Swelling and delamination of inorganic homoionic montmorillonite clay in water–polar organic mixed solvents

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ARTICLE

Swelling and delamination of inorganic homoionic montmorillonite clay in water–polar organic mixed solvents

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Smectite group of clay minerals (smectites) consists of negatively charged clay layers and interlayer exchangeable cations. They are spontaneously delaminated in water to form single clay layers when the interlayer cations are small alkaline cations such as Na$^+$ or Li$^+$. This phenomenon known as osmotic swelling has fundamental importance in constructing novel clay-based nanomaterials. However, osmotic swelling of smectites has not been systematically investigated in organic solvents although this phenomenon should be useful for developing novel clay-organic nanocomposites. We report herein that montmorillonite, a typical smectite, with monovalent and divalent inorganic interlayer cations show osmotic swelling accompanied by delamination of clay layers in water–acetonitrile and water–2-propanol mixed solvents, although inorgnic interlayer cations have been believed to be inappropriate for delamination of smectites in organic solvents. The delamination is confirmed by combination of macroscopic sample appearances, XRD patterns, and SEM images. Montmorillonite with interlayer Na$^+$ or Li$^+$ ions show osmotic swelling in pure water and the mixed solvents but not in pure organic solvents. Montmorillonite with alkaline earth dications in the interlayer spaces are swollen in water–organic mixed solvents but not in both of the pure water and organic solvents. Partial delamination in several systems can be clarified by SEM images even though the sample appearances and XRD patterns do not give firm evidence. Such non-uniform swelling behavior of montmorillonite is related to disordered stacking of the aluminosilicate layers with different morphology in the clay powders as observed by SEM.

Introduction

The smectite group of clay minerals (smectites) are layered aluminosilicates, which consists of negatively charged oxide layers and interlayer exchangeable cations.[1] They are composed of most abundant and environmentally friendly elements and physicochemically stable. Thus, the clay minerals have been utilized as raw materials of various practical materials for a long time, and investigated as future advanced materials. Examples are drilling fluid, barrier materials for waste landfills, various adsorbents, clay–polymer nanocomposites, and clay–organic hybrids.[1-7]

Most fundamental property of smectites for their applications is intercalation of guest molecules into the interlayer spaces.[1, 2] The interlayer cations in natural smectites are Na$^+$ and Ca^{2+} in many cases, and they adsorb polar molecules. In particular, smectites with interlayer Na$^+$ ions are readily hydrated to incorporate a huge amount of water molecules into the interlayer spaces.[8-11] This property results in hydration of individual interlayer cations followed by infinite swelling of the clay minerals to form stable aqueous colloids of smectites. The former and the latter processes are also known as crystalline and osmotic swelling, respectively.[12] The latter has recently been recognized as delamination driven by repulsive interactions between adjacent layers in the layered crystals. In the state of osmotic swelling, the layered crystallites of the clay minerals are delaminated (or exfoliated) into single aluminosilicate layers, which have often been called nanosheets.[12, 13] This property facilitates cation exchange and adsorption of the guest species. Smectites with interlayer Ca^{2+} ions do not show osmotic swelling in water although the Ca^{2+} ions are hydrated. This behavior is explained by strong electrostatic attraction between the negatively charged clay layers and the divalent interlayer cations.

In contrast to hydration, smectites with inorganic exchangeable cations are difficult to be solvated by organic molecules. This property is not favorable for the preparation of clay–organic hybrids, and thus inorganic interlayer cations have often been exchanged for organic cations represented by organoammonium ions to change the interlayer environments into organophilic in order to prepare clay–organic hybrids.[3, 4, 11] Investigations of the affinity of smectites with inorganic

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interlayer cations to organic molecules have possibility of developing facile procedures of preparing clay–organic hybrids by skipping the exchange for organic cations. This type of hybrids obtained from smectites with inorganic interlayer cations also has possibility of exhibiting unusual functions based on interactions between the inorganic cations and organic guest molecules.

In fact, several groups have sporadically reported swelling of smectites with inorganic interlayer cations in organic or water–organic mixed solvents, as concisely summarized in a recent paper of Breu et al.[14] Olejnik et al. examined osmotic swelling of various inorganic homoionic montmorillonite (Mont) in several organic solvents.[15] They found that Mont with Na^+ ions (Na^+-Mont) is swollen in formamide (FA) and *N*-methylformamide (NMF), and Cs^+-Mont is swollen in FA. Onikata et al. reported osmotic swelling of Li^+-, Na^+-, Mg^{2+}-, Ca^{2+}-, Ba^{2+}-Mont in water–propylene carbonate (PC) mixed solvents in the presence of NaCl.[16] They proposed coordination of PC molecules as the outer shell to the water molecules hydrated to the interlayer Na^+ ions as the inner shell. Most recently, Breu et al. reported osmotic swelling of synthetic fluorohectorite with Na^+ ions in mixed solvents of water and acetonitrile (ACN) or dimethylsulfoxide (DMSO).[14, 17, 18] These studies also report dependencies of swelling behavior on solvent composition; several tens of volume percent of organic solvents are favorable for osmotic swelling.

From these previous studies, we can expect that Na^+ homoionic smectites can be osmotically swollen and delaminated in various mixed solvents of water and organic compounds such as FA, NMF, PC, ACN, and DMSO. Possibility of swelling is also suggested for smectites with other inorganic cations. However, effects of inorganic exchangeable cations and solvent composition on the swelling and delamination of smectites have yet been investigated. Such data are most fundamental knowledge for preparing clay–organic hybrids without interlayer hydrophobization and handling delaminated clay layers in organic solvents toward construction of novel clay-based nanostructured materials.

Therefore, we report herein colloid dispersibility of various inorganic homoionic smectites in mixed solvents of water and ACN or 2-propanol (IPA) with different water/organic ratio. We employ Mont as a typical smectite and compared monovalent (alkaline) and divalent (alkaline earth) ions as the interlayer cations in order to systematically understand conditions for swelling and delamination of inorganic homoionic smectites in water–polar organic mixed solvents. Li^+- and Na^+-Mont, which are infinitely swollen in water, are found to undergo osmotic swelling in both of water and water–polar organic mixed solvents. Mont with divalent cations is also found to be swollen in the mixed solvents although they are not swollen in pure water or organic solvents. Delamination of the Mont layers caused by the osmotic swelling is confirmed by low-voltage SEM observations.

Methods

Sample preparation

Inorganic salts and organic solvents were purchased from FUJIFILM Wako Pure Chemical Co. and used as received. Organic solvents were guaranteed grade reagents whose wate contents were less than 0.1 mass%. Milli-Q water was used in all of the experiments. Inorganic homoionic Mont samples were prepared from natural purified Mont (Kunipia F, Tsukinuno mine, Yamagata Prefecture, Japan; ideal formula $Na_{0.33}Al_{1.67}Mg_{0.33}Si_4O_{12}H_2$, cation exchange capacity 1.2 meq g^{-1}) provided by Kunimine Industries Co. Ltd., being the same as the JCSS–3101 reference clay sample delivered by the Clay Science Society of Japan.[19] Mont was stirred in an NaCl solution, washed with water for several times and finally with acetone, dried under ambient conditions, and ground to obtain Na^+-Mont powders.

Na^+-Mont was then stirred in an aqueous solution of alkaline or alkaline earth chloride salt for a day. LiCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ were used as the chloride salt. The obtained samples were washed with water for several times and finally with acetone, dried under ambient conditions, and ground to obtain powdery Mont with monovalent or divalent interlayer cations other than Na^+. Powder XRD patterns of these inorganic homoionic Mont are shown in Figures S1 and S2 (ESI). They show typical XRD patterns of "air-dried" inorganic homoionic Mont with the basal spacings of 1.1–1.5 nm depending on the interlayer cations. These basal spacings correspond to one to three water layers in the interlayer regions.[20] TG-DTA curves of Na^+-, K^+- and Ca^+-Mont indicate typical shapes of inorganic homoionic Mont, as shown in Figure S3 (ESI). The water content in Na^+-, K^+- and Ca^+-Mont is estimated from the TG mass losses lower than 400°C[21] as 9.7, 5.5, and 12%, respectively.

Then, dispersion behavior of inorganic homoionic Mont was examined. Water–ACN and water–IPA mixed solvents were tested. The water/organic volume ratio was set to 100/0 (pure water), 75/25, 50/50, 25/75, and 0/100 (pure organic). Mont powders (0.3 g) were added to a solvent (9 mL) in a glass vial, and stirred for 24 h to obtain a suspension sample. After stopping the stirring, the clay powders were stable in dispersed state or gradually settled down, depending on the sample. For the latter case, it took several weeks to reach sedimentation equilibrium. Thus, dispersed state of the Mont powders in the suspension was judged by naked eyes with photographs of the sample vial after standing the suspension for 6 weeks.

Characterization

XRD patterns of Mont suspended in the solvents were recorded on a Rigaku Ultima IV diffractometer (monochromatic CuKα radiation) after sealing a suspension sample in a glass capillary (Hilgenberg, Mark-tube, 2.0 mm diameter, 0.01 mm wall thickness). TG-DTA curves were obtained by using a Rigaku TG-DTA 8122 apparatus with heating rate of 10°C/min under a nitrogen atmosphere. Low-voltage SEM observations were performed with a Zeiss GeminiSEM 560 microscope. A small amount of a suspension sample was cast on a piece of silicon wafer and dried under ambient conditions, and then subjected to the SEM observations without coating.

Results

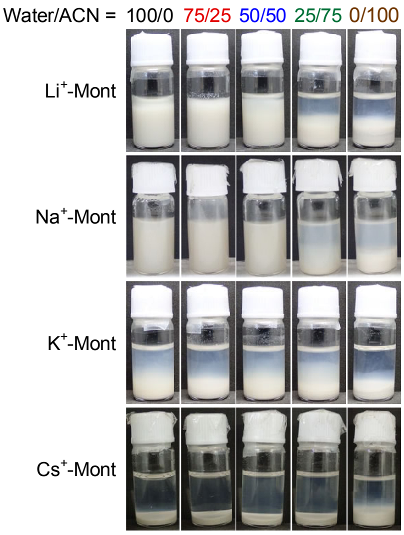

Figure 1. Photographs of Li$^+$-, Na$^+$-, K$^+$-, and Cs$^+$-Mont suspended in pure water, water–ACN mixed solvents with different water/ACN ratio, and pure ACN.

Dispersibility in water–ACN mixed solvents

We evaluate the dispersibility of inorganic homoionic Mont in water–polar organic mixed solvents by macroscopic appearance of the sample after reaching the sedimentation equilibrium. Figure 1 shows the photographs of Li$^+$-, Na$^+$-, K$^+$-, and Cs$^+$-Mont in water–ACN mixed solvents. Among the samples, Li$^+$- and Na$^+$-Mont are well dispersed in pure water and water–ACN mixed solvents up to the composition of water/ACN = 50/50. Osmotic swelling in water accompanied by delamination of the aluminosilicate crystallites into single clay sheets has been well known for Li$^+$- and Na$^+$-smectites. The sample appearances indicate the osmotic swelling of Li$^+$- and Na$^+$-Mont in pure water as well as in the water-dominant mixed solvents. In contrast, the clay powders are not entirely dispersed in the ACN-dominant mixed solvent (water/ACN = 25/75) and pure ACN, suggesting the absence of osmotic swelling. However, turbidity of the upper supernatant phase of these samples suggests a part of the clay particles are well dispersed in the ACN-dominant solvents.

We characterize the structure of the clay particles in the solvents by the XRD measurements of the clay suspensions. Figure 2 shows the XRD patterns of Li$^+$- and Na$^+$-Mont in in water–ACN mixed solvents. Na$^+$-Mont in water and water-dominant mixed solvents (water/ACN = 75/25 and 50/50) does not indicate any peaks (Figure 2B). This result is in harmony with the macroscopic sample appearance, and thus evidences osmotic swelling. In contrast, the sample in ACN dominant mixed solvent (water/ACN = 25/75) shows very broad peaks at 2θ = 2–3° and around 4°, the latter which is probably the second order of the peak at 2–3°, suggesting a small degree of the stacking of clay layers. This means that Na$^+$-Mont is in the swollen state but clay layers are stacked in part. Moreover, the sample in pure ACN exhibits a peak at d = 2.0 nm (2θ = 4.5°). This value corresponds to the basal spacing of Na$^+$-Mont incorporating three layers of molecules like water and small organics.[20] In other words, Na$^+$-Mont in pure ACN is not swollen in the solvent liquid phase but molecularly incorporating a small amount of solvent molecules. The XRD patterns of Li$^+$-Mont are almost the same as those of Na$^+$-Mont, in accordance with the similar sample appearances between the Na$^+$- and Li$^+$-Mont series. An exception is the Li$^+$-Mont in pure water indicating a peak at d = 1.9 nm (2θ = 4.7°); some of the clay particles would not be completely delaminated. From these results, we conclude that Li$^+$- and Na$^+$-Mont, known to be delaminated in water through osmotic swelling, retain their swelling properties in water–ACN mixed solvents.

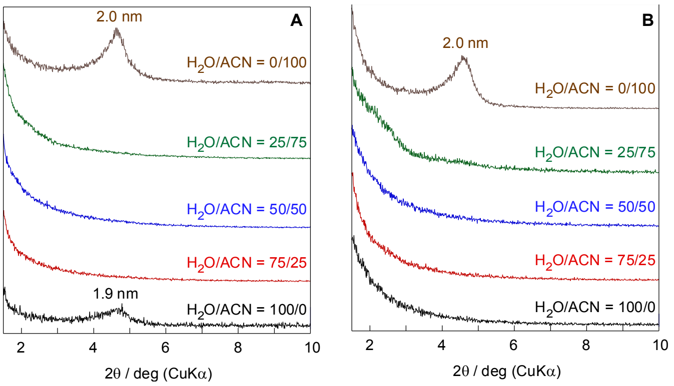

Figure 2. XRD patterns of (A) Li$^+$- and (B) Na$^+$-Mont suspended in pure water, water–ACN mixed solvents with different water/ACN ratio, and pure ACN.

In contrast, K$^+$- and Cs$^+$-Mont are not well dispersed in the water–ACN solvent system. As shown in the photographs of Figure 1, they are settled down in all of the solvents: from water/ACN = 100/0 to 0/100. For K$^+$-Mont, partial osmotic swelling and delamination are expected because of the turbidity of supernatant liquid phase. For Cs$^+$-Mont, the transparent supernatants suggest the absence of swelling and delamination of clay crystallites. Their XRD patterns shown in Figure 3 are almost consistent with such sample appearances. Most of the suspension samples of K$^+$- and Cs$^+$-Mont exhibit a diffraction peak at d = 1.5 nm corresponding to the basal spacing of the stacked clay layers incorporating two molecular layers of solvents; the peak at d = 1.2 nm seen for Cs$^+$-Mont in water/ACN = 100/0 and 75/25 indicates incorporation of one molecular

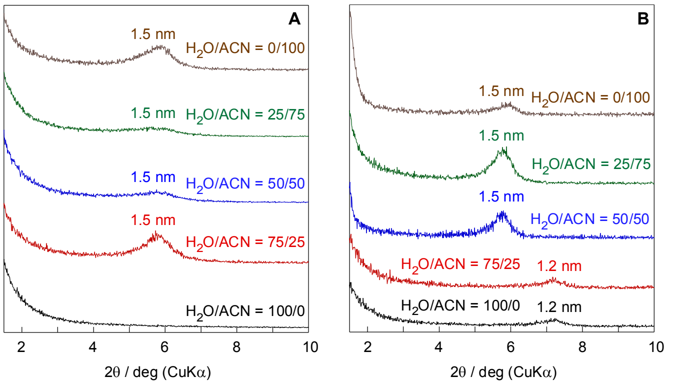

Figure 3. XRD patterns of (A) K$^+$- and (B) Cs$^+$-Mont suspended in pure water, water–ACN mixed solvents with different water/ACN ratio, and pure ACN.

layer of solvation.[20] These results are rationalized by lower solvation power of K^+ and Cs^+ than Li^+ and Na^+ for water and polar organic molecules.

Dispersibility of Mont with divalent interlayer cations, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, are similar to each other, but different from that with monovalent cations. Figure 4 shows photographs of the suspension samples at the sedimentation equilibrium. All of the Mont powders are almost settled down in pure water and ACN, but they are well dispersed in the water–ACN mixed solvents, especially in water-dominant ones (water/ACN = 75:25 and 50/50). In particular Mg^{2+}- and Ca^{2+}-Mont are entirely dispersed in the mixed solvents of these compositions, suggesting osmotic swelling with delamination, while finite swelling is suggested in the ACN-dominant solvent (water/ACN = 27/75). Sr^{2+}- and Ba^{2+}-Mont also show essentially the same behavior.

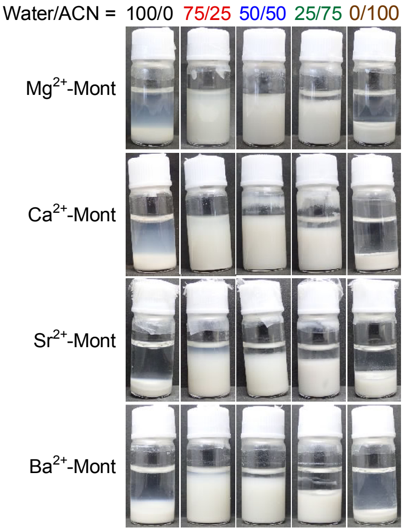

Figure 4. Photographs of Mg^{2+}-, Ca^{2+}-, Sr^{2+}-, and Ba^{2+}-Mont suspended in pure water, water–ACN mixed solvents with different water/ACN ratio, and pure ACN.

Figure 5 shows the XRD patterns of the suspension samples of Mont with four divalent cations. The XRD patterns depend on the solvent composition, and almost independent of the cation species. Mont in pure water and ACN show a peak at d = 1.9 nm, corresponding to the basal spacing of the stacked clay layers with three layers of solvent molecules. These patterns agree with the sample appearances where the clay powders are present as sediments. On the other hand, the suspension samples in the mixed solvents of water/ACN = 75/25 and 50/50 indicate the patterns without peaks or with a very weak and broad peak, indicating osmotic swelling of clay into delaminated clay layers. The samples of water/ACN = 25:75 show a peak at d = 2.9 nm (2θ = 3°) accompanied by the second-order peak. The d-value larger than those expected for solvation by solvent molecules at the inner shell; hence, it indicates finite swelling of the interlayer spaces of Mont without delamination by intercalating certain amounts of solvent molecules. These results demonstrate that Mont with divalent inorganic cations are specifically swollen in water–ACN mixed solvents although they are not swollen in pure water or ACN. In particular, osmotic swelling accompanied by delamination of the clay layers is realized in the water-dominant mixed solvents.

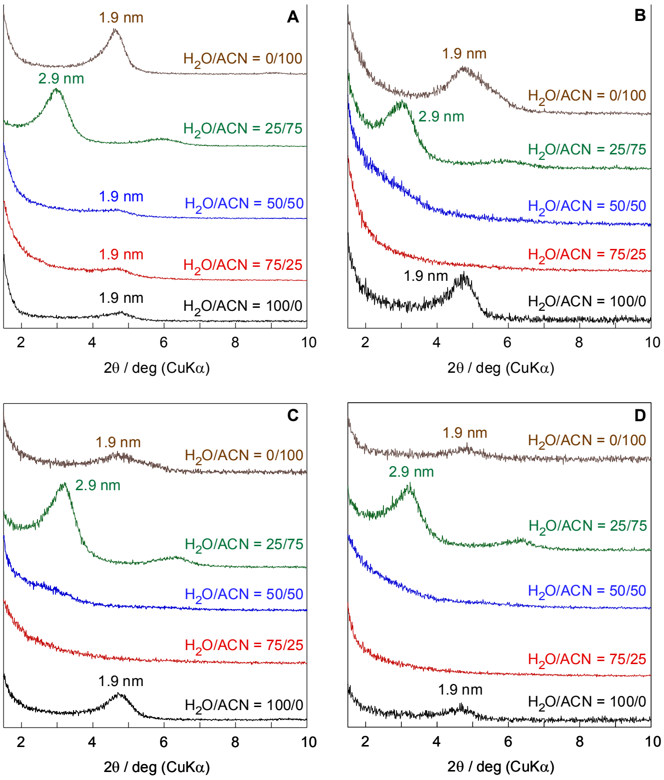

Figure 5. XRD patterns of (A) Mg^{2+}-, (B) Ca^{2+}-, (C) Sr^{2+}-, and (D) Ba^{2+}-Mont suspended in pure water, water–ACN mixed solvents with different water/ACN ratio, and pure ACN.

Dispersibility in water–IPA mixed solvents

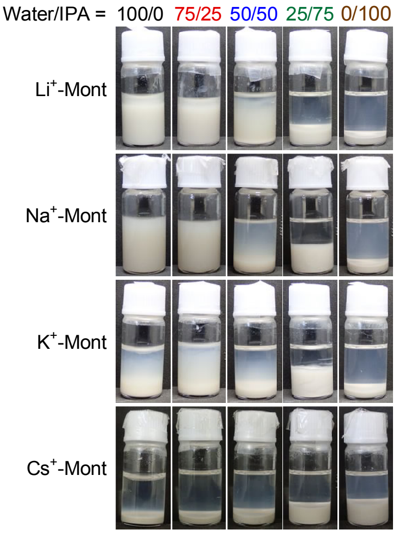

Figure 6. Photographs of Li^+-, Na^+-, K^+-, and Cs^+-Mont suspended in pure water, water–IPA mixed solvents with different water/IPA ratio, and pure IPA.

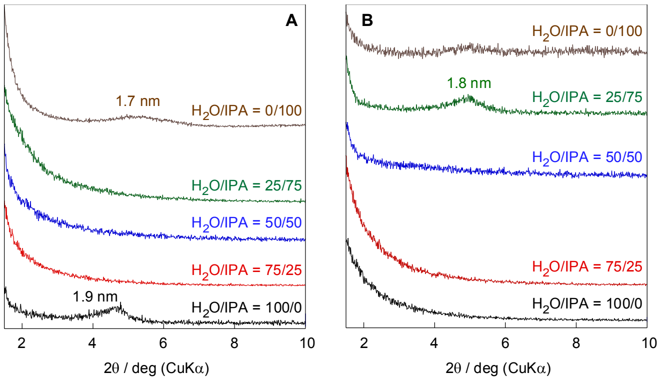

Figure 7. XRD patterns of (A) Li^+- and (B) Na^+-Mont suspended in pure water, water–IPA mixed solvents with different water/IPA ratio, and pure IPA.

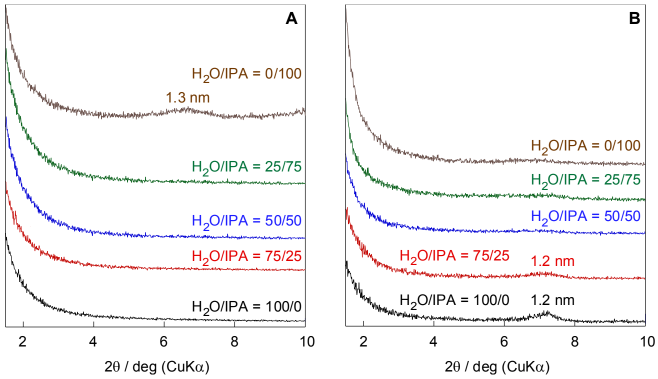

Figure 8. XRD patterns of (A) K^+- and (B) Cs^+-Mont suspended in pure water, water–IPA mixed solvents with different water/IPA ratio, and pure IPA.

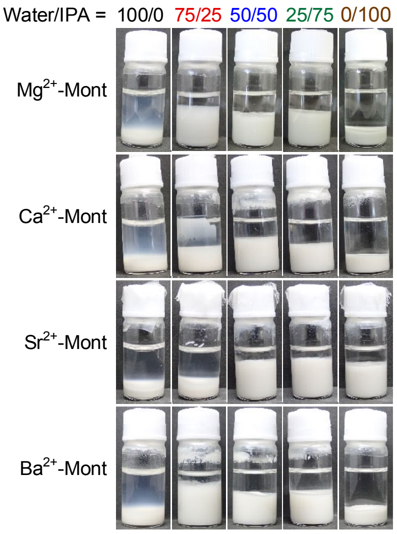

Figure 9. Photographs of Mg^{2+}-, Ca^{2+}-, Sr^{2+}-, and Ba^{2+}-Mont suspended in pure water, water–IPA mixed solvents with different water/IPA ratio, and pure IPA.

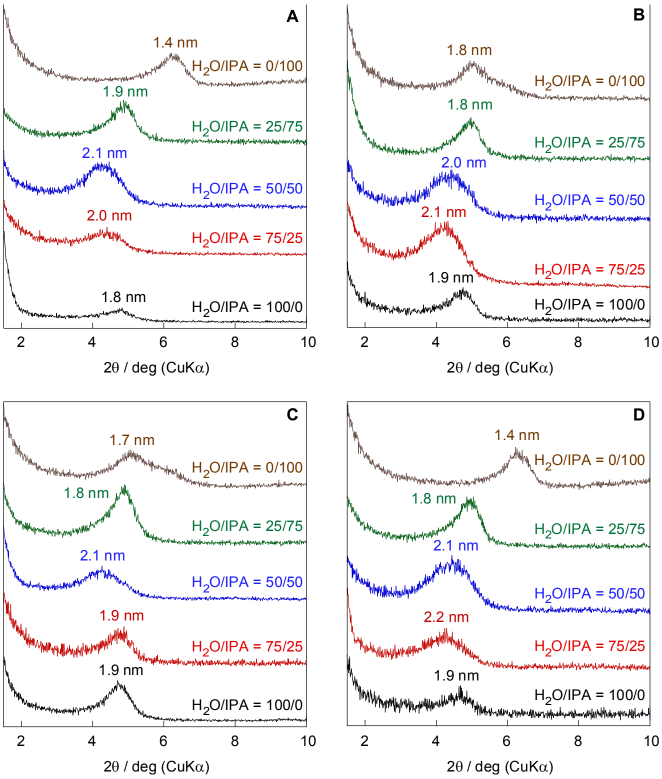

Figure 10. XRD patterns of (A) Mg^{2+}-, (B) Ca^{2+}-, (C) Sr^{2+}-, and (D) Ba^{2+}-Mont suspended in pure water, water–IPA mixed solvents with different water/IPA ratio, and pure IPA.

Dispersion of inorganic homoionic Mont in water–IPA mixed solvents shows a trend similar to that of the water–ACN system. Figure 6 shows the photographs of Li^+-, Na^+-, K^+-, and Cs^+-Mont in water–IPA mixed solvents. Li^+- and Na^+-Mont are well dispersed in the mixed solvent of water/IPA = 75/25. The volume fraction of the solvent occupied by the dispersed clay particles decreases with the increase in the fraction of IPA in the mixed solvent, and the clay powders are settled down in pure IPA. The XRD patterns of Li^+- and Na^+-Mont in the mixed solvents of water/IPA = 75/25 and 50/50 (and 25/75 for Li^+-Mont) do not give any peaks of stacked clay layers, as shown in Figure 7, being in harmony with the sample appearances. These results suggest osmotic swelling of Li^+- and Na^+-Mont in water–IPA mixed solvents.

In contrast, K^+- and Cs^+-Mont are mostly settled in the water–IPA mixed solvents as seen in the photographs of the samples (Figure 6c and d). Their behavior is similar to that in the water–ACN system. However, their XRD patterns of the suspension samples, shown in Figure 8, do not give rigid evidence for stacking of clay layers. Diffraction peaks indicating basal spacing of the stacked clay layers are absent for K^+-Mont or very weak for Cs^+-Mont in the mixed solvents. The sample appearances are in harmony with the XRD results. Dispersed particles coexist with the settled ones in the K^+-Mont samples, and finite swelling is recognized from the volume occupancy of settled particles in Cs^+-Mont. Hence, partial delamination can be suggested in these samples.

The tendency of particle dispersion of Mont with divalent inorganic interlayer cations in water–IPA mixed solvents is also

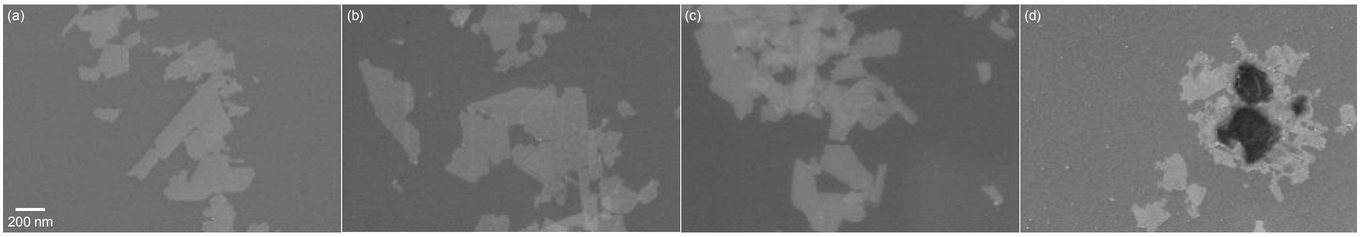

Figure 11. SEM images of Na$^+$-Mont recovered from (a) pure water, (b) water–ACN mixed solvent (water/ACN = 75/25), (c) water–ACN mixed solvent (water/ACN = 25/75), and (d) pure ACN.

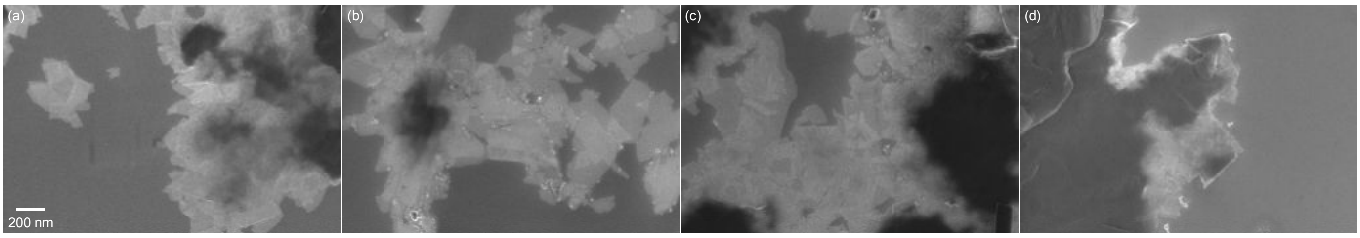

Figure 12. SEM images of Ca^{2+}-Mont recovered from (a) pure water, (b) water–ACN mixed solvent (water/ACN = 75/25), (c) water–ACN mixed solvent (water/ACN = 25/75), and (d) pure ACN.

similar to that in water–ACN mixed solvents. Figure 9 shows photographs of the suspensions of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}-Mont. In all of the divalent-cation samples, clay powders are almost settled down in pure water and IPA, but dispersed in their mixed solvents to some extent. This dependency of the solvent composition is basically the same as that found in water-ACN mixed solvents, although entire dispersion suggesting osmotic swelling of the clay powders in the solvents is not observed. The XRD patterns of the suspension samples, shown in Figure 10, agree with the sample appearances. All of the samples show diffraction peaks ascribable to the basal spacings of the stacked clay layers. The XRD patterns depend on the solvent composition, and almost independent of the cation species. The basal spacings in the mixed solvents are at around 2.1 nm for most of the samples in the mixed solvents, and the value is larger than that in pure water or IPA. The basal spacings suggest the amounts of solvent molecules incorporated into the interlayer spaces in the mixed solvents are somewhat larger than those in the pure solvents. Because the increment of the basal spacing is only several sub-nanometers, we do not assign the increased basal spacings to the swelling of Mont. From these results, we conclude that Mont with divalent inorganic cations are not osmotically swollen with delamination but somewhat dispersed in the water–IPA mixed solvents through incorporating the solvent molecules into the interlayer spaces.

SEM observations

We observed Na$^+$- and Ca^{2+}-Mont powders recovered from the suspension samples with a low-voltage high-resolution SEM, as representatives of the monovalent and divalent homoionic Mont which show swelling in the water–organic mixed solvents. We found that SEM images of the dried samples reflect the swollen states of the clay mineral in the solvents. Figure 11 shows the SEM images of Na$^+$-Mont samples of the water–ACN system. The sample recovered from pure water, where Na$^+$-Mont is delaminated, exhibits many thin rectangular plates with uniform contrast (Figure 11a). The lateral size of the plates is 50–500 nm, agreeing with the reported size of a single sheet of the employed clay mineral.[19] Hence, the delaminated clay layers are successfully detected by SEM, which supports the conclusion obtained by the sample appearance and XRD.

Similar thin plates are also observed for Na$^+$-Mont recovered from water–ACN mixed solvents (Figures 11b and c), demonstrating delamination of Na$^+$-Mont into single clay layers in these mixed solvents. However, the sample recovered from pure ACN shows both of thin plates and stacked particles (Figure 11d). The stacking is not regular like a “card stock” but disordered as a “discard pile”. The disordered structure is due to the different shape and size of each clay layer in the stacks. This is rationalized by the sample history; the raw clay was purified by sedimentation in water and then exchanged for Na$^+$ ions in an aqueous solution. With such a disordered structure, periphery of a pile consists of smaller number of sheets and more easily delaminated than the center of the pile. We therefore conclude that Na$^+$-Mont particles are partly delaminated even in pure ACN. Such real conditions of Mont are not exactly given by the sample appearances and XRD patterns because they only show average structure of the clay mineral.

Partial delamination is similarly observed for Ca^{2+}-Mont in the water–ACN mixed solvents. The SEM images shown in Figure 12 demonstrate partial delamination for all of the samples recovered from pure water and the mixed solvents as evidenced by the coexistence of thin plates and discard piles. On the other hand, the SEM image of Ca^{2+}-Mont recovered from pure ACN only shows stacked particles (Figure 12d), indicating the absence of delamination. These images indicate that Ca^{2+}-

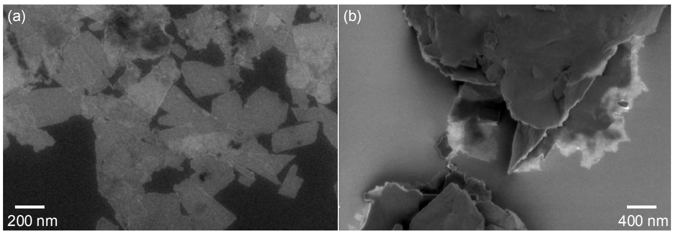

Figure 13. SEM images of Na$^+$-Mont recovered from (a) water–IPA mixed solvent (water/IPA = 75/25) and (b) pure IPA.

Mont is swollen and delaminated to some extent in the water–ACN mixed solvents. The SEM results are in harmony with the sample appearances and XRD patterns, as in the case of Na$^+$-Mont of the water–ACN system.

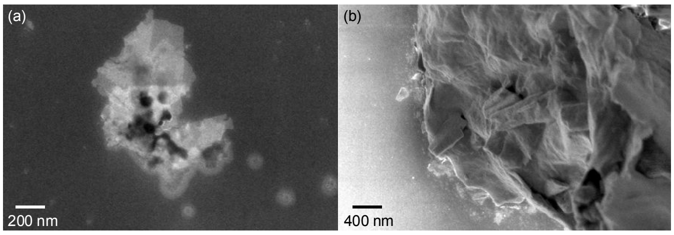

Figure 14. SEM images of Ca^{2+}-Mont recovered from (a) water–IPA mixed solvent (water/IPA = 75/25) and (b) pure IPA.

Delaminated Na$^+$- and Ca^{2+}-Mont plates are also found in the SEM images of the samples recovered from a water–IPA mixed solvent, as shown in Figures 13 and 14. The images indicate the coexistence of thin plates and discard piles. On the other hand, the images of both Na$^+$- and Ca^{2+}-Mont recovered from pure IPA only indicate aggregated particles, suggesting the non-swellable nature of these Mont in IPA. The SEM images together with the sample appearances and XRD patterns indicate that Na$^+$- and Ca^{2+}-Mont can be swollen in water–IPA mixed solvents to some extent but IPA more obstructs the delamination than ACN.

Discussion

The present study demonstrates osmotic swelling of inorganic homoionic Mont accompanied by delamination into single aluminosilicate layers in water–polar organic mixed solvents for many interlayer monovalent and divalent cations even if the swelling occurs partly in some cases. The swelling and delamination can be assessed by combining the sample appearance, XRD, and SEM observations. Typical osmotic swelling, such as Na$^+$-Mont in water causes dispersion of the delaminated clay layers entirely in the solvent to give no XRD peaks ($2\theta > 1.5°$ with CuKα radiation) and uniform thin plates in SEM images.

However, partially swollen samples can give apparent discrepancy in the results of the above three observations. SEM observations clarify that the Mont powders purified from natural clay soil are disordered stacks consisting of piled aluminosilicate plates. Hence, we can reasonably assume that all of the Mont powders do not show exactly the same swelling behavior in solvents; there should be a broad distribution in their swollen state. Because the XRD analysis only indicates an average structure of the sample, it can mislead the local structure of rather disordered clay particles and their dispersion states. The non-uniform morphology (size and shape) of the clay layers observed by SEM as well as charge density heterogeneity in the clay crystallites are responsible for the non-uniform swelling behavior.

The swelling mechanism in the water–organic mixed solvents can be rationalized by considering the inner and outer solvation shells of the interlayer inorganic cations as proposed by Onikata et al.[16] This is schematically illustrated in Figure 15. Note that this schematic model focuses only on the solvation of the cations but ignores their location in the interlayer space. Because of the strong hydration tendency of alkaline and alkaline earth metal cations, we can assume the formation of inner shell of water molecules around these cations in the water–polar organic mixed solvents. Then, the organic molecules would be coordinated to the cations as the outer solvation shell through the inner hydration shell.

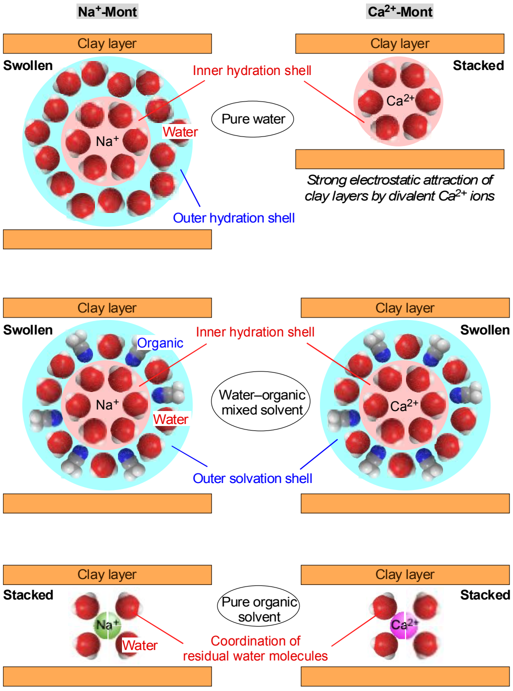

Figure 15. Schematic representations of Na$^+$- and Ca^{2+}-Mont suspended in pure water, water–polar organic mixed solvents, and pure organic solvents.

For Li$^+$- and Na$^+$-Mont, the aluminosilicate layers are osmotically swollen in pure water because the hydration energy of the interlayer cations overwhelms the electrostatic attraction between the monovalent interlayer cations and negatively charged clay layers; both of the inner and outer solvation shells are occupied by water molecules. In the mixed solvents, water molecules in the outer solvation shell are supposed to be partly displaced by the organic molecules, and the swollen structure is retained. However, in pure organic solvents, the interlayer cations are coordinated by a limited amount of water molecules, which are still present in the system because we did not thoroughly dehydrate the clay powders and organic solvents, and the interlayer cations are exposed to many organic solvent molecules. Because the organic solvents stabilize the interlayer cations to a lesser degree than water, the electrostatic attraction between the interlayer cations and clay layers is more preferrable than swelling by the solvent at this stage. For K$^+$- and Cs$^+$-Mont, the interlayer cations are not strongly hydrated as Li$^+$ and Na$^+$, and thus would not be swollen in both of water and water–organic mixed solvents.

For Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}-Mont, the lack of osmotic swelling in pure water is rationalized by the strong electrostatic attraction between the divalent cations and the anionic clay layers. The electrostatic stabilization would inhibit the formation of outer hydration shells around the interlayer cations. In contrast, phenomenology of the present study suggests solvation at the outer shell is allowed in the examined water–organic mixed solvents. Contributions of smaller dielectric constants of the system or asymmetric distribution of the solvent molecules[22] to overcome the electrostatic attraction; however, more concrete quantitative and/or theoretical considerations will be necessary in the future. Partial delamination found by SEM observations is in harmony with the assumption of the competition between the formation of the outer solvation shell and the electrostatic attraction. Finally, the non-swollen state in pure organic solvents is explained like as Li^+- and Na^+-Mont.

Contribution of the water molecules present in the initial Mont powders kept under ambient conditions is estimated to be small, and the dispersion behavior is not explained by the hydrated water molecules. XRD patterns of the homoionic Mont powders indicate the presence of water forming one to three interlayer water layers by hydration to the interlayer cations (Figures S1 and S2). The amount of water molecules in such crystalline swelling had been examined for a long time, and is summarized in a recent book chapter as up to 0.6 g-H_2O / 1 g-clay.[23] The water content of our clay powders is estimated as 0.06–0.12 g-H_2O / 1 g-clay (6-12 mass%) by TG-DTA (see Experimental), being in the range of this literature value. If we adopt the value of 0.12 g-H_2O / 1 g-clay, the amount of water given by the clay powders in each suspension (0.3 g clay in 9 mL solvent) is calculated to be 0.36 mL, being 0.4 vol% of the solvent volume. In addition, Mont with divalent interlayer cations are swollen only in the mixed solvents. Moreover, the basal spacings of the powder Mont samples are not retained in the solvents even for the non-swollen samples. Hence, the observed dispersion behavior is not ascribed to the hydrated water molecules present in the clay powders but induced by the introduced organic solvents.

Conclusions

Our results clarify that osmotic swelling of inorganic homoionic smectites together with delamination of clay crystallites to single clay layers is a general phenomenon in water–polar organic mixed solvents, although we have usually exchanged the interlayer inorganic cations for organic ones for delaminating the clay mineral in organic solvents. Li^+- and Na^+-Mont are known to cause osmotic swelling in pure water, and this property is retained in the mixed solvents. In contrast, Mont with divalent interlayer cations are non-swellable in pure water but swollen in the mixed solvents. This property is common to divalent alkaline earth interlayer cations, which will be applied to develop new ways of preparing novel materials composed of clay minerals and organic substances. SEM images of the clay powders recovered from the solvents indicate non-uniform piled-up structures of clay layers related to the non-uniform swelling. The SEM observations directly indicate the disordered layered structure of clay minerals, which has been recognized as an essential structural character of clay minerals, indicating a limitation of understanding clay minerals and clay–organic nanocomposites based on an average structure analyzed by XRD.

Author Contributions

Teruyuki Nakato: conceptualization, supervison, discussion, writing, editing. Munehiro Kubota: conceptualization, preliminary experiments, discussion, editing. Yuuki Otsuka, Yuta Yane: sample preparation, data collection. Kosei Orio: sample preparation. Emiko Mouri: discussion, editing. Yusuke Yamauchi: discussion, editing. Hirokatsu Miyata: SEM observations, TG analysis, discussion, editing.

Conflicts of interest

There are no conflicts to declare.

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