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# Intercalation of Polyfluorinated Surfactants into Clay Minerals and the Characterization of the Hybrid Compounds

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Intercalation of seven types of cationic surfactants, including polyfluorinated surfactants, into a cation-exchangeable clay mineral, saponite, was investigated. All of the surfactants were found to intercalate in amounts exceeding the cation exchange capacity (CEC). This tendency was more evident in the cases of the polyfluorinated surfactants, (((perfluoroalkanoylethyl)hexadecyl)dimethylammonium bromide ( $C_nF$ -S, where  $n$  indicates the number of carbons in the perfluoroalkyl group, F denotes a fluorinated surfactant, and S denotes a surfactant having a single, long alkyl chain);  $C_3F$ -S exhibited intercalation up to 4.4 times CEC as a saturated adsorption limit. The saponite interlayer distance increased upon surfactant intercalation and reached a constant value at intercalation levels exceeding CEC. The occupied areas for each surfactant molecule decreased in the order  $C_1F$ -S >  $C_2F$ -S >  $C_3F$ -S among the polyfluorinated surfactants. All of the experimental results, including the saturated intercalation levels, the occupied areas, the interlayer distances, and the DSC measurements, suggest that  $C_nF$ -S intercalated in saponite forms a rigidly packed bilayer structure in which the long alkyl chains tilt at an angle of ca.  $35^\circ$  with respect to the clay surface. The microscopic structure of the hybrid compounds is discussed.

## Introduction

Fluorocarbons and their derivatives have attracted much attention due to their strong hydrophobicity, lipophobicity, high gas solubility, high resistance against oxidation, and high stability in the presence of strong acid and bases.<sup>1–3</sup> Organic fluorinated compounds as solvent molecules are expected to induce a relative enhancement of solute–solute intermolecular interactions, since solvent–solute interactions are minimized in the fluorinated environment. The polyfluorinated environment is thus both promising and interesting from the viewpoint of a novel microenvironment for chemical reactions. Recently, we have synthesized a novel series of polyfluorinated surfactants on the basis of this viewpoint and found that they formed micelles and vesicles with unique microscopic structures.<sup>4–5</sup> The micelles and vesicles were revealed to have been coated by a perfluorinated layer and to exhibit a strong protective effect against the attack of strong oxidizing agents such as the hydroxide radical. These were termed “surface polyfluorinated micelles” and “surface polyfluorinated vesicles”, respectively.<sup>4,5</sup>

Saponite is an example of a silicate having a layered structure. Substitution of Si atoms in the network of the layered structure with various metal ions such as  $Al^{3+}$ ,  $Mg^{2+}$ , and so forth renders the layer surface nega-

tively charged.<sup>6</sup> Into the interlayer space of saponite, various positively charged organic and inorganic compounds and polar substances, including ketones, nitriles, and alcohols, can thus be incorporated to form a sandwich-like structure, that is, an intercalation process.<sup>7–12</sup> In many cases, the intercalated molecules are known to align themselves in an ordered structure within the interlayer space.<sup>6–8</sup> When compared with nano- or mesoporous materials such as zeolites,<sup>13</sup> a greater variety of larger molecules can be intercalated into the interlayer space, since it is two-dimensionally wide and moreover can adjust itself to accommodate guest molecules by expanding, that is, increasing the interlayer distance.<sup>14</sup> The interlayer space can be modified with a large variety of molecules.<sup>8</sup> The concept of preparing unique hybrid polyfluorinated environments provided by the novel

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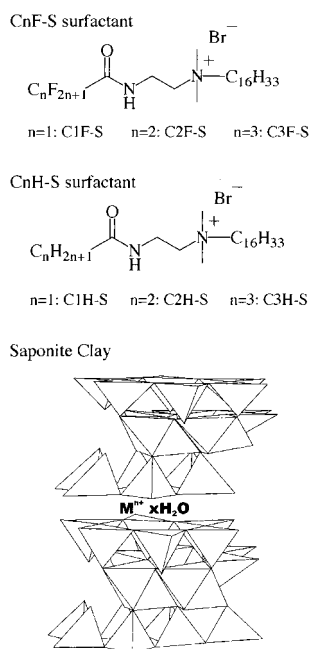
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Chart 1



cationic polyfluorinated surfactants and clay minerals such as saponite is promising from the viewpoint of microenvironments for chemical reactions, since each component has such unique characteristics.<sup>6–8</sup> The polyfluorinated surfactants are expected to form a two-dimensionally wide polyfluorinated phase. Their microscopic structure, molecular alignment, phase-transition properties, and other characteristics relevant to the chemical reaction environment provide much interest. In this paper, we report on the intercalation of cationic polyfluorinated surfactants into cation-exchangeable clay minerals and the characterization of the resulting structures.

### Experimental Section

**Materials.** The synthesis of polyfluorinated surfactants (CnF-S) and their hydrocarbon analogues (CnH-S) has been reported elsewhere.<sup>4</sup> The symbol  $n$  denotes the number of carbons in the acyl group, F indicates a polyfluorinated surfactant, H indicates a hydrocarbon analogue, and S indicates a surfactant type with a single long alkyl chain. Cetyltrimethylammonium bromide (CTAB; WAKO Pure Chemical Industries, Co.) was recrystallized from acetone three times. Cation-exchangeable clay (Sumecton SA) was kindly provided by Kunimine Industries and was used as received. Sumecton SA is a type of sodium saponite synthesized via a hydrothermal reaction. The properties of Sumecton SA are as follows: the composition is  $[(\text{Si}_{7.20}\text{Al}_{0.80})(\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{-0.77}(\text{Na}_{0.49}\text{Mg}_{0.14})^{+0.77}$ , the surface area is  $750 \text{ m}^2 \text{ g}^{-1}$ , and the cation-exchange capacity (CEC) is  $0.997 \text{ mequiv g}^{-1}$ .<sup>15</sup> The structures of CnF-S and CnH-S surfactants and saponite clay are shown in Chart 1. Deionized water (conductivity  $< 0.1 \mu\text{S/cm}$ ) was used as a solvent.

**Sample Preparation.** The syntheses of surfactant–clay hybrid compounds were carried out by the following procedure. As a typical condition, 30 mL of surfactant aqueous solution (5 mM) was added to 10 mL of clay aqueous dispersion (5 g/L). Under these conditions, the loading levels (amounts) of surfactants were 300% with respect to the CEC of the clay. Control of the surfactant loading levels allowed control of the adsorbed surfactant level. An aqueous mixture of clay/surfactant was stirred at  $65^\circ\text{C}$  for 3 h. The precipitate was filtered (ADVANTEC, Toyo Roshi Kaisha, Ltd.; pore size =  $0.2 \mu\text{m}$ ), washed with water on filter paper, and then dried in air at  $80^\circ\text{C}$  to constant weight.

The compositions of the clay/surfactant hybrid compounds were determined by the weight gain of the clay and were confirmed by elemental analysis.

**Instrumentation and Methods.** X-ray powder diffraction (XRD) was performed on a MXP-18 (MAC Co., Ltd.) diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.15405 \text{ nm}$ ). Differential scanning calorimetry (DSC) was measured with a Seiko DSC-200 (Seiko Instruments) (scan range,  $5\text{--}90^\circ\text{C}$ ; heating rate,  $5^\circ\text{C/min}$ ). A small-angle X-ray scattering (SAXS) instrument was attached to the small-angle X-ray scattering optics (DSC–SRXRD) at beam-line BL-10C at the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of the monochromatic X-rays for DSC–SRXRD was  $0.1488 \text{ nm}$ . The scattered X-rays were detected by a one-dimensional position-sensitive proportional counter (PSPC). The distance between the specimen and the PSPC was  $680 \text{ nm}$ , which covered  $1.25 \text{ nm} < S^{-1} = (2 \sin \theta / \lambda)^{-1} < 200 \text{ nm}$  (scan range,  $21\text{--}90^\circ\text{C}$ ; heating rate,  $0.2^\circ\text{C/min}$ ). The temperature was calibrated by measurement of the melting points of pure indium and tin. Thermal gravimetric analysis was measured with a TG-DTA 6200 (Seiko Instruments) (scan range  $25\text{--}450^\circ\text{C}$ ; scan rate,  $5^\circ\text{C/min}$ ). Fourier transform infrared spectra (FT-IR) were measured on a FT/IR-620 (JASCO) spectrometer equipped with the attenuated total reflection (ATR) unit for ATR–FT-IR measurement.

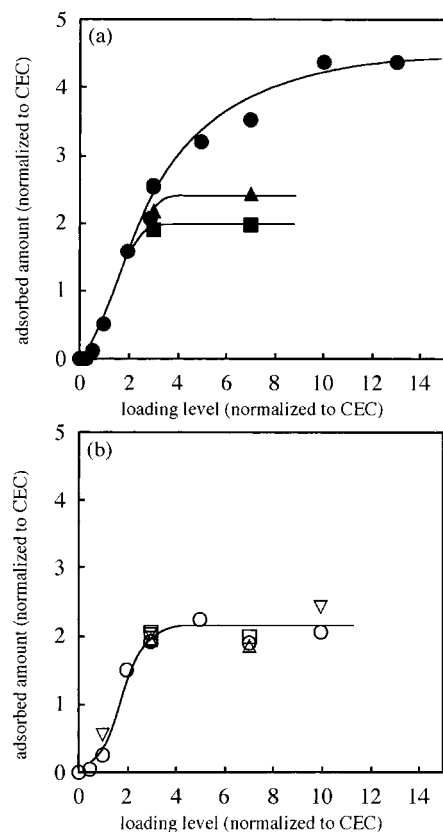
### Results and Discussion

#### Formation of Clay/Surfactant Hybrid Compounds.

Saponite was found to disperse well in water by means of vigorous stirring. An aqueous solution of surfactant, when poured into the aqueous saponite suspension, also with vigorous stirring, forms a white precipitate under the conditions described in the Experimental Section. The weight gain of the precipitate, compared with the initial weight of saponite, strongly indicates that the surfactant is incorporated into the clay. Elemental analysis also indicated that the precipitate contained surfactant molecules, as described later. The amounts of surfactant intercalated into saponite under various conditions are shown in Figure 1.

The intercalation levels increased monotonically with the surfactant loading level in the aqueous mixture and in most cases saturated for loading levels that were a factor of ca. 3 with respect to CEC (referred to hereafter as  $3 \times \text{CEC}$ ). For all surfactants, excess intercalation of surfactant above the amount equivalent to CEC was observed, as shown in Figure 1. Hydrocarbon-type surfactants CnH-S and CTAB (Figure 1b) exhibited saturated intercalation amounts that were similar ( $1.9\text{--}2.4 \times \text{CEC}$ ) to each other, while the polyfluorinated surfactants CnF-S showed larger saturation levels; the level increased with the number of carbons in the perfluoroalkyl chain. C3F-S exhibited a very large saturation level ( $4.4 \times \text{CEC}$ ). For the intercalation of alkylammonium bromide surfactants into clay layers, one of the most curious points is whether and how the bromide ions are incorporated within the interlayer space. The major driving force for the adsorption of the cationic surfactant on the cation-exchangeable clay surface should be a Coulombic stabilization by the neutralization of the charges on the surfactant and clay. The bromide counterions are thus expected to be expelled from the surface for adsorption levels below CEC, and the bromide ions may remain in the interlayer as counterions for the ammonium group when the surfactant is incorporated at levels in excess of CEC after attaining charge neutralization. One of the most powerful tools for clarifying this point should be elemental analysis. To fully understand the latter, thermal gravimetric analyses (TGA) were carried out; these clearly indicated that for the C3F-S/clay hybrid sample only trace amounts of water, less than 0.03% of the total weight, are incorporated in the sample after being dried in air at  $80^\circ\text{C}$  to a constant weight,

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**Figure 1.** Adsorbed amount of surfactant intercalated in saponite clay on various loading levels of (a) polyfluorinated surfactant and (b) hydrocarbon analogue: (●) C3F-S, (▲) C2F-S, (■) C1F-S, (○) C3H-S, (△) C2H-S, (□) C1H-S, and (▽) CTAB.

whereas the original clay itself contains 10.4% water. The elemental analyses were thus carefully inspected on the basis of the TGA data. Supposing a ratio  $x$  between surfactant intercalated without bromide ion and that with bromide ion and varying the ratio systematically, a calculated elemental percentage was compared carefully with the experimentally obtained one. The elemental analyses of the sample prepared with various surfactant loading levels can be best explained as follows: the surfactants in the form of ammonium ions adsorb at the cation-exchangeable sites without the bromide counteranion below  $1.7 \times \text{CEC}$ , while they are incorporated as neutral molecules, with the bromide ion, above  $1.7 \times \text{CEC}$ . The analyses are as follows. Calcd for (%)  $4.4 \times \text{CEC}$  of C3F-S/saponite: C, 37.09; N, 3.61. Found (%): C, 36.84; N, 3.75. Calcd for (%)  $3.6 \times \text{CEC}$  for C3F-S/saponite: C, 35.05; N, 3.41. Found (%): C, 34.99; N, 3.13. Calcd for (%)  $2.6 \times \text{CEC}$  for C3F-S/saponite: C, 31.56; N, 3.07. Found (%): C, 32.01; N, 3.40. These strongly suggest that the actual number of anionic sites in the saponite is larger than the CEC value. The reason for this discrepancy is not clear, but surface hydroxyl groups may provide additional anionic sites.<sup>16</sup> At present, it cannot be definitely specified where they are located. As far as the experimental results indicate, the amount of the anionic sites other than those existing within the clay layer is  $0.7 \times \text{CEC}$ , which at present can only be simply expressed as "surface hydroxyl groups". Supposing that the actual number of anionic sites is  $1.7 \times \text{CEC}$ , the above explanation concerning the elemental analyses would be reasonable,

(16) The pH value of an aqueous dispersion of Sumecton SA (10 g/L) was found to be 9.01, indicating that the clay itself has basic sites on its surface.

**Table 1. Structural Data of Surfactant/Clay Hybrid Compounds**

| surfactant | adsorbed amount for saturation vs CEC | occupied area, Å <sup>2</sup> | clearance space, Å | molecular length, <sup>a</sup> Å | tilt angle, deg |
|------------|---------------------------------------|-------------------------------|--------------------|----------------------------------|-----------------|
| C1F-S      | 2.0                                   | 63                            | 31.3               | 25.1                             | 38.6            |
| C2F-S      | 2.4                                   | 52                            | 29.8               | 25.9                             | 35.1            |
| C3F-S      | 4.4                                   | 28                            | 29.7               | 26.7                             | 33.8            |
| C1H-S      | 2.0                                   | 63                            | 31.8               | 24.9                             | 39.6            |
| C2H-S      | 1.9                                   | 66                            | 29.8               | 25.7                             | 35.4            |
| C3H-S      | 2.0                                   | 63                            | 30.8               | 26.5                             | 35.5            |
| CTAB       | 2.4                                   | 52                            | 11.8               | 24.6                             | 13.9            |

<sup>a</sup> Side opposite to the triangular structure of each surfactant.

because the anionic sites of the clay surface should be electrically neutralized by the ammonium surfactant in the region below  $1.7 \times \text{CEC}$ , driving the intercalation and removing sodium bromide from the interlayer. In contrast, the surfactant molecules in excess of  $1.7 \times \text{CEC}$  would be incorporated as neutral tetraalkylammonium bromide molecules to the already neutralized interlayer space due to hydrophobic interactions between the long alkyl chains of the surfactants and also due to relatively strong hydrophobic ones among the polyfluorinated alkyl chains. Neutral polar organic molecules such as alcohols, nitriles, ketones, and so forth have been reported to be intercalated into clays,<sup>9–12</sup> and intercalation in excess of CEC has also been reported in some cases.<sup>15,17–19</sup> However, the intercalation of such a large excess ( $4.4 \times \text{CEC}$ ), as observed in the case of C3F-S, has never been reported. The polyfluorinated surfactants thus offer most interesting examples for excess intercalation. The fact that the intercalation was not observed at all when the clay and the surfactants were dispersed in various organic solvents such as dichloromethane, acetonitrile, acetone, 2-propanol, and benzene strongly suggests that hydrophobic interaction between the surfactant molecules is the driving force for the intercalation.

**Occupied Area of the Intercalated Surfactant Molecule.** Two key questions arise: (1) how is such a large excess in terms of intercalation possible for the polyfluorinated surfactants and (2) how do the polyfluorinated molecules align within the interlayer space of the clay? To clarify these points, the occupied area for each surfactant on the clay surface was calculated from the values of the surface area of the saponite ( $\sim 750 \text{ m}^2/\text{g}$ )<sup>6c,20</sup> and the saturated amount (number of molecules) of intercalation for each surfactant. The estimated occupied areas for each surfactant molecule are compared in Table 1.

The values of occupied area decreased in the order  $\text{C}_n\text{H-S}$ ,  $\text{C1F-S} > \text{C2F-S} > \text{C3F-S}$ . The area decreased systematically with increasing number of carbon atoms in the perfluoroalkyl group. The cross-sectional area of a single long hydrocarbon chain in the all-trans conformation is calculated to be around  $18\text{--}20 \text{ Å}^2$ .<sup>21</sup> In the actual system, however, the cross-sectional area of the most rigidly packed alkyl chain of an ammonium-

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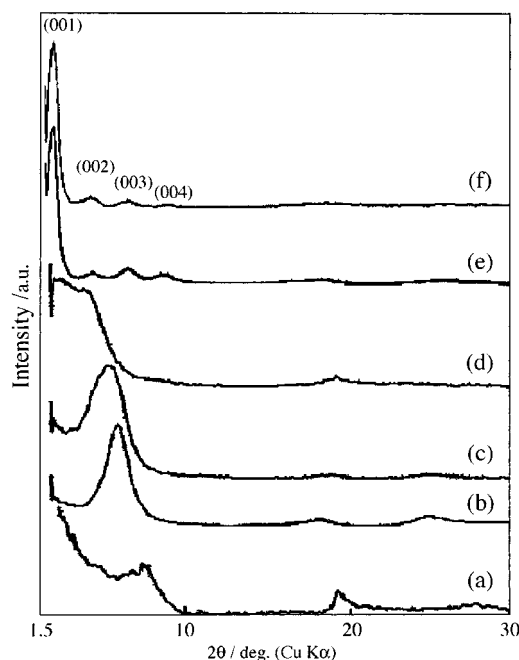
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type surfactant in a Langmuir–Blodgett (LB) membrane on mica has been reported to be around  $26 \text{ \AA}^2$ , depending on the tilt angle and the configuration of the ammonium headgroup with respect to the chain.<sup>22</sup> As indicated in Table 1, C3F-S has the smallest cross-sectional area ( $28 \text{ \AA}^2$ ), strongly suggesting that it has a microscopic structure similar to that of the long alkyl chains that are the most tightly packed within LB membranes. The values of intrinsic surface area of saponite ( $750 \text{ m}^2/\text{g}$ ) divided by  $26 \text{ \AA}^2$  would afford a maximum amount of surfactant intercalated within the clay layer, supposing a microscopic orientation of surfactant molecules similar to that in the LB membrane:  $750 \text{ m}^2 \text{ g}^{-1} / (26 \text{ \AA}^2 \times N_A) = 4.8 \times 10^{-3} \text{ mol/g}$ , where  $N_A$  is Avogadro's constant. Thus, the maximum intercalation amount for surfactant molecules ( $4.8 \text{ mmol/g}$ ) corresponds to  $4.8 (= 4.8 \text{ mmol} / 0.997 \text{ mequiv})$  equiv versus CEC.<sup>19</sup> The observed saturation level for the intercalation for C3F-S ( $4.4 \text{ equiv}$  vs CEC) corresponds well to the maximum limit where all of the surface area of the clay is covered by the surfactant headgroup, as estimated from the cross-sectional area given in the literature. These results clearly indicate that C3F-S has a bilayer structure within the interlayer space of the clay. If the surfactant is incorporated in the form of a single layer, the saturated amount of intercalation should be around  $2.4$  ( $1/2$  of  $4.8$ ). But the observed value is close to twice this value. The results in Table 1 can be summarized as follows: (1) the occupied areas of intercalated surfactants decrease systematically with increasing number of carbon atoms in the perfluoroalkyl chain and (2) the hydrocarbon analogues of the surfactants have larger occupied areas than those of the polyfluorinated surfactants. These characteristics strongly suggest that the microscopic orientations of the surfactants are delicately controlled by the short chains of the surfactants. A larger area suggests a bulkier microscopic configuration around the ammonium headgroup of the surfactant, that is, the surfactant should have a bent-type structure of the ammonium group with respect to the chain. In studies on surface polyfluorinated micelles and vesicles formed by  $C_n\text{F-S}$ , the perfluoroalkyl chains have been found to extend straight into the bulk water phase, while the short alkyl chains of the corresponding hydrocarbon analogues ( $C_n\text{H-S}$ ) penetrate into the core of the micelles or vesicles.<sup>4,5</sup> These contrasting microscopic orientations can be rationalized by hydrophobic and lipophobic interactions between the perfluoroalkyl groups in the case of  $C_n\text{F-S}$  and hydrophobic interactions alone in the case of  $C_n\text{H-S}$ .<sup>4,5</sup> These interactions should also contribute to the control of the microscopic structure of the surfactant molecules in the interlayer spaces in clays. The polyfluorinated surfactants are understood to have smaller occupied areas and thus increase intercalation levels owing to the aggregative interactions between the short perfluoroalkyl chains. On the other hand, the short alkyl chains of the hydrocarbon-type surfactants incorporated into the clay structure might be able to bend around to provide appreciable hydrophobic interactions with the long alkyl chains. Very interestingly, C1F-S and C1H-S have almost the same occupied areas, suggesting similar microscopic orientation. Thus, the effect of the perfluoroalkyl group appears to be minimized for C1F-S. A similar tendency was also observed in the formation of micelles and vesicles.<sup>4,5</sup>

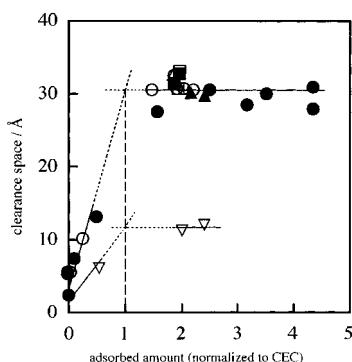


**Figure 2.** X-ray diffraction profiles of C3F-S/saponite clay hybrid compounds with various adsorbed amounts of C3F-S molecules: (a) 0 CEC (original saponite), (b)  $<0.01$  CEC, (c)  $0.11$  CEC, (d)  $0.5$  CEC, (e)  $2.7$  CEC, and (f)  $4.4$  CEC.

**Determination of Layer Distances of Clay/Surfactant Hybrid Compounds by XRD Analysis.** Another powerful piece of information that helps to clarify the microscopic orientation of surfactant molecules in the clay structure is the distance between clay layers. Clay minerals are known to vary their interlayer distances depending on the nature of the intercalated molecules and their microscopic orientation.<sup>6–8</sup> XRD measurements were carried out on the present samples, and typical XRD profiles are shown in Figure 2 for C3F-S.

The rather broad peak of  $d(001)$  ( $2\theta = 7.5^\circ$ ;  $d = 12 \text{ \AA}$ ) of the original saponite with weak intensity underwent an obvious shift to smaller angles as a sharp peak with the appearance of higher angle diffraction peaks upon intercalation of C3F-S. The shift depended on the amount of intercalation (Figure 2). In the region of intercalation in excess of CEC, the sharp peak for  $d(001)$  ( $2\theta = 2.2^\circ$ ;  $d = 39 \text{ \AA}$ ) remained unchanged. The layer distances, as expanded by the intercalation of the surfactants, were estimated from the position of the (001) diffraction peak. An excess distance or “clearance space” can be defined as the value obtained by subtraction of the intrinsic layer thickness ( $9.6 \text{ \AA}$ )<sup>20</sup> from the observed layer distance. The clearance space depends on the degree of intercalation, as seen in Figure 3, increasing with increasing intercalation levels. Despite considerable efforts to obtain additional data points between  $0.5$  and  $1.5 \times \text{CEC}$ , the experiments in this region did not yield stable results, presumably owing to the metastable aspect of the intercalation prior to formation of the bilayer structure. Interestingly, the clearance space appeared to reach constant values for two different types of surfactants at equal adsorption levels normalized to CEC (Figure 3), even as the intercalation continued to increase well above CEC (Figure 1). The maximum clearance space for  $C_n\text{H-S}$  and  $C_n\text{F-S}$  were almost the same ( $\sim 30 \text{ \AA}$ ), but CTAB exhibited a smaller value ( $\sim 12 \text{ \AA}$ ). CTAB has been presumed to have a *pseudo*-

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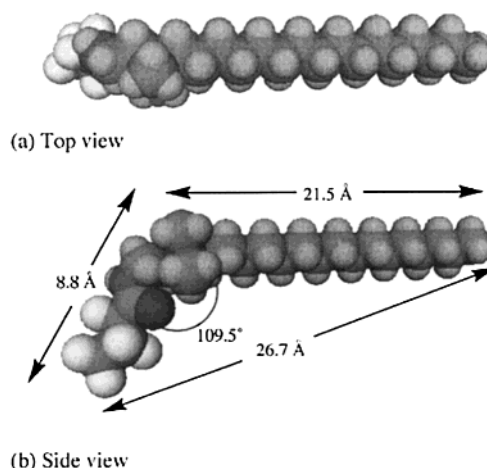
**Figure 3.** Relation between adsorbed amount of surfactant and layer clearance space of surfactant/saponite clay hybrid compounds: (●) C3F-S, (▲) C2F-S, (■) C1F-S, (○) C3H-S, (△) C2H-S, (□) C1H-S, and (▽) CTAB.

trimolecular layer.<sup>14a,23</sup> In the present work, it also appears to have a microscopic structure different from those of  $C_nH-S$  and  $C_nF-S$ . The results obtained can be summarized as follows: (1) an ordered structure is formed even for small intercalation levels; (2) even for different types of surfactants, the structural ordering is almost complete at equal intercalation levels versus CEC; and (3) upon further intercalation above CEC, the clearance space ( $\sim 30$  Å) remained constant, indicating no change in the ordered structure.

The data obtained for the occupied areas and clearance space strongly suggest that C3F-S has a fully packed bilayer structure. This idea prompted us to carry out DSC measurements, to obtain information as to whether the long alkyl chains undergo a phase transition.<sup>5,24</sup> If the surfactants have a highly ordered bilayer structure, a phase transition involving the long alkyl chains, for example, a gel–liquid crystal phase transition, might be expected to be observed. In the DSC measurements, saponite itself did not show any peak in the temperature range of 20–90 °C, while the hybrid compound intercalated with C3F-S at  $4.4 \times$  CEC showed a broad but distinct endothermic peak centered at around 50 °C. The endothermic peak area clearly increased with increased levels of intercalated C3F-S, although quantitative analysis was difficult owing to peak broadening. SAXS measurements on the same sample also showed a distinct phase transition at around 59 °C. These results suggest that C3F-S has a highly ordered structure that undergoes a gel–liquid phase transition as the temperature is raised.<sup>5</sup> The results obtained for the calorimetry and SAXS measurements all support the discussion derived from the results on the occupied areas of the surfactants and clearance space.

**Molecular Orientation of the Intercalated Polyfluorinated Surfactants and Their Microscopic Structure in the Clay Layer.** The optimized structures of the C3F-S surfactant molecules were calculated by means of the PM3 MO method, as depicted schematically in Figure 4, where each dimension, including the length of the long alkyl chain, the short alkyl chain, the bending angle, and the side opposite to the triangular structure, is described.

The molecular length can thus be defined in various ways. The distance of the side opposite to the triangular structure is 26.7 Å for the longest molecules (C3F-S) and 24.9 Å for the shortest (C1H-S). A simple comparison of



**Figure 4.** Molecular model of C3F-S surfactant.

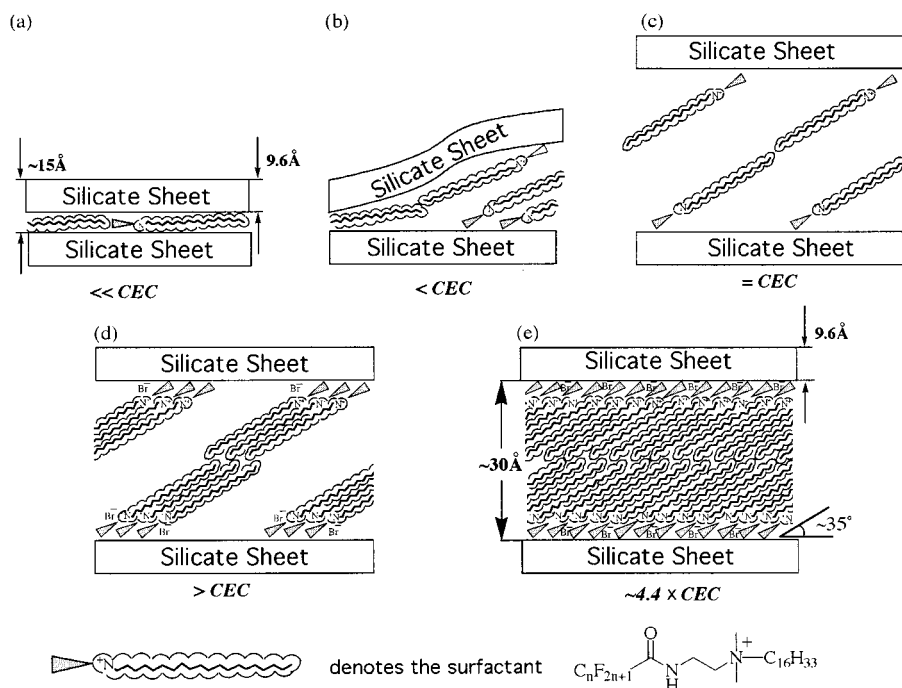
these lengths with the similar values for clearance space ( $\sim 30$  Å, Figure 3) for the  $C_nF-S$  and  $C_nH-S$  series might lead to the conclusion that the surfactant molecules are oriented perpendicular to the clay surface in a single layer. However, all of the experimental results, that is, occupied areas, saturated intercalation levels, DSC, and SAXS measurements, clearly indicate that these molecules form bilayer structures within the clay layer. On the basis of the bilayer structure, the surfactant molecules are expected to tilt at a fixed angle in the interlayer space. By use of the distance of the side opposite to the optimized triangular structure, the tilt angles for each surfactant were calculated, as compared in Table 1. The opposite sides of the surfactant molecules all tilt in the range of ca. 34–39° with respect to the clay surface. The proposed microscopic structure is depicted schematically in Figure 5.

The ion-exchange replacement of sodium ions by the ammonium surfactant molecules can induce the formation of an ordered structure (Figure 5a). With an increase in the amount of intercalated surfactant, the interlayer distance expands (Figure 5b), reaching a constant value at the same adsorption level, that is, 1.0 versus CEC (Figure 5c). Under these conditions, the surfactant molecules form a bilayer structure. At loadings greater than ca.  $1.7 \times$  CEC, the excess intercalation proceeds by an incorporation of alkylammonium bromide surfactant as a neutral molecule (Figure 5d) via a different mechanism, that is, one due to hydrophobic interactions involving the polyfluorinated chains and long hydrocarbon alkyl chains, as distinct from the electrostatic ion-exchange mechanism operative in the region below  $1.7 \times$  CEC. The maximum limit of the intercalation depends on the microscopic structure around the ammonium headgroup of the surfactant; C3F-S, having the smallest occupied area, showed the largest intercalation, up to  $4.4 \times$  CEC (Figure 5e). To confirm the orientation, the following experiments are now in progress, and very interesting preliminary results are obtained. By increasing the number of carbon atom of the perfluoroalkyl chains systematically, such as C4F-S, C5F-S, C6F-S, and C10F-S, the layer distance increased systematically, well in accord with the orientation shown in Figure 5.

A simple question arises here: why does the surfactant molecule tilt with respect to the clay surface? The following discussion might partly answer the question. As discussed above, the primary driving force for the intercalation of the ammonium surfactant should be the electrostatic interaction between the ammonium cation and the negative charge on the clay surface. The

(23) (a) Ogawa, M.; Aono, T.; Kuroda, K.; Kato, C. *Langmuir* **1993**, 9, 1529. (b) Ogawa, M.; Wada, T.; Kuroda, K. *Langmuir* **1995**, 11, 4598.

(24) (a) Okahata, Y.; Shimizu, A. *Langmuir* **1989**, 5, 954. (b) Kanzaki, Y.; Hayasi, M.; Minami, C.; Inoue, Y.; Kogure, M.; Watanabe, Y.; Tanaka, T. *Langmuir* **1997**, 13, 3674.



**Figure 5.** Schematic structure of C3F-S/saponite clay hybrid compound for various amounts of adsorbed C3F-S molecules: (a) very small amounts vs CEC, (b) less than CEC, (c) equal amount approximately to CEC, (d) amounts in excess of CEC, and (e) 4.4 times CEC. The surfactant represents the top view shown in Figure 4. The tilt angle shown in (e) represents that of the side opposite to the triangle structure of the surfactant.

surfactant molecules would tend to orientate themselves in such a way as to minimize their distance from the negative charge of the clay surface. However, with increasing numbers of molecules, both the bulkiness associated with the ammonium headgroup and the mutual electrostatic repulsion between the ammonium groups would force the surfactant molecules to modify their positions. In micelles, the ammonium groups are known to be situated in a zigzag position so as to minimize the repulsive interactions, forming a Stern layer.<sup>25</sup> On the clay surface, however, due to the anisotropic restriction of the surface, the surfactant molecules are obliged to avoid the mutual close contact of the ammonium groups by *tilting in a fixed direction*. The orientations of the surfactant molecules are thus considered to be governed by a delicate balance among the following factors: (1) stabilization through cation–anion electrostatic interaction between the ammonium group and the negative charge on the clay surface; (2) destabilization by the electrostatic repulsion between the ammonium cations; (3) destabilization through the steric crowding among the substituents on the ammonium group; and (4) stabilization by hydrophobic interactions between the long alkyl chains. The microscopic orientation around the ammonium headgroup would be further influenced by the strong repulsive lipophobic interactions of the short perfluoroalkyl chain with the long hydrocarbon chains and attractive hydrophobic interactions between the perfluoroalkyl chains in the case of  $\text{C}_n\text{F}-\text{S}$ , which would lead to formation of separate fluorocarbon and hydrocarbon phases as shown in Figure 5e. As already noted, however, relatively attractive hydrophobic interactions between the short alkyl chains and the long alkyl chains would be important in the case of  $\text{C}_n\text{H}-\text{S}$ , leading to a bent-type structure. More detailed studies on the microscopic structure around the ammonium headgroup are now in progress. In addition to the above factors,

**Table 2.** IR Spectral Data of Original Surfactants and Surfactant/Clay Hybrid Compounds at Carbonyl Stretching Band ( $\text{cm}^{-1}$ )

|       | hybrid <sup>a</sup> |      | original surfactant <sup>b</sup> |
|-------|---------------------|------|----------------------------------|
| C3F-S | 1714                | 1685 | 1716                             |
| C2F-S | 1714                | 1681 | 1717                             |
| C1F-S | 1731                | 1672 | 1735                             |
| C3H-S | 1669                | 1652 | 1670                             |
| C2H-S | 1651                |      | 1653                             |
| C1H-S | 1663                |      | 1672                             |

<sup>a</sup> Measured by ATR technique. <sup>b</sup> Measured by KBr method.

stabilization by hydrogen-bonding interactions between the amide groups of the aligned polyfluorinated surfactants on the clay surface are thought to contribute substantially to the formation of the bilayer structure. ATR–FT-IR measurements of the surfactant/clay hybrid compounds showed that two strong carbonyl stretching peaks were observed for each of the  $\text{C}_n\text{F}-\text{S}$  surfactants, as well as for C3H-S, in the clay environment, as listed in Table 2. The new peak at the smaller wavenumber was assigned to a hydrogen-bonded carbonyl. In contrast, the shift or appearance of another peak of carbonyl was not obvious in the cases of C1H-S and C2H-S in clay. Since almost no water is involved in the dried hybrid compound, as confirmed by TGA, the peak shift of the carbonyl can be understood by assuming the formation of intermolecular hydrogen bonds between the adjacent amide groups of the aligned surfactants on the clay surface. In summary, a novel series of polyfluorinated surfactants  $\text{C}_n\text{F}-\text{S}$  has been found to form very interesting hybrid compounds with saponite, as described above. The interlayer space in the hybrid compounds promises to provide unique types of reaction microcavities having a polyfluorinated microenvironment.