Intercalation of a Cationic Surfactant in the Interlayer Space of Smectites

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(Received April 8, 2002)

The properties of cationic surfactant-clay mixtures were examined by measurements of the electric conductivity, absorption spectra, and X-ray diffraction patterns. The orientation of *N*-[[4-(aminoiminomethyl)amino]butyl]dodecanamide (DAG) as a intercalated cationic surfactant and the thickness of the interlayer space of clay using Na-saponite (Sumecton SA) were investigated. DAG molecules were intercalated in a 1 nm gap in the interlayer space of clay. It is speculated that alkyl groups of the surfactant molecules are placed not parallel, but inclined slightly vertical to the internal surface of Na-saponite.

Smectites, classified as clay minerals, have a lamellar structure, of which the specific surface is comparable to that of active carbon. Smectites, which are characterized as a negatively charged surface, are easily modified by compounds having positively charged groups, and various compounds are intercalated in their interlayer space. Recently, processed materials made from smectites have attracted remarkable attention for applications as absorbents for organic pollutants,[1–3] optical materials,[4–8] catalysts,[9–11] and polymer/clay composites.[12–15] Smectites are used in many articles, such as hair-care products, body soaps, cleansing foams, bath agents, and skin care products.[16,17] It is known by experience that processed montmorillonite, as one type of smectites, is efficient to protect skin and hair from irritant materials. It was considered that irritant materials are adsorbed on the external surface and/or interlayer space of Na-saponite.

Cationic surfactants are widely used as a rinse and hair conditioner. *N*-[[4-(aminoiminomethyl)amino]butyl]dodecanamide (DAG) was developed as a cationic surfactant, which has an affinity for hair.[18] DAG is composed of a hydrophilic guanidinium group and a hydrophobic alkyl group connected with an amide group as a joint. There have been many papers concerning the intercalation of cationic surfactants containing an alkyltrimethylammonium group or neutral surfactants onto smectites.[19–21] However, no paper has been found so far on DAG adsorption onto smectites. Therefore, it is worth investigating the intercalation of a surfactant into the interlayer space of smectites.

The purpose on this paper is to discuss the orientation of intercalated molecules and the thickness of the interlayer space of a silicate layer using Na-saponite, which can intercalate molecules of the surfactant. The properties of DAG-clay mixtures were examined by measurements of the electric conductivity, absorption spectra and X-ray diffraction patterns.

Experimental

Materials. Na-saponite (Sumecton SA supplied from Kunimine Industries Co., $(Na_{0.49}Mg_{0.14})^{0.77+}[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{0.77-}$ as the ideal formula, very minute particles synthesized by a hydrothermal reaction) was used as a host material. The property of Sumecton SA is as follows: The viscosity of a 3.5% suspension is more than 25,000 cp, the pH of a 2% suspension is 8.5–10.5, and the cationic-exchange capacity (CEC) is 0.7 meq g^{-1}.

DAG acetate was used as a cationic surfactant. The other chemicals were of reagent grade, or the best commercially available.

Apparatus. Various measurements were performed using an electric-conductivity meter (Horiba ES-14) for the electric conductivity, an X-ray diffractometer (RINT-2100) using monochromatic Cu Kα radiation for the X-ray diffraction patterns, and a Shimadzu spectrophotometer (UV-2400PC) for the absorption spectra. The clay used was separated from aqueous suspensions by centrifugation with a centrifugal separator (Tommy, RS-18GL).

Electric Conductivity. Aqueous suspensions of 2, 4, 8, and 16 g dm^{-3} clay were prepared. Eighty cm^{-3} each of the suspension in a bottle was immersed in a water bath to keep the temperature constant at 25 °C. The electric conductivity was measured. Into these aqueous clay suspensions, 0.4 mmol of DAG was dissolved, and the electric conductivity was measured. This process was repeated by adding another 0.4 mmol of DAG into the clay suspensions until the concentration of DAG reached to around 20 mM (= mmol dm^{-3}). The volume change of the aqueous suspensions was very small regardless of the DAG addition, and the volume was considered to be constant.

Measurement of Adsorbed DAG. Twenty cm^{-3} of a mixture containing 0.61–1.30 mM DAG, and 0.5 g dm^{-3} Na-saponite was stirred gently at 25 ± 1 °C for one day. The DAG concentration of the mixture in the supernatant after full sedimentation was determined by a photometric measurement. The absorbances of 1 mM DAG and 0.5 g dm^{-3} Na-saponite were obtained to be 4.7 and 0.09 at 205 nm, and 0.006 and 0.03 at 250 nm, respectively. The absorbance of the mixture in the top clear layer was measured at 205 and 250 nm. Since the absorbance of DAG was negligible at 250 nm, the clay concentration could be estimated from a measurement of the absorbance at 250 nm in the mixture. The absorbance at 205 nm in the mixture consisted of both the absorbance of DAG and clay. Therefore, the absorbance of DAG at 205 nm was obtained by subtracting the absorbance of the clay at 205 nm. The amount of DAG adsorbed to clay was calculated by subtracting the equilibrated concentration from the initial one.

X-ray Diffraction Patterns. Mixtures of DAG and clay were prepared for measurements of the X-ray diffraction patterns in the same way as for that of the electric conductivity. Each aqueous suspension was cast to make a thin layer on a plate of glass (38 mm × 30 mm × 1.8 mm). The cast films were placed and dried up in a desiccator for more than 3 days. The X-ray diffraction patters of the dried cast films were measured. The basal spacing of clay was calculated according to Bragg's equation. The X-ray diffraction pattern of clay alone was also measured.

Results and Discussion

Electric Conductivity of the DAG–Clay Mixtures. The electric conductivities of the DAG-clay mixtures were measured by varying the concentration of DAG at the designated concentration of clay. The results are shown in Fig. 1. As compared with the conductivity of salt solutions, such as potassium chloride (0.15 mS cm^{-1} for 1 mM KCl, 25 °C), Fig. 1 shows a reasonable conductivity of DAG solutions. In the case of a DAG solution without clay, the slope of the conductivity–concentration line was found to change at 7.8 mM DAG. This result indicates that DAG molecules aggregate to form micells in the solution at higher than 7.8 mM. In the case of 16 g dm^{-3} clay, the conductivity increased linearly up to around 10 mM DAG (first stage), and then the plots lined up on a gentle slope in the region of 10–17 mM DAG (second stage). The conductivity increased linearly with a slightly steep slope of the solid line at higher than 17 mM DAG (third stage).

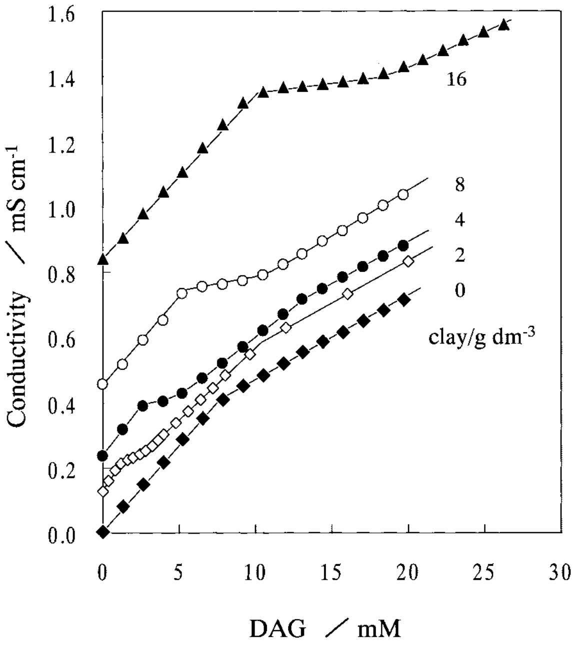

Fig. 1. Conductivities for DAG-clay mixtures. Clay concentrations (g dm^{-3}): 0 (◆), 2 (◇), 4 (●), 8 (○), and 16 (▲).

At the first stage, the cationic surfactant, DAG, could be adsorbed on the surface of the silicate layer, while Na$^+$ was released from the surface of the silicate layer. Consequently, Na$^+$ and acetate ion (counter ion of DAG) participate in the conductivity. It could be explained that DAG molecules were adsorbed on the clay surface, caused by cation exchange. In the second stage, the ionic exchange on the surface of clay was completed for the adsorption of DAG. The conductivity scarcely increased in spite of the addition of DAG acetate. Therefore, it was considered that DAG molecules in the bulk suspension were intercalated in the interlayer space of the silicate layer due to a hydrophobic interaction. The conductivity increased with increasing the DAG concentration in the third stage. It is evident from the presence of free DAG and acetate ion in the suspension that the interlayer space of the silicate layer is saturated by the intercalation of DAG molecules. The same tendency was observed in the case of 2–8 g dm^{-3} clay. In the case of 2 g dm^{-3} clay, the dotted line was bent at 1.3, 2.5, and 10.5 mM DAG. DAG molecules were intercalated in the interlayer space of clay at lower than 2.5 mM DAG in the first and second stage. Free DAG increased in the suspension at higher than 2.5 mM DAG in the third stage. It seems that no more DAG was adsorbed into the clay. In the cases of 2 and 4 g dm^{-3} clay, the solid line made a gentle slope at higher than 10.5 and 13.5 mM DAG, respectively (fourth stage). This is explains why the concentration of free DAG reached cmc (= 7.8 mM free DAG in the mixture). The intercalation of DAG in the interlayer space of clay appears at a higher concentration of DAG than cmc. The saturated adsorption of DAG in the interlayer space of clay is estimated to be 1.4 mmol g^{-1}.

Figure 2 shows the relationship between the concentrations of DAG and clay at the beginning of the second stage. The plots of DAG against the clay concentration fell on a straight

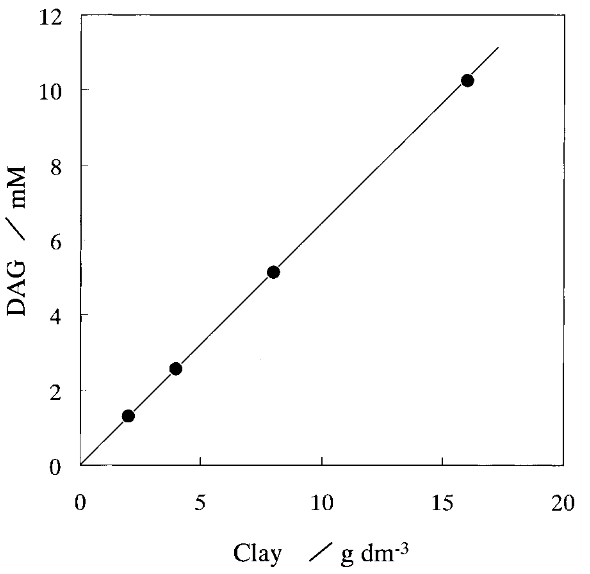

Fig. 2. The relationship between DAG and clay concentration.

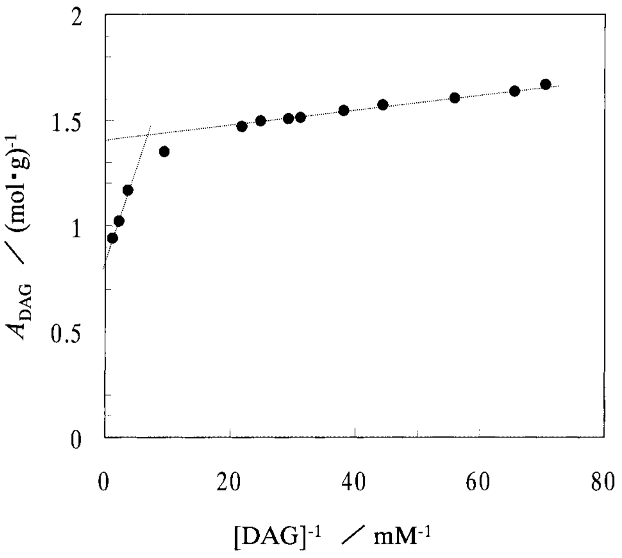

Fig. 3. Langmuir's adsorption isotherm of DAG onto Na-saponite at 25 °C [DAG] and A_{DAG} are expressed as the equilibrated concentration of DAG in the mixture and the amount of DAG adsorbed onto 1 g of Na-saponite after one day, respectively.

line. From the slope up to 1.3 mM DAG in the first stage, we obtained CEC = 0.64 mmol g^{-1} DAG. This is almost in accord with 70 meq/100 g clay.[21] At this stage, cations are exchanged by DAG$^+$ in the interlayer space of clay. The alkyl groups of DAG may bring about hydrophobic circumstances in the interlayer space of clay. Therefore, it was considered in the second stage that DAG was adsorbed on the surface of clay due to a hydrophobic interaction.

Langmuir's Adsorption Isotherm of DAG onto Na-Saponite. Figure 3 shows Langmuir plots between the equilibrated concentration of free DAG and the amount of DAG adsorbed to clay in a mixture using 0.5 g dm^{-3} clay. The plotted line is bent around 0.17 mM in Fig. 3. It seems that DAG molecules are adsorbed to clay due to two different affinities. In less than 0.17 mM DAG, the slope of the plotted line is gentle, which means a strong affinity of DAG to clay. Judging from the slope in Fig. 3, the affinity in the first stage was found to be 20-times greater than that in the second stage. From each intercept derived from two lines, the saturated adsorption of DAG was estimated to be about 0.7 and 1.2 mM g^{-1}, respectively. These results are explained in the same way as those of the electric conductivity in Fig. 1. The first stage appears due to the ionic adsorption of DAG to clay, and the second stage may follow with weak adsorption due to the hydrophobic interaction.

X-ray Diffraction Patterns of DAG-Clay Mixtures. X-ray diffraction patterns were measured in order to demonstrate the configuration of DAG molecules in the interlayer space of clay. X-ray diffraction patterns of various DAG/clay ratios (mmol g^{-1}) are shown in Fig. 4. The basal spacing of the clay, d, was obtained from Fig. 4. The relationship between d and DAG/clay ratio (mmol g^{-1}) is shown in Fig. 5.

Two peaks, one broad and one sharp, appeared in the region of $2\theta < 7°$, as shown in Fig. 4. The former shifted 2θ to a smaller region with increasing DAG/clay up to 0.7–0.8 mmol g^{-1}. The latter appeared at $2\theta = 2.8°$ at higher than 1 mmol g^{-1}. Both d's were determined to be 2.0 and 3.0 nm in the region of DAG/clay > 1.5. From the result of DAG alone, d = 3.0 nm was assigned to be due to the micells of DAG. Taking into consideration the results on conductivity, it was deduced that d = 2.0 nm came from the intercalation of DAG in the interlayer space of clay. The silicate layer of Sumecton SA is approximately 1.0 nm thick.[21] Therefore, the interlayer space of clay expanded to 1.0 nm due to the intercalation of DAG

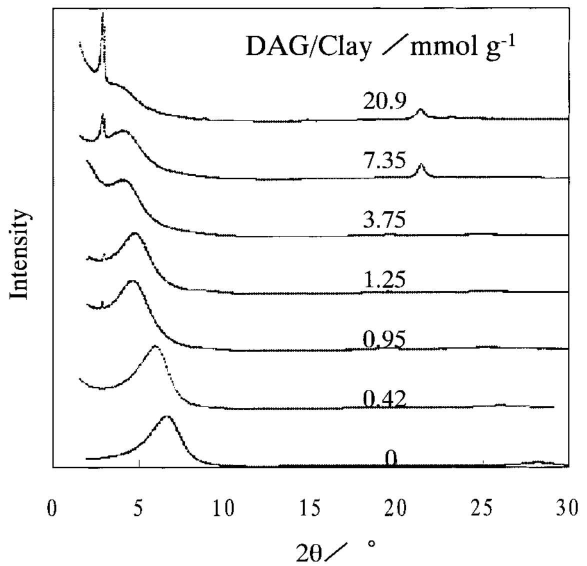

Fig. 4. X-ray diffraction patterns for DAG-clay mixtures.

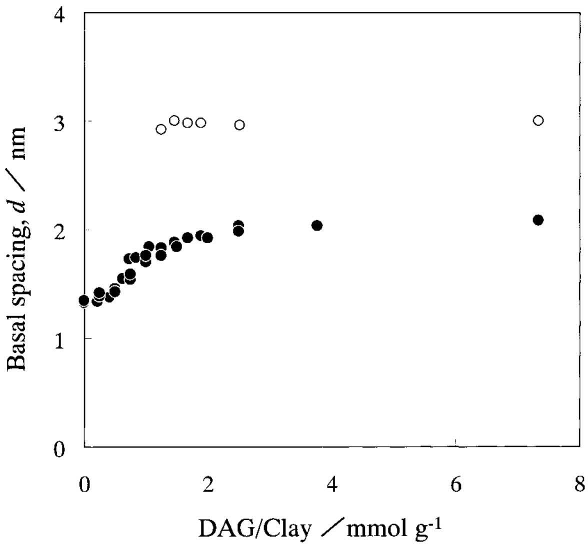

Fig. 5. The distance of basal spacing for DAG-clay mixtures.

The Configuration of DAG in the Interlayer Space of Clay. It has been reported that N-dodecyldimethylamine N-oxide is intercalated in a gap of approximately 0.8 nm in the interlayer space of clay to make a bimolecular layer oriented parallel to the internal surface of clay.[21] On the other hand, our results on conductivity in the previous section might lead to different speculation. The basal spacing is 2.0 nm, where

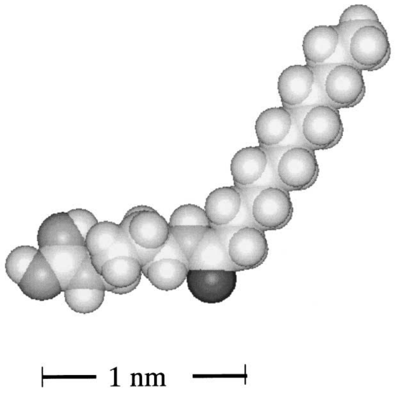

Fig. 6. Model configuration of DAG^+.

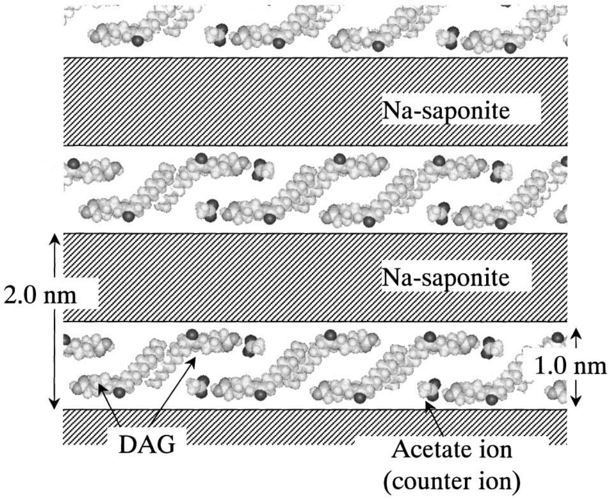

Fig. 7. Configuration of DAG molecules in the clay lamellar.

DAG/clay is in higher than 1.5 mmol g^{-1}. DAG could be intercalated more than CEC in the clay. The total length of dodecanamide group and the guanidinium group could be estimated to be around 2.4 nm.

A DAG molecule is bent at an amide group as a joint between a hydrophobic alkyl group and a hydrophilic guanidinium group. This configuration was assessed using the MM+ molecular mechanics program with the conjugate gradient method and Adapted Newton Rapson method (HyperChem, Ver. 6.0, MM+, Hypercube inc.). The model configuration of DAG^+ is shown in Fig. 6. The area of the occupied surface for one DAG^+ might be 1.1 nm × 0.5 nm, which is estimated from the length and thickness of a hydrophilic group. The axis of the hydrophilic group can plausibly orient parallel to the surface of clay. On the other hand, the specific surface area of Sumecton SA was calculated to be approximately 800 m^2 g^{-1}, based upon 2.3 as the specific gravity and 1.1 nm as the thickness of clay plate (Na salt), of which the side and edge areas were neglected. This roughly corresponds to 750–850 m^2 g^{-1} as the specific surface area, which was obtained from the result on methylene blue adsorption in an organic solvent. It is estimated to be 0.64 mmol/g as DAG^+ and 0.76 mmol/g as DAG acetate in saturated adsorption. In the case of 0.64 mmol/g, the hydrophilic groups of DAG^+ might cover approximately 200 m^2 g^{-1} of the clay surface. This surface area occupied by DAG^+ is smaller than the specific surface area of Sumecton SA. Therefore, it was considered that DAG acetate was intercalated in addition to DAG^+ adsorption due to ion exchange, and that these alkyl groups of DAG made a hydrophobic interaction with each other on the same interlayer surface of clay. In the case of 1.4 mmol/g DAG^+, the hydrophilic groups of DAG^+ might cover a clay surface of nearly 500 m^2 g^{-1}. Acetate as a counter ion might intercalate with DAG^+.

Judging from all our results, the axis hydrophobic alkyl group was suggested to orient diagonally from the clay surface, as shown in Fig. 7, due to a 1.0 nm expansion of the interlayer space. The clay lamellar was considered to stack with each other to make thick-layered particles.

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