

Direct Surface Force Measurement for Synthetic Smectites Using the Atomic Force Microscope

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An atomic force microscope with a colloid probe technique was used to measure forces interacting between smectites, that is, saponite and hectorite. The measured forces fit well to the forces calculated by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory at separations larger than 4 nm over concentrations of 10^{-5} – 10^{-2} M NaCl and the pH range of 4–10. There is also a good agreement between zeta potential and the electrical double-layer (EDL) potential extracted from the best fit to the DLVO force curve. According to the analysis on the pH dependence of the EDL potential using the Gouy–Chapman–Stern–Graham model, the inner Helmholtz layer capacitance for the good fit of the outer Helmholtz plane potential to the EDL potential required a much lower value for hectorite ($\sim 5 \mu\text{F}/\text{cm}^2$) than that for saponite ($\sim 500 \mu\text{F}/\text{cm}^2$), reflecting the difference in the location of the lattice charge between saponite and hectorite. This provided evidence for the fact that the EDL force for smectites is dominated by the location of the charges as well as the density of the charges. Extra short-range repulsion was observed at separations below ~ 3 nm with increasing NaCl concentration and pH and then disappeared with decreasing pH or the NaCl concentration. The short-range repulsion was extracted as a double-exponential function, that is, $F/R = A_1 \exp(-D/D_1) + A_2 \exp(-D/D_2)$, by subtracting the DLVO forces from the measured forces in the same way as the study with a surface force apparatus (Pashley, R. M. *J. Colloid Interface Sci.* **1981**, *83*, 531). The values of two decay lengths (D_1 and D_2) for smectites showed a very similar result to those for muscovite mica rather than silica. It was also found that the sum of the force constants ($A_1 + A_2$) was closely related to the density and structure of the lattice charge.

Introduction

Interparticle forces between clay platelets have been extensively investigated in relation to swelling, colloid stability, and cation-exchange properties because of a wide range of industrial applications as well as scientific interests.

Most of the previous studies on the interparticle interaction in clay dispersions have been performed using indirect or macroscopic techniques such as rheology,^{1–7} swelling pressure, and the determination of interlayer space using X-ray diffraction.^{8–15} However, the dispersion

of arbitrary-shape particles and the coexistence of positively charged edges and negatively charged faces have made it difficult to understand the interparticle forces between clay surfaces. For the last two decades, more pronounced understanding of forces interacting for two surfaces in solutions has been available with the development of a surface force apparatus (SFA)¹⁶ and the colloid probe technique with atomic force microscopy (AFM).¹⁷ More recently, we reported that the colloid probe technique using AFM allowed a direct surface force measurement between two isolate faces (basal planes) of expandable fluorine mica.¹⁸ It was suggested that the direct surface force measurement could be expected to be available for other swellable clay minerals with a variety of origins, crystal structures, and chemical compositions.

In this study, we applied the colloid probe technique with AFM to directly measure the face-to-face force interacting between synthetic smectites with different locations of lattice charge, that is, saponite and hectorite. Smectites, which are the most typical swellable clay minerals, possess the structure of 2:1 layered silicates in which one alumina– or magnesia–oxygen–hydroxy octahedral sheet shares oxygen atoms with two identical silica–oxygen–hydroxy tetrahedral sheets, one on each side, and exchangeable Na^+ ions are sandwiched between the silicate layers. Saponite and hectorite stand for both extremes in the location of the lattice charge: the face of saponite is negatively charged due to isomorphous sub-

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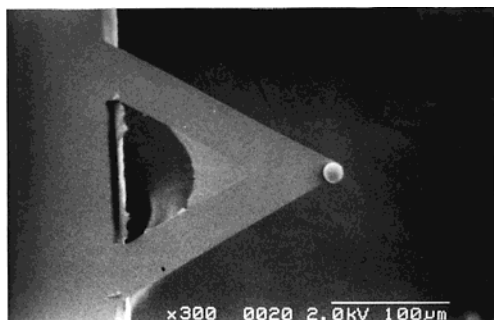


Figure 1. SEM photograph of a colloid probe with which smectite platelets are covered.

stitution of Si^{4+} by Al^{3+} ions in the tetrahedral silica sheet, while the negative charge of hectorite is due to isomorphous substitution of Mg^{2+} by Li^+ ions in the magnesia octahedral sheet.¹⁹

In general, the forces interacting between surfaces in water have been well explained by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory,^{20,21} that is, the combination of the electric double-layer (EDL) repulsion and the attractive van der Waals (VDW) force, involving some extra forces such as hydration repulsion^{22,23} and hydrophobic attraction.²⁴ It has been also accepted that interparticle forces between clay platelets behave as predicted from the above view and successfully provide a reasonable explanation for a variety of phenomena in clay suspensions.²⁵ In particular, the effects of variation in the density and location of charge on the interparticle forces between clay platelets have been extensively examined with the intention of clarifying the behavior of swelling and interlayer cation-exchange peculiar to clays; nevertheless, the relation between the location of the lattice charge and interparticle force remains unclear. In this study, our main concern is how the location of charges and the density of charge may influence the interparticle forces between clay surfaces.

Experimental Section

Colloid Probe Preparation. A poly(methyl methacrylate) (PMMA) sphere with a diameter of about $10\ \mu\text{m}$ (Sekisui Kasei, Co., Ltd., Osaka) was attached to a standard AFM cantilever (Digital Instruments, Inc., Santa Barbara, CA) with epoxy glue. The dispersion of smectites was prepared by dispersing 0.01 g of the particles in 1 L of water. A drop of the dispersion was placed on the probe to produce a smectite-topped surface on the PMMA sphere (see Figure 1), followed by drying in a laminar flow cabinet at room temperature overnight. The probe was heated at a temperature of $120\ ^\circ\text{C}$ for several minutes to firmly stick the delaminated flakes of smectites onto the surface of the PMMA sphere. The macroscopic flat surface of smectites, which was mounted on a piezoelectric tube driven toward and away from the probe, was prepared by drying a dispersion of smectites on a mica sheet covered with the epoxy glue in the same way as the preparation for the colloid probe.

Force Measurement. The force measurements were conducted using the AFM Nanoscope III (Digital Instruments, Inc.,

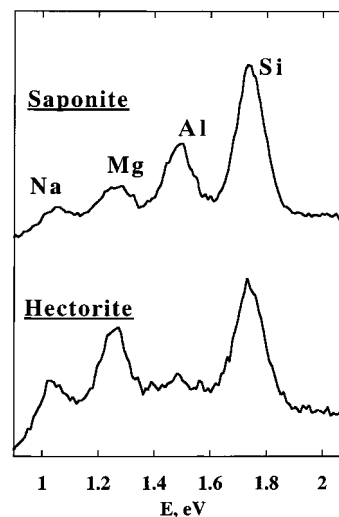
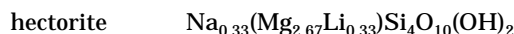
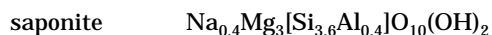


Figure 2. Chemical analysis of a smectite-topped colloid probe with electron spectroscopy.

Santa Barbara, CA). The smectite-coated surface is displaced in a controlled manner toward and away from the smectite-topped probe in aqueous solution. The interacting forces between the probe and the flat surface can be obtained from the deflection of the cantilever. The deflection of the cantilever versus the displacement of the flat surface was converted into surface force versus separation by assuming that the zero point of separation was defined as the compliance region where the probe and the flat surface are in contact and the zero force was determined at large surface separations. The force measurements were performed at a scan rate of 0.5 or 1 Hz over a scanning distance from 200 to 500 nm. The spring constants of the cantilevers were determined with tungsten balls (Fukuda Metal Foil & Powder Co., Ltd.) in accordance with the method presented by Cleveland.²⁶ The spring constants of the cantilevers used in this study were found to be $0.071 \pm 0.002\ \text{N/m}$.

Materials. We used two kinds of synthetic smectites, that is, saponite and hectorite, which were kindly supplied from Kunimine Industries Co., Ltd., and Coop Chemical Co. Ltd., respectively. The structural formulas of saponite and hectorite were shown as follows:



The pH of solutions was adjusted with HCl and NaOH. NaCl used for a supporting electrolyte was baked at $500\ ^\circ\text{C}$ for 3 h to remove organic impurities. All reagents used in this work were analytical grade. The water used in all experiments was supplied by a Milli-Q system.

Results

Characterization of Surfaces for Force Measurement. The scanning electron microscopy (SEM) image of a smectite-topped probe is shown in Figure 1. We verified the presence of smectite platelets on a PMMA sphere after force measurements by SEM observation with chemical analysis. As can be seen in Figure 2, the clear signals corresponding to the elements noted in the above structural formula can be detected from the probe surface. The AFM images of smectite cast on the epoxy resin are shown in Figure 3. It can be seen that smectite platelets were highly oriented (Figure 3a). The image of the face of smectite showed molecular arrangements of oxygen atoms with the root mean square (rms) roughness of $\sim 1\ \text{nm}$ across an area of $50\ \text{nm} \times 50\ \text{nm}$ as shown in Figure 3b. The

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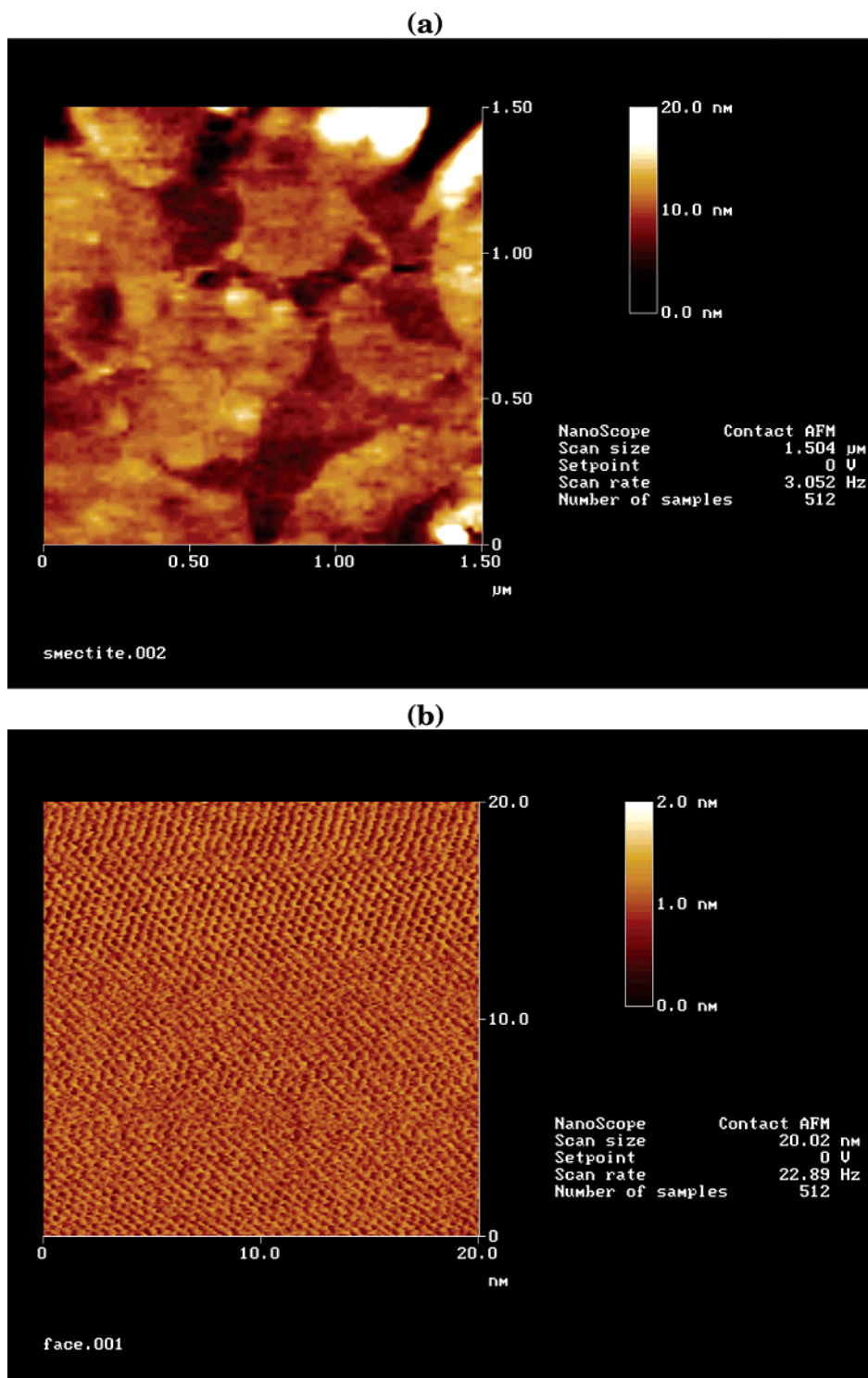


Figure 3. AFM images of a flat surface where smectites were coated on epoxy glue: (a) a top view image of the smectite-coated surface; (b) a molecular-scale top view image of the face of a smectite platelet.

molecularly smooth area of smectite is limited compared with that of muscovite mica, but the area required for a contact in AFM with the colloid probe (radius $\sim 10^{-5}$ m) should be much smaller than that in the SFA with muscovite mica (radius $\sim 10^{-2}$ m). Therefore, the places for force measurements were carefully selected by confirming the jump-in contact (primary minimum) in pure water or dilute salt solution.

The Effect of NaCl Concentrations on Force Curves. The forces measured between smectites with changing NaCl concentration at pH 5.6–5.8 are shown in Figure 4 and Figure 5. The force curves for saponite behave

in the same manner as that for hectorite totally. At large separations, the measured forces agreed well with the conventional DLVO force calculated on the basis of the DLVO theory where the constant surface potential model or the constant surface charge model²⁷ was assumed with the nonretarded VDW force. For the calculation of the nonretarded VDW force, the Hamaker constant for smectites was assumed to be 2.2×10^{-20} J for muscovite mica.¹⁶ Good agreement between the decay length of the force

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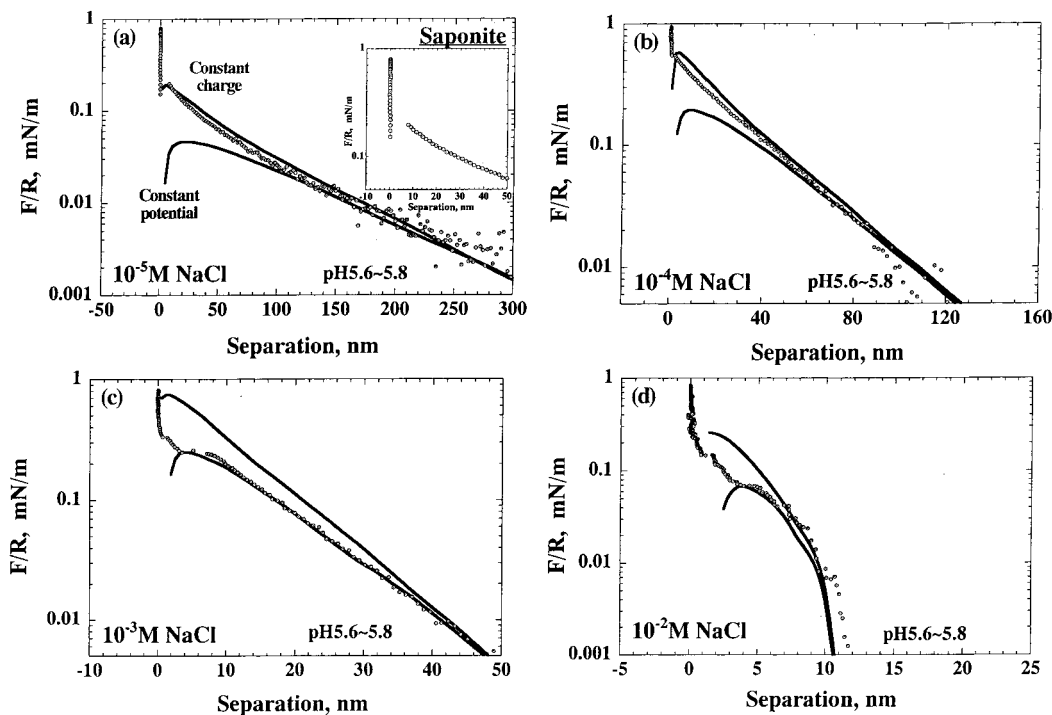


Figure 4. Force–separation curves for the interaction between saponite which were obtained with changing a background electrolyte concentration from 10^{-5} to 10^{-2} M NaCl at pH 5.6–5.8. The upper and lower lines correspond to the constant charge curve and the constant potential curve, respectively. The best fit parameters were (a) $|\Psi_s| = 45$ mV (EDL potential) and $\kappa^{-1} = 96.5$ nm; (b) $|\Psi_s| = 40$ mV and $\kappa^{-1} = 30.5$ nm; (c) $|\Psi_s| = 32$ mV and $\kappa^{-1} = 9.7$ nm; (d) $|\Psi_s| = 22$ mV and $\kappa^{-1} = 3.2$ nm.

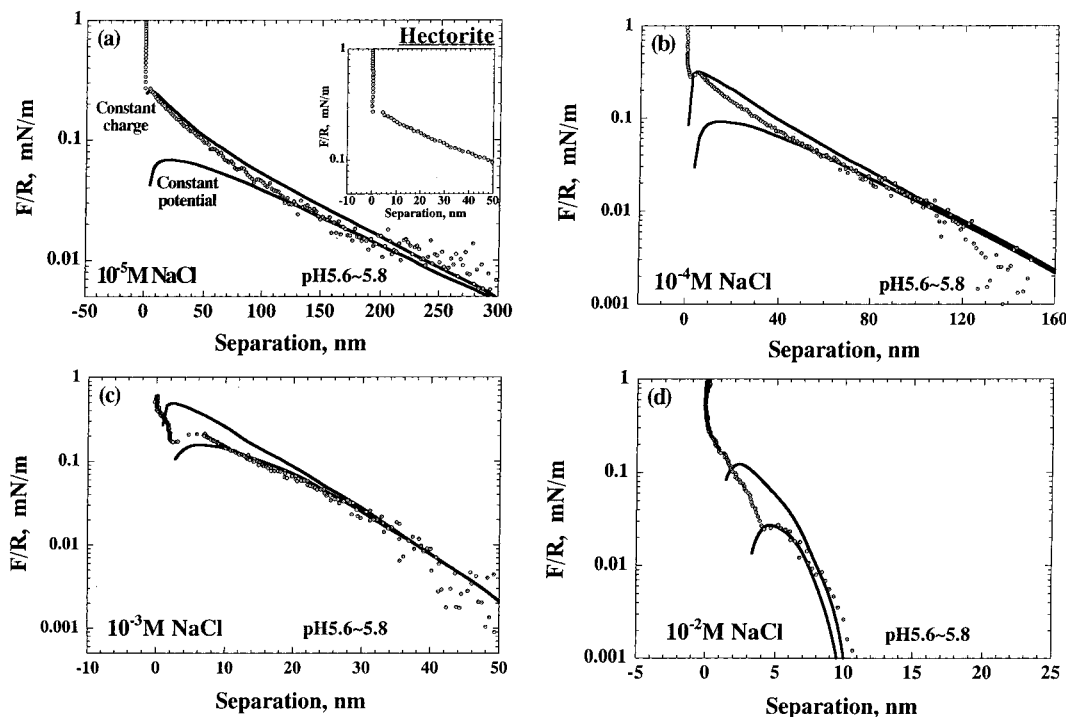


Figure 5. Force–separation curves for the interaction between hectorite which were obtained with changing a background electrolyte concentration from 10^{-5} to 10^{-2} M NaCl at pH 5.6–5.8. The best fit parameters were (a) $|\Psi_s| = 42$ mV and $\kappa^{-1} = 96.5$ nm; (b) $|\Psi_s| = 35$ mV and $\kappa^{-1} = 30.5$ nm; (c) $|\Psi_s| = 30$ mV and $\kappa^{-1} = 9.7$ nm; (d) $|\Psi_s| = 20$ mV and $\kappa^{-1} = 3.2$ nm.

curves at larger separations and the Debye length obtained from the known concentration of NaCl was also recognized. The forces measured at separations larger than 4 nm tend to fit well to the DLVO force with the constant surface potential model rather than the constant surface charge model with increasing NaCl concentration. This suggested that Na^+ ions compensate negative surface charges on

the faces of smectites more effectively when approaching the two surfaces in the higher NaCl concentration regime.

A primary minimum was clearly confirmed at concentrations of 10^{-5} M NaCl as seen in the insets of Figure 4 and Figure 5. Quirk and Pashley²⁸ suggested

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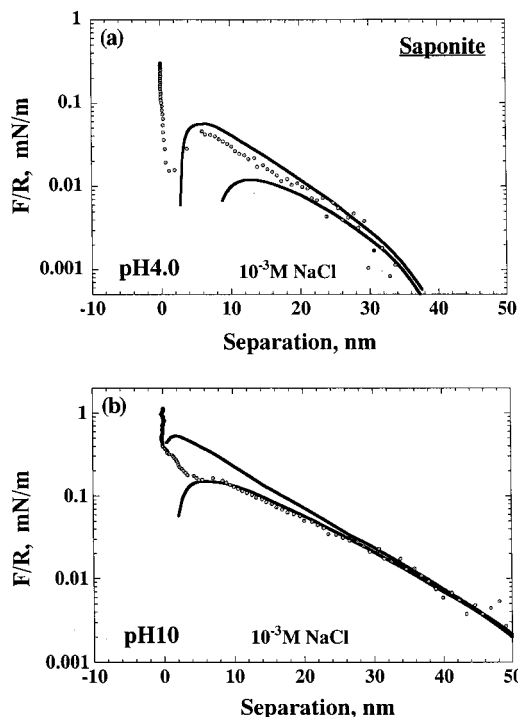


Figure 6. Force–separation curves for the interaction between saponite at a background electrolyte concentration of 10^{-3} M NaCl with changing pH from 4 to 10. The best fit parameters were as follows: (a) $|\Psi_s| = 12$ mV and $\kappa^{-1} = 9.2$ nm at pH 4; (b) $|\Psi_s| = 28$ mV and $\kappa^{-1} = 9.7$ nm at pH 10.

that “contact” in the force measuring apparatus involves the separation of surfaces by the diameter of a water molecule, that is, about 0.2 nm. The contact observed here may correspond to the one mentioned above. With increasing NaCl concentration, such a primary minimum contact disappeared and an extra short-range repulsion was observed at a concentration of 10^{-2} M NaCl at separations below ~ 3 nm. When the solution of 10^{-5} M NaCl was introduced into the measuring cell again after the measurement in the solution of 10^{-2} M NaCl, such a short-range repulsion disappeared and a primary minimum could be recognized. This indicated that the short-range repulsion for smectites was reversibly dominated by the change in the concentration of NaCl.

The pH Dependence of the Force Curve. The forces interacting between smectites were measured with changing the pH of solution from 4 to 10 at a concentration of 10^{-3} M NaCl. The forces measured at pH 4 and 10 are shown in Figure 6 and Figure 7. The forces measured at separations larger than 4 nm fit well to the forces calculated from the DLVO theory. When the pH of the solution was increased from pH 5.6 to 10, the magnitude of the short-range repulsion increased. When the pH of the solution was lowered from 10 to 4, such a short-range repulsion disappeared for hectorite and saponite. We also confirmed that the short-range repulsion for smectites appeared again in the solution with natural pH (\sim pH 5.6). Hence, the short-range repulsion showed a reversible dependence on pH as well as on the change in NaCl concentration.

The short-range repulsion for smectites behaves quite identically to the “secondary hydration force” observed for muscovite mica.^{22,23} Moreover, there is apparently no difference in the behavior of the short-range force between saponite and hectorite.

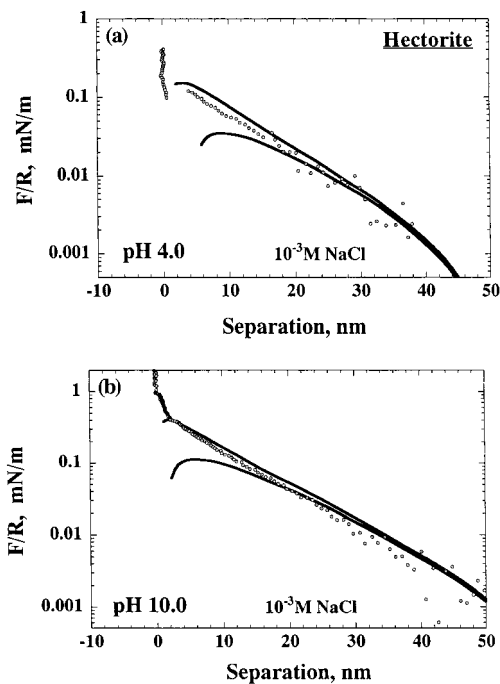


Figure 7. Force–separation curves for the interaction between saponite at a background electrolyte concentration of 10^{-3} M NaCl with changing pH from 4 to 10. The best fit parameters were as follows: (a) $|\Psi_s| = 18$ mV and $\kappa^{-1} = 9.5$ nm at pH 4; (b) $|\Psi_s| = 30$ mV and $\kappa^{-1} = 9.7$ nm at pH 10.

Discussion

The Effect of the Location of Lattice Charges for Smectites on EDL Force. In our recent study,²⁹ the zeta potential for saponite was found to be more sensitive to the change in pH of the solution than that for hectorite in lower pH regions, leading to the conclusion that such a behavior was due to the difference in the location of the lattice charges between saponite and hectorite. Most of the studies on the comparison between force measurements and electrokinetic study supported that the EDL potential obtained with the DLVO fitting was consistent with zeta potential if the asperity of the surface for force measurement could be neglected or was small in comparison with the thickness of the EDL.¹⁸ Hence, the EDL potential obtained here for smectites was compared with zeta potential measured by a flat plate streaming potential in our recent study.²⁹ In Figure 8, the EDL and zeta potentials were plotted against pH at a concentration of 10^{-3} M NaCl as a supporting electrolyte. A good agreement between the EDL and zeta potentials can be observed for both saponite and hectorites.

The outer Helmholtz plane (OHP) potential calculated using the triple-layer model of Gouy–Chapman–Stern–Graham (GCSG) for muscovite mica^{30–32} was shown as dotted lines in Figure 8. The OHP potential is defined as the potential at the plane of the closest approach of hydrated ions to the surface and then considered to correspond to the EDL potential and zeta potential. In this model, we assumed that H^+ ions behave as a specifically adsorbed ion at the inner Helmholtz plane (IHP) rather than a potential-determining ion adsorbed

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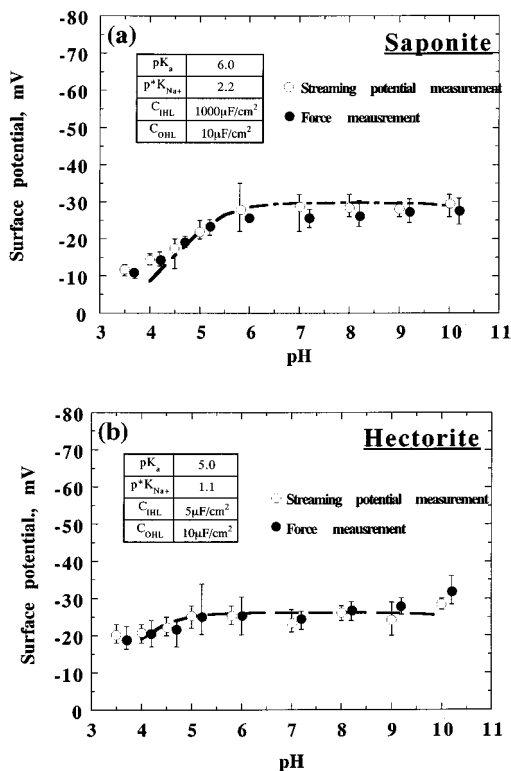


Figure 8. Comparison between EDL potential and zeta potential at pH 5.6–5.8 as a function of pH. Fitting of the OHP potential calculated using the GCSG model with dissociation-binding equilibria of surface groups was shown as dotted lines: (a) $N_s = 8 \times 10^{13} \text{ cm}^{-1}$, $pK_a = 6.0$, $p^*K_{Na^+} = 2.2$, $C_{IHL} = 1000 \mu\text{F}/\text{cm}^2$, and $C_{OHL} = 10 \mu\text{F}/\text{cm}^2$; (b) $N_s = 6 \times 10^{13} \text{ cm}^{-1}$, $pK_a = 5.0$, $p^*K_{Na^+} = 1.1$, $C_{IHL} = 5 \mu\text{F}/\text{cm}^2$, and $C_{OHL} = 10 \mu\text{F}/\text{cm}^2$.

at the siloxane network of the face. The EDL and zeta potentials for smectites were totally insensitive to the change in pH as noted in Figure 8 except for a low-pH region in the case of saponite, implying that the H^+ ion for smectites would not behave as a potential-determining ion. In fact, we confirmed that the fits of calculated OHP potential to zeta potential were significantly improved by assuming that H^+ ions play a role as a specifically adsorbed ion rather than a potential-determining ion.²⁹ This assumption is contrary to the fact that H^+ ions play a role as a potential-determining ion for most metal oxide–water interfaces. Quirk and Pashley indicated that H_3O^+ ions could occupy a position between muscovite mica surfaces even at “contact” in water and the desolvation of H_3O^+ ions to achieve the pristine contact of mica surfaces would not appear feasible.²⁸ They also suggested that because of the strong affinity of H_3O^+ ions for tetrahedral sites with the isomorphous substitution of Si^{4+} by Al^{3+} ions, H_3O^+ ions could approach more closely than any other hydrated cations.³⁴ This argument implies further support for the assumption that the H^+ ion behaves as a specifically adsorbed ion. The capacitance of the inner Helmholtz layer (IHL), that is, C_{IHL} , required for the good fit of the potentials to the diffuse-layer potentials showed a much lower value for hectorite ($\sim 5 \mu\text{F}/\text{cm}^2$) than that for saponite ($\sim 500 \mu\text{F}/\text{cm}^2$). As the IHL is considered to be the layer intervening between the plane of the lattice charges and the plane of the closest approach of dehydrated ions to the surface, that is, the inner Helmholtz plane, C_{IHL} is given as $C = \epsilon\epsilon_0/d$ where ϵ_0 is the dielectric constant in a vacuum, ϵ is the relative dielectric constant in the inner or outer layer, and d is the thickness of IHL. The lattice charges of hectorite are located in the octahedral magnesia layer at a depth of $\sim 0.5 \text{ nm}$ from the crystal surface, while

saponite possesses its own lattice charge at a depth of $\sim 0.1 \text{ nm}$ in the tetrahedral silica sheet.³³ In addition, the value of ϵ for hectorite should be lower than that of saponite since there exists a siloxane tetrahedral layer with a much lower value of ϵ (4–7) than that of the water phase (~ 80), between the plane of the lattice charges and IHP for hectorite. The difference in the value of the capacitance of the IHL reflects the location of the lattice charge for smectites. From these observations, it can be said that the EDL force for smectites, which is directly dominated by the EDL potential, is clearly dependent on the location of the lattice charge as well as the charge density which has been justified by the conventional DLVO theory.

Short-Range Repulsion. The extra short-range repulsive forces, which appear at separations around 3–4 nm, are encountered in a wide range of colloids and biological surfaces. The origins of the repulsive short-range forces are extremely system dependent although the appearance of the repulsion is very similar for any case. Recently, the occurrence of the short-range repulsion was classified into three cases:³⁵ (1) for soft and mobile amphiphilic or biological surfaces, the undulation mode of a bilayer due to its thermal flexibility becomes restricted with approaching two surfaces in the short-range separation; (2) for silica surfaces, a short-range steric effect and/or an outward shift of the EDL force from the surface removes the VDW attraction because of the presence of an amorphous “gel layer” with protruding silica “hair”; (3) for muscovite mica, the short-range repulsion referred to as secondary hydration force is observed as the sum of the standard free energy for exchanging adsorbed hydrated cations with H^+ ions prior to contact and the mixing free energy for replacing H^+ with hydrated cations in bulk solution becomes unfavorable. The origin of the short-range repulsion for smectites would be identical to that of the secondary hydration force for muscovite mica^{22,23} since there exists a strong resemblance in the behavior of short-range repulsion and the siloxane network structure on the basal plane between smectites and muscovite mica.

The short-range repulsive forces for smectites were extracted by subtracting the DLVO forces from the forces measured at a concentration of 10^{-2} M NaCl . In this case, the DLVO forces assumed the constant EDL potential model because the long-range measured forces were entirely consistent with the DLVO forces calculated using the constant potential model as shown in Figures 3 and 4. The short-range repulsive forces for smectites were shown in Figure 7 where the hydration forces reported in the previous studies on muscovite mica³⁶ and silica³⁷ are also shown as dotted lines. The short-range repulsive forces for smectites are found to be substantially smaller than that for muscovite mica for all separations even though the short-range forces for smectite would be overestimated by assuming the constant potential model. In addition, the short-range repulsive forces for saponite are larger in magnitude than that for hectorite. For comparison, the short-range repulsive force for expandable fluorine mica (ME) reported in our previous work¹⁸ was extracted in the same way as in this study and plotted also in Figure 9. The short-range repulsion for ME is as small as that for hectorite and smaller than that for saponite. The lattice charges of ME are present in the magnesia octahedral sheet like those of hectorite, but the density of the lattice

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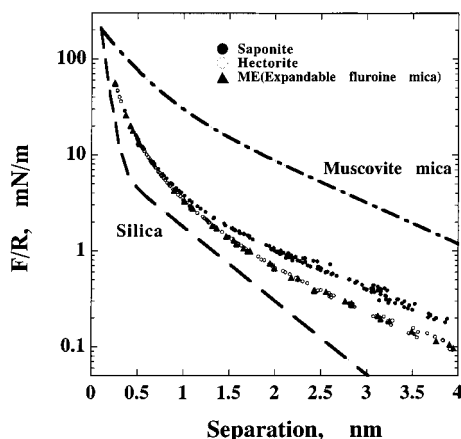


Figure 9. Short-range repulsive force obtained by subtracting the DLVO force from the measured forces for smectites at a concentration of 10^{-2} M NaCl at pH 5.6–5.8. The upper and lower dotted lines correspond to the hydration forces for muscovite mica and silica, respectively.

Table 1. Parameters of the Double-Exponential Fit for Short-Range Repulsion Derived by Subtraction of the DLVO Force from the Measured Force

	double exponential: $F(D)/R = A_1 \exp(-D/D_1) + A_2 \exp(-D/D_2)$				ref
	A_1 (mN/m)	D_1 (nm)	A_2 (mN/m)	D_2 (nm)	
muscovite mica	210	0.30	60.0	1.02	35
saponite	91	0.27	6.2	1.11	this work
hectorite	50	0.32	3.5	1.12	this work
expandable mica	49	0.34	2.5	1.30	18
silica	1167	0.57	10.5	5.63	37

charge is at least 1.5 times higher than that for saponite and hectorite. The most likely explanation for the smaller short-range repulsion for ME than for saponite and hectorite may be that the charge arising from isomorphous substitution in the octahedral sheet is distributed over a wider area of oxygens on the basal plane than that in the tetrahedral sheet and then regarded as smeared out.³⁸ However, the lattice charge of layer silicates and hydration force cannot be correlated to each other simply as described later.

Following an empirical procedure reported in the previous studies,^{36,37} the hydration forces for smectites were fitted by a double-exponential function,

$$F(D)/R = A_1 \exp(-D/D_1) + A_2 \exp(-D/D_2) \quad (1)$$

The obtained constants were listed in Table 1 where the constants for muscovite mica³⁶ and silica³⁷ were also listed. The two decay lengths, that is, D_1 and D_2 , for smectites and ME are very similar to those for muscovite mica. The decay lengths for silica are apart from those for the four-layer silicates. Though the physical picture of a double-exponential decay for hydration force seems to be unclear, a possible explanation for the two decay lengths for muscovite mica was two steps of dehydration of adsorbed hydrated cations while approaching the two surfaces.³⁶ This explanation appears quite different from the above-mentioned origin of the hydration force for silica. The similarities in the two decay lengths between smectites and muscovite provide further justification for the belief that the origin of the hydration force for smectites should be identical to that of secondary hydration for muscovite mica rather than the short-range repulsion for silica.

(38) Farmer, V. C.; Russell, J. D. *Trans. Faraday Soc.* **1971**, *67*, 2737.

To clarify the relation between hydration forces and adsorbed Na^+ ions on the face of the layered silicates, the adsorbed amount of Na^+ ions was estimated. $F(0)/2\pi R = (A_1 + A_2)/2\pi$, which corresponds to the work required to approach the two surfaces against the repulsive hydration forces, should be identical to the sum of the standard free energy ($\Delta G^\circ_{\text{ex}}$) for replacing adsorbed Na^+ by H^+ ions and the mixing free energy ($\Delta G^\circ_{\text{mix}}$) for removing H^+ and adding Na^+ ions to bulk solution²³ as shown in the SFA studies on muscovite mica (Table 2). The densities of Na^+ ions adsorbed on the face for smectites and ME ($n_{\text{Na}^+}^{\text{S}}$) can be numerically obtained by the following equations:

$$(A_1 + A_2)/2\pi = \Delta G^\circ_{\text{ex}} + \Delta G^\circ_{\text{mix}} \quad (2)$$

$$\Delta G^\circ_{\text{ex}} = -n_{\text{Na}^+}^{\text{S}} kT \ln(*K_{\text{Na}^+}) \quad (3)$$

$$\Delta G^\circ_{\text{mix}} = kT \{ (n'_{\text{H}^+} \ln X'_{\text{H}^+} + n'_{\text{Na}^+} \ln X'_{\text{Na}^+}) - (n_{\text{H}^+} \ln X_{\text{H}^+} + n_{\text{Na}^+} \ln X_{\text{Na}^+}) \} \quad (4)$$

where $*K_{\text{Na}^+}$ is a cation-exchange equilibrium constant,^{18,28} and n (n') and X (X') are the number of cations per unit volume and the molar ratio of cations in bulk solution before (after) removing H^+ and adding Na^+ ions to bulk solution, respectively. The occupied ratios of Na^+ ions adsorbed on the face of saponite and muscovite mica to the lattice charges in the tetrahedral sheet are higher than those of hectorite and ME to the lattice charges in the octahedral sheet. The density of Na^+ ions adsorbed on the face follows the order in the magnitude of hydration forces as well as in the density of lattice charge when the location of lattice charge is same. Thus, it can be said that the hydration repulsion is dominated by the density of Na^+ ions adsorbed on the face that is dependent on the difference in destiny and structural origin of the lattice charge.

Interparticle Forces and Swelling. A number of studies presented in the field of soil and clay science have been extensively making an effort to explain the swelling of smectites including montmorillonite using interparticle forces substantiated by the DLVO theory invoking the short-range repulsion. Two different interpretations for the expansion of the interlayer referred to as crystalline swelling or short-range swelling have been proposed for smectites. One explanation is that such a sort of swelling can be totally assessed by the DLVO theory.^{8–12} Another explanation is that the role of the EDL force is not significant and the additional hydration force due to the structural perturbation of the interfacial water is dominant for swelling.^{13–15} However, these arguments have remained unsettled. In the present study, we noticed some inconsistencies with the observation in the studies on interlayer distance versus swelling pressure for montmorillonite. First, the EDL potentials extracted from the measured forces for smectites by the fittings with the DLVO theory were quite consistent with zeta potential, whereas the Gouy plane potentials extracted from the relation between swelling pressure and interlayer distance for montmorillonite were much larger in magnitude than zeta potential. The zeta potential for montmorillonite showed values ranging from -40 to -70 mV,^{39–42} which are in the same order as the EDL potential presented

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(41) Gonzalez-Caballero, F. *J. Colloid Interface Sci.* **1985**, *113*, 203.

(42) Horikawa, Y.; Murray, R. S.; Quirk, J. P. *Colloids Surf., A* **1988**, *32*, 181.

Table 2. Adsorbed Amount of Na⁺ Ions Estimated from the Force Constants of the Exponential Function for Short-Range Repulsion

	$A_1 + A_2$ (mN/m)	$2\pi(\Delta G^{\text{ex}} + \Delta G^{\text{mix}})$ (mJ/m ²)	$p^*K_{\text{Na}^+}$	$n_{\text{Na}^+}^{\text{S}}$ (no. per cm ⁻²)	Ns (no. per cm ⁻²)	$n_{\text{Na}^+}^{\text{S}}/Ns$
muscovite mica	270 ^a	270 ^b	2.5 ^b	1.9×10^{14}	2.0×10^{14}	0.95
saponite	97		2.2 ^c	5.0×10^{13}	8.0×10^{13}	0.63
hectorite	54		1.1 ^c	1.7×10^{13}	6.6×10^{13}	0.26
expandable mica	52		1.5 (3.0 ^d)	1.9×10^{13}	1.2×10^{14}	0.16

^a Reference 35. ^b Reference 23. ^c Reference 29. ^d Reference 18. The value of $p^*K_{\text{Na}^+}$ for expandable mica was recalculated by assuming that the H⁺ ion was a specific adsorption ion rather than a potential-determining ion.

here. Second, the behavior of EDL forces for smectites shifts from the constant charge to the constant potential with increasing the NaCl concentration independently of the structural origin of the lattice charge for smectites (see Figures 3 and 4). All of the other force curves observed at various pHs exist in the intermediate range between the constant charge and constant potential models. These results are inconsistent with the experimental observation in the studies on swelling that the Gouy plane charge should be constant and the EDL forces behave as the constant charge model for montmorillonite. Third, there exists the short-range repulsion for smectites at separations below 3 nm but much smaller than that for muscovite mica. The short-range repulsion showed a reversible dependence on pH as well as NaCl concentration and then behaves quite identically to the secondary hydration force observed for muscovite mica. So it is concluded that the origin of the short-range force for smectites studied here is due to secondary hydration force^{22,23} but not the structural perturbation of the interfacial water.¹¹

As a key for explaining the above inconsistencies, the difference in the measuring situation between the direct force measurements and the determination of interlayer space corresponding to swelling pressure is considered. The force measurement in this study allowed the forces interacting between two isolated surfaces for smectites, whereas the dependence of interlayer distance on swelling pressure has been usually measured for a suspension or gel of montmorillonite where platelets with a thickness of 1 nm may not be regarded as a rigid surface.¹² The hindrance of other platelets against the interaction between two concerned platelets would be unavoidable. Montmorillonite is generally contaminated with organic and/or inorganic impurities of natural origin, making the properties of interparticle forces ambiguous. For that reason, synthetic smectites were used to avoid the effect of impurities in the present study. It is true that most of the studies on swelling have carefully prepared montmorillonite using dialysis with a cation-exchange process to eliminate impurities, but it appears insufficient for the evaluation of the short-range surface forces, especially for organic impurities. As a technical aspect, it seems to be somewhat difficult that the small magnitude of the short-range force is experimentally distinguished from the DLVO forces with the constant charge model with increasing the slope of EDL forces versus separation in the higher electrolyte concentration regime. The magnitude of the secondary hydration force for smectites is so small that the presence of the short-range force could be barely confirmed as an inflection point appearing at a separation of ~3 nm (see Figure 4d and Figure 5d).

Although some likely explanations for the inconsistencies between the present study and swelling measurements

could be discussed, no clear understanding is yet available and so further work should be required. Nevertheless, we believe that the present study proposed the forces interacting between two ideally isolated faces of smectites for the first time.

Conclusion

Using AFM with the colloid probe technique, we measured the face-to-face force interacting in NaCl aqueous solution between synthetic smectites with different locations of lattice charge, that is, saponite and hectorite. The experimentally measured forces have a good fit to the forces theoretically calculated according to the DLVO theory. The short-range repulsive hydration forces for smectites could be clearly observed at separations below ~3 nm and varied in magnitude with NaCl concentration and pH. According to the comparison in the pH dependence between the EDL potential and zeta potential with the analysis using the GCSG model, the IHL capacitance for the good fit of the OHP potential to the EDL potential required an much lower value for hectorite (~5 $\mu\text{F}/\text{cm}^2$) than that for saponite (~500 $\mu\text{F}/\text{cm}^2$), reflecting the difference in the location of the lattice charge between saponite and hectorite. Hence, we have suggested that the EDL force for smectites is dominated by the location of the charges as well as the density of the charges.

The hydration forces for smectites were fitted by a double-exponential function. The two decay lengths for smectites and ME are very similar to those for muscovite mica and are apart from those for silica. The similarities in the two decay lengths between smectites and muscovite supported that the source of the hydration force for smectites should be similar to that for muscovite mica rather than that for silica. According to the estimation of the density of Na⁺ ions from the work required to approach the two surfaces against the repulsive hydration forces, that is, the sum of the two force constants ($A_1 + A_2$), it was recognized that the density of Na⁺ cations adsorbed on the basal plane follows the order in the density of lattice charge as well as the magnitude of hydration forces. In addition, the densities of Na⁺ ions adsorbed on the face of saponite and muscovite mica with the lattice charges in the tetrahedral sheet are higher than those of hectorite and ME with the lattice charges in the octahedral sheet. These observations suggested that the hydration repulsion observed for smectite was dominated by the difference in density and structure of the lattice charge for smectites.

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