayer opening should be ~ 20.6 Å (Brindley and Moll, 1965). If the fatty acid molecules were horizontally organized, the interlayer space should accommodate the CH_2 groups in a staggered position. To have a double layer of horizontally oriented organic molecules, however, the minimum interlayer spacing should be >4.2 Å. In all the systems studied here, the inter-

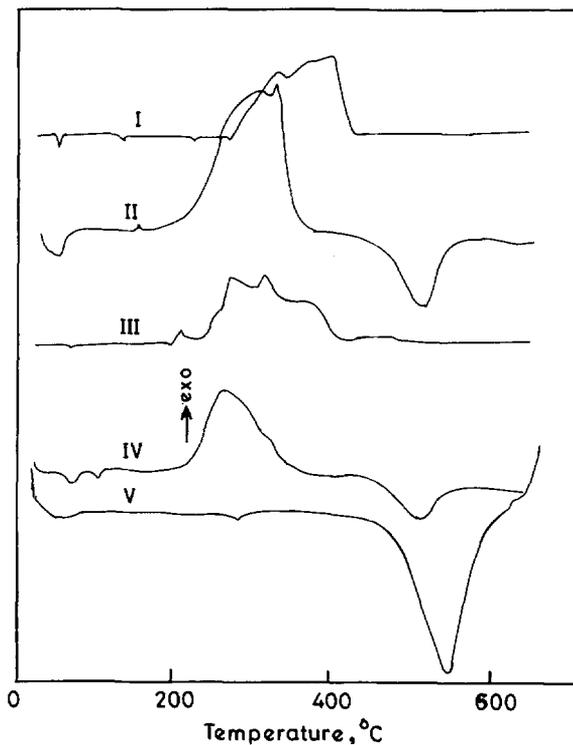


Figure 4. Differential scanning calorimetry tracings. I = K-laurate; II = intercalated K-laurate; III = K-stearate; IV = intercalated K-stearate; V = kaolinite.

layer spacing of the intercalates was 11 Å, which is just sufficient to fit the FAS molecule in a nearly horizontal orientation. This explains the fairly constant c spacing value for FAS of varying chain lengths.

Nuclear magnetic resonance. Proton-free induction decay curves for kaolinite, hydrazine hydrate-treated kaolinite, sodium stearate, potassium laurate, and their corresponding intercalates in the time scale 11–200 μs are given in Figure 3. These data were recorded under the following instrumental parameters: precessional frequency 20 MHz, 90° pulse width 2 μs , repetition delay of 2 s. The FAS samples were recrystallized from hydrazine hydrate to simulate conditions under which they were intercalated into the kaolinite. The FID has two distinct features (1) a fast decaying signal ≤ 40 μs indicating highly ordered protons and (2) a slow decaying signal ≥ 40 μs , indicating protons of relatively greater mobility.

The free-induction decay profile (Figure 3) indicates that protons in the kaolinite (O–H groups) tended to attain a relatively higher mobility after removal of hydrazine hydrate, although XRD studies of the same materials indicated no change in interlayer spacing. Sodium stearate and its intercalate showed similar proton mobility curves. In contrast, potassium laurate appears to have undergone significant ordering in the intercalate.

Thermal analysis. Thermogravimetric studies of the intercalates showed a stepwise decomposition of the fatty acid salt followed by the dehydroxylation of the kaolinite. Figure 4 shows the DSC curves for kaolinite, potassium laurate, potassium stearate, and their intercalates. The decomposition temperature of the fatty acid salt decreased from 430° to 365°C for K laurate intercalate and from 400° to 355°C for K stearate intercalate. The dehydroxylation temperature of kaolinite decreased from about 540° to about 500°C. These results are similar to earlier findings on thermal decomposition of intercalates of potassium salts of short-chain carboxylic acids in which decarboxylation temperatures were considerably reduced and the temperature for dehydroxylation of kaolinite was lowered by 50°–70°C from the original 525°C (Sidheswaran *et al.*, 1987).

Comparison with bentonite

For kaolinite, breaking of the interlayer hydrogen bonds by an entrainer appears to be essential to initiate intercalation of most carboxylic acid salts, except potassium acetate (Sidheswaran *et al.*, 1987; Theng, 1974). In contrast, bentonites can be intercalated by fatty acid salts even in an aqueous medium, in which the exchangeable cations hydrate to expand the interlayer and facilitate the intercalation process. In the present investigation, a solution of potassium laurate intercalated readily with bentonite and no entrainer was found to be necessary for this purpose. Even when hydrazine hydrate was used as an entrainer along with FAS, the interlayer spacing in the final intercalate changed only slightly.

ACKNOWLEDGMENTS

The authors thank K. C. Gounden for his help in the NMR studies.

REFERENCES

Breen, C. and Lynch, S. (1988) Reexamination of kinetics of the thermal desorption of dimethyl sulphoxides N-meth-

- yl formamide from Greensplatt kaolin: *Clays & Clay Minerals* **36**, 19–24.
- Brindley, G. W. and Moll, W. F., Jr. (1965) Complexes of natural and synthetic Ca montmorillonites with fatty acids: *Amer. Mineral.* **50**, 1355–1370.
- Chadbourne, F. G. (1921) Patent No. GB 160892.
- Chadbourne, F. G. (1922) Patent No. GB 176577.
- James, F. O. (1953) Patent No. GB 688466.
- Jurg, J. W. and Eisma, E. (1964) Petroleum hydrocarbons generation from fatty acids: *Science* **144**, 1451–1452.
- Kanfer, J. S., Monson, J. A., and Krieger, J. J. (1987) Patent GB 2190096 A.
- Lagaly, G. (1984) Clay organic interactions: *Phil. Trans. R. Soc. London A* **311**, 315–332.
- Lipsicas, M., Raythatha, R., Giese, R. F., Jr., and Costanzo, P. M. (1986) Molecular motions, surface interactions and stacking disorders in kaolinite intercalates: *Clays & Clay Minerals* **34**, 635–644.
- Raupach, M., Barron, P. F., and Thompson, J. G. (1987) Nuclear magnetic resonance, infra-red and X-ray diffraction study of dimethyl sulphoxide and dimethyl selenoxide intercalates with kaolinite: *Clays & Clay Minerals* **35**, 208–219.
- Ridley, G. (1987) 0210842; Priority 26.07.85; GB 8518910.
- Shimoyama, A. and Johns, W. D. (1971) Catalytic conversions of fatty acids into petroleum like paraffins and their maturation: *Nature* **232**, 140–144.
- Sidheswaran, P., Ganguli, P., and Bhat, A. N. (1988) Thermal behaviour of intercalated kaolinite: *Thermochim. Acta* **118**, 195–303.
- Sidheswaran, P., Ram Mohan, S. V., Ganguli, P., and Bhat, A. N. (1987) Intercalation of kaolinite with potassium salts of carboxylic acids: X-ray diffraction and infrared studies: *Ind. J. Chem.* **26A**, 994–998.
- Sieskind, O. and Ourisson, G. (1971) Interactions argile matiere organique: Formation de complexes entre la montmorillonite et les acides stearique et beheni. *C. R. Acad. Sci. Paris* **272**, 1985–1988.
- Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions*: Adam-Hilger, London, 343 pp.
- Theng, B. K. G. (1982) Clay-polymer interactions: Summary and perspectives: *Clays & Clay Minerals* **30**, 1–10.
- Thompson, J. G. and Cuff, C. (1985) Crystal structure of kaolinite dimethylsulphoxide intercalate: *Clays & Clay Minerals* **33**, 490–500.

(Received 15 December 1988; accepted 7 June 1989; Ms. 1862)