

Intercalation Behavior of Fluorinated Surfactant Cation into The Gallery of Smectite Clays

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Intercalation behavior of fluorinated surfactant cation into the gallery of smectite clays with different size and layer charge was investigated using $C_8F_{17}SO_2NHC_3H_6N(CH_3)_3I$ as the intercalant and sodium fluoride tetrasilic mica and saponite as the host clays. The adsorption isotherms of the surfactant onto the smectite from water/methanol mixed solution at room temperature were determined. The structures appearing in various levels of loading were studied with TG, XRD and FT-IR analyses. The results were compared with the results for montmorillonite previously reported. The results indicated that mono-layer type of intercalation proceeds in the gallery of the mica and montmorillonite, whereas multi-layer adsorption occurs in the case of saponite.

1. INTRODUCTION

Recently, much attention has been paid on nanometer sized composite based on layered inorganic materials hosting functional organic molecules aiming at new advanced materials. Fluorinated surfactant with perfluoro alkyl chain has fascinating features with compared to hydrocarbon-based organic, e.g. thermal stability, water- and oil-repellency, low surface tension associated with the stiff perfluoro chain^{1,2)}. In the previous paper, the authors reported that the fluorinated surfactant cation, $C_8F_{17}SO_2NHC_3H_6N(CH_3)_3^+$ can be easily intercalated into the gallery of the montmorillonite clay through ion-exchange reaction with sodium ion to form intercalation compound with layered structure having a basal spacing of 3.0 nm³⁾. It was also found that the basal spacing reduced to 1.5 nm when the quantity of intercalated surfactant ions was smaller than the cation exchange capacity (CEC) of the montmorillonite. In general, the conformation of the intercalant molecular ions inside the gallery changes depending upon the charge density of the clay as well as the size of the molecule ion. In addition, size of the clay should also be a sensitive factor for the mode of aggregation of the molecules inside the gallery.

The purpose of this paper is to present the difference in intercalation behavior of the fluorinated surfactant into the gallery of the clays depending on the charge density of the silicate layer and also on the lateral size of the clays. For this purpose, intercalation of the fluorinated surfactant into two kinds of smectite clays with different layer charge and size, sodium fluoride tetrasilic mica with swelling property and synthetic saponite, will be investigated and compared with the result of montmorillonite previously presented.

2. EXPERIMENTAL SECTION

2.1 Materials

A quaternary ammonium type cationic fluorinated surfactant, $C_8F_{17}SO_2NHC_3H_6N(CH_3)_3I$, provided from Tohkem-Products Co. Ltd., was used throughout the study. The clays used for this study were sodium fluoride tetrasilic mica (Somasif provided from CO-OP CHEMICAL Co. Ltd.; nominal composition: $Na_2[Si_8Mg_5O_{20}F_4]$; chemical analysis data: SiO₂ 58.73%; MgO 27.58%; Na₂O 4.96%; F 8.02%; CaO 0.16%; Fe₂O₃ 0.07%; Al₂O₃ 0.48%; CEC: 115 meq. / 100 g; lateral crystallite size: . 5 μm) and saponite (Smecton SA provided from Kunimine Industries Co. Ltd.; chemical composition: $(Na_{0.49}Mg_{0.14})[(Si_{7.20}Al_{0.8})(Mg_{5.97}Al_{0.03}O_{20}(OH)_4)]$; CEC: 100 meq. / 100g; lateral crystallite size: . 0.1 μm). These smectite clays are essentially isomorphous to montmorillonite, adopting so-called 2:1 type layered silicate structure with thickness of silicate layer of 0.96 nm.

2.2 Intercalation

The intercalation reaction of the cationic fluorinated surfactant into the clays was carried out through ion-exchange reaction between Na⁺ and $[C_8F_{17}SO_2NHC_3H_6N(CH_3)_3]^+$. One gram of the clay was added in 200 ml of deionized water under vigorous stirring for 3 hours. The suspension was mixed with 200 ml water / methanol mixed solution (the mixing ratio was 1:1) containing the surfactant with different amount 0.4-5.4 times as much as CEC. The suspensions were vigorously stirred for 3 hours under lowered pressures with suction. They were allowed to age overnight, and the products were separated by centrifugation, washed with deionized water and dried in vacuo.

In the previous paper, it was found that iodide salts of the surfactant were cointercalated into the gallery of the clay in addition to the surfactant ions. To separate the surfactant salt, here, the as-prepared samples were rinsed with methanol, followed by filtration. These methanol-rinsed samples as well as the as-prepared samples were together analyzed with following methods.

For convenience, a nomenclature, REF-A-B will be used hereafter for convenience. Here, R is the molar ratio of the surfactant to CEC of the clays, A represents the sort of clay, Mi : mica; Sp : saponite, and B represents whether the sample was washed with methanol: rMeOH; or not: non.

2.3 Characterization of the products.

X-ray diffraction (XRD) patterns for powder and oriented film samples were obtained with a Rigaku diffractometer RAD-C using Ni-filtered $CuK\alpha$ radiation. FT-IR spectra were obtained with a Perkin-Elmer 1640 spectrometer. The sample was ground finely with KBr to make a pellet. Thermogravimetric analysis (TG) was performed with a Rigaku TG8120.

3. RESULTS AND DISCUSSION

3.1 XRD study

The XRD patterns for the as-prepared intercalation compounds are summarized as a function of amount of the surfactant in the solution used in Figure 1. From this figure, basal reflections corresponding to a basal spacing of 2.9 nm can be observed at $2\theta = 3.0, 6.0$ and 9.0 degree for R -value lower than 2. On the other hand, for higher R -value than 2, basal reflections corresponding to a basal spacing of 3.6 nm at $2\theta = 2.5, 4.9, 7.4$ degree. These

results indicate that there are two phases in this composite system with different basal spacing depending on the amount of intercalated surfactants. However, the basal spacing of high R -samples was found to reduce to 2.9 nm when these samples were rinsed with methanol, as shown in Figure 2. On the other hand, $R = 0.9$ sample showed no significant change despite of methanol rinse.

In case of saponite, the XRD patterns were found to be weak and broad due to small crystallite size of the silicate. When we focus our attention to the as-prepared samples, only one basal reflection centered at $2\theta = 6.0$ degree ($d = 1.5$ nm) was observed for $R = 1.1$ (Figure 3). However, for $R = 5.4$, no significant reflection attributable to a certain basal reflection was found. This profile indicates that the composite has a disordered structure through exfoliation of the silicate layers. On the other hand, when the samples were rinsed with methanol, essentially the same profiles as the $R = 1$ sample appeared.

3.2 FT-IR Study.

From FT-IR spectra for mica-based composites and saponite-based ones, at least four absorption bands were observed in addition to typical absorption bands due to layered silicate. They were (1) 1150 and 1210 cm^{-1} due to C-F stretching vibration; (2) 1370 cm^{-1} due to SO_2 stretching one; (3) 1470 cm^{-1} due to C-H bending one. These absorption bands are characteristic for the fluorinated surfactant ion used, thus we can realize the intercalation or adsorption of the surfactant into or on the clay silicates. The absorbance of these bands changed depending upon the amount of surfactant used, whereas the difference became small in case of methanol rinsed samples.

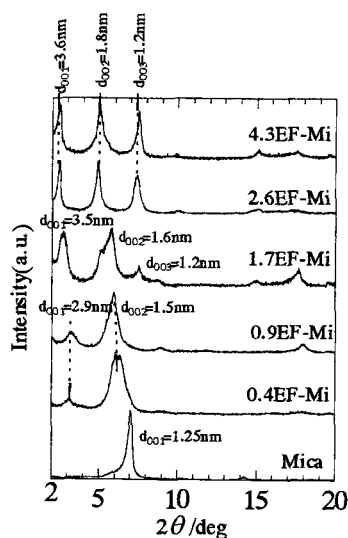


Figure 1. XRD patterns for the as-Prepared fluorinated surfactant / mica composites.

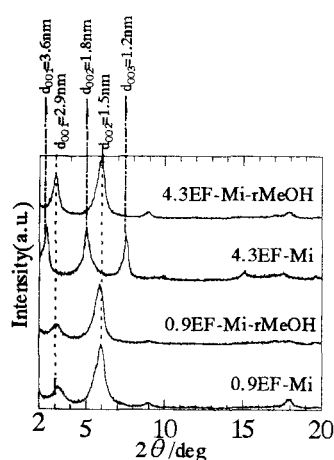


Figure 2. Comparison in XRD patterns between as-prepared and methanol-rinsed mica-based composites.

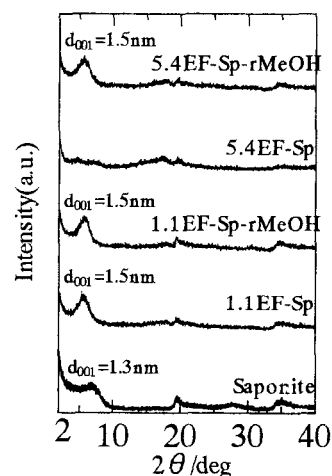


Figure 3. Comparison in XRD patterns between as-prepared and methanol-rinsed saponite-based composites.

3.3 TG Study.

TG profiles are presented in Figures 4 a and b for the composites based on mica and saponite, respectively. In case of mica base composites, two-step behavior was observed; (1) relatively sharp weight loss at around 250 °C; (2) moderate loss from 250 through 400 °C. The temperature of the first loss is close to but significantly higher than the decomposition temperature of the pure original surfactant salt, and the amount changes depending on the sample. Thus the first loss includes the decomposition of the extra surfactant salt intercalated into the mica. The second loss can be assigned to decomposition of the surfactant ions anchored on the internal surface of the silicate through ionic interaction.

For saponite-based composites, similar behaviors were observed except for large weight loss in the case of $R = 5.4$ as-prepared sample. In this case, the temperature of the first loss is very close to that of the decomposition of the pure surfactant salt, suggesting that the surfactant salt deposited in a position spatially separated from the silicate layers.

3.4 Structural Consideration on the Composites

To advance the argument further on quantitative basis, we estimated the quantities of the surfactant

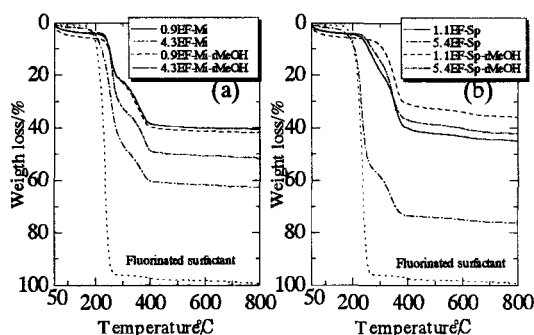


Figure 4. TG profiles for mica-based composites: (a); and those for saponite-based composites: (b).

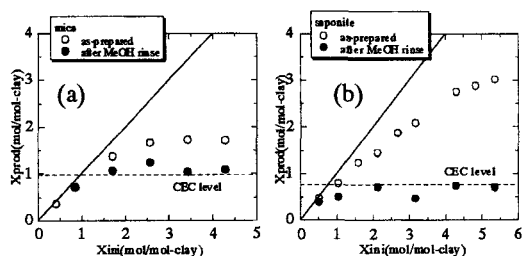


Figure 5. Molar ratios of the surfactant to the clay silicate in the product, X_{prod} , as a function of that in the initial suspension, X_{ini} ; for mica-based system: (a) and saponite-based system: (b). Open keys represent the as-prepared composites and solid keys methanol-rinsed ones.

adsorbed on the silicate with using the TG data. In calculation, we assumed that the weight loss from 200 to 300 °C and that from 300 to 400 °C were assigned to decomposition of surfactant iodide salts, and that of surfactant ions. The total numbers of the surfactant adsorbed on or into the clays per clay structure unit (O_{20}F_4 for mica and $\text{O}_{20}(\text{OH})_4$ for saponite), X_{prod} , are summarized in Figures 5 a and b as a function of the molar ratio of surfactant to clay in the initial suspension (X_{ini}). In these figures, open and solid keys represent the data for as-prepared composites and methanol-rinsed composite, respectively.

In the case of as-prepared mica-based composite, in the light loading region of $X_{\text{ini}} < 1.0$, the X_{prod} increased as the X_{ini} increased, whereas it saturated at around 1.7 when X_{ini} increased over 2. However, after methanol-rinse, the X_{prod} reduced to 1.0, which is very close to CEC level of this clay, in heavy loading region. Taking account of the XRD and TG results described above, we can point out three features as follows. (1) The mica can accommodate the surfactant ions as well as iodide salts at most 1.7 times as much as the molar unit of the clay, resulting in the basal spacing of 3.6 nm. (2) The salts adsorbed can be released from the interlayer space by extraction with methanol, resulting in a basal spacing of 2.9 nm. (3) However, the surfactant molecules introduced as ions have durability against the methanol rinse. The schematic illustration of the structure model is presented in Figure 6.

The first feature is basically the same as that found for the montmorillonite-based composite reported in the previous paper except for a little difference in the basal spacing. Here, the mode of the intercalation should be a monolayer type one with the perfluoro chains standing with respect to the plane of the silicate. And the intercalation extending over CEC level can be interpreted as cointercalation of iodide salts induced hydrophobic interaction between perfluoro chains.

The upper limit of the amount of intercalated surfactant, $X_{\text{prod}} = 1.7$, can be interpreted by a simple geometric consideration. The effective coverage of a perfluoro chain in the closest packing mode is 0.29 nm², on the other hand, the area of the basal plane of the unit cell of mica is 0.47 nm². Thus the mica can accommodate the perfluoro chains 1.62 times as much as the clay unit in the interlayer space on the basis of monolayer-type intercalation. This value is close to the observed value.

However, the situation seems to be different in the case of saponite-based composite. In this case, the intercalation proceeds extending over the level observed for mica, reaching 3 times as much as the clay molar unit, which is corresponding to about 4

times as much as the CEC. This feature of massive adsorption is consistent with the result reported by Inoue's group⁵⁾. Taking account of the faint XRD reflection from the heavily loaded saponite as described above, it is hypothesized that a highly disordered structure such as "card-house" structure was progressed in this case, which enabled to accommodate the massive surfactant salts in addition to surfactant ions. The "card-house" structure is often formed through edge-surface bonding between different silicate layers of clay in dilute acidic suspension. Especially when the size of the silicate crystallite is small, as is the case of saponite, the silicate layers tend to be organized in this structure. It also provides a large number of open pores in the structure to accommodate massive surfactant salts. Even in this case, the surfactants introduced as ions have durability against the methanol rinse.

The basal spacing of 1.5 nm observed for the lightly loaded or methanol-rinsed samples, has been also found for the montmorillonite-based composite with light loading. This has been interpreted as a configuration of the surfactant ions lying parallel to the plane of the silicate. However, intercalation composite with this basal spacing was not observed in the case of the mica with loading of CEC-level. The difference in this point may relate with the difference in the charge density among these clays. The average

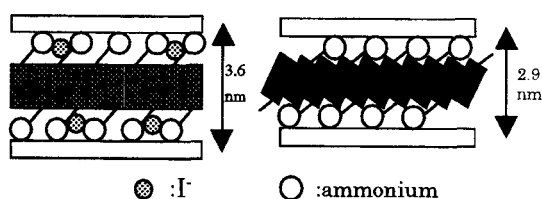


Fig 6. Schematic illustration of the structure model for the as-prepared and methanol-rinsed mica-based composites

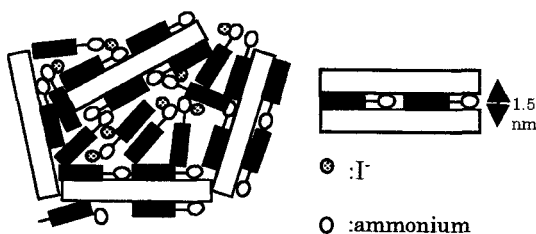


Fig 7. Schematic illustration of the structure model for the as-prepared and methanol-rinsed saponite-based composites

areas on silicate layer per negative unit charge can be calculated to be 0.67, 0.54 and 0.48 nm² for saponite, montmorillonite and mica used in our study, respectively. It is likely that there should be a tendency that lower charge density leads to the lying-type configuration, whereas higher charge density leads to the standing-type one in the interlayer space of the clays. The schematic illustration of the structure model for saponite-based composites is presented in Figure 7.

4. CONCLUSION

The conclusions obtained in the present study are summarized as follows:

- (1) The intercalation of quaternary ammonium ions with perfluoro chain into the gallery of mica and saponite clays can proceed with ion-change method just as previously demonstrated for montmorillonite.
- (2) The intercalation of the ions is accompanied with cointercalation of the surfactant iodide salts with different amounts depending on the kind of clay.
- (3) The mica can accommodate the surfactant totally 1.7 times as much as the clay on molar basis whereas the saponite can do about 3 times.
- (4) Corresponding to these uptakes, nanocomposites with different structure are suggested: (i) monolayer-type intercalation with basal spacing of 3.6 nm for mica; (ii) multilayer adsorption in a card-house type open structure for saponite.
- (5) In both clays, the excess salts are removed with methanol-rinse.

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REFERENCES

- 1) E. Kissa, "Fluorinated surfactant synthesis, properties, applications", *Surfactant Science*, 50 (1994)
- 2) K. Ihara and S. Kouja, "Fluorinated Polymer" (in Japanese), Kyoritsu-shuppan, (1990)
- 3) K. Fuda, H. Shida, K. Murakami and T. Matsunaga, *Trans. Mat. Res. Soc. Jpn.*, 24 (1999), in press.
- 4) G. Lagly, *Solid State Ionics.*, 22, 43 (1986)
- 5) M. Yui, H. Inoue, abstracts of symposium organized by division of colloid and surface chemistry, The Chemical Society of Japan, p122 (1997)