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Staging of Organic and Inorganic Gallery Cations in Layered Silicate Heterostructures

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Heterostructured fluorohectorite clays with regularly alternating interlayers of inorganic and organic exchange cations have been prepared through ion exchange reaction of the sodium clay in aqueous suspension with half an equivalent of alkylammonium ions. In order to elucidate this staging-like behavior of the intercalates, the exchange process was examined for a series of onium ion surfactants of the type $[C_nH_{(2n+1)}N(C_mH_{(2m+1)})_3]^+$. One set of onium ions varied the alkyl chain length ($n = 4$–22), while maintaining a constant onium head group size ($m = 4$). A second set varied the head group size ($m = 1$–5), while the chain length remained fixed ($n = 16$). Two fundamental factors, namely, alkyl chain length and head group size determined staging behavior. The surfactant alkyl chain length determined the extent of Na^+ replacement by onium ions. Relatively little Na^+ exchange ($\sim 10\%$) occurred for the short chain onium ions with $n = 4$, $m = 4$ and $n = 6$, $m = 4$. The replacement of Na^+ by onium ions became more favorable as the alkyl chain length was increased to $n = 8$ or 10. For very hydrophobic surfactants with $n \geq 12$, onium ion uptake was essentially quantitative, affording 1:1 mixed Na^+–onium ion intercalates. The "footprint" or area covered by the onium ion head group on the interlayer surface controlled heterostructure formation for the 1:1 intercalates. For $m \geq 3$ the head group footprint matched the clay surface charge density and precluded the mixing of organic and inorganic exchange cations within the same gallery. The segregation of the hydrophobic organic cations and the hydrophilic inorganic cations on the internal and external surfaces of two-nanolayer tactoids during the ion exchange process was proposed as the pathway for staging behavior in the heterostructured intercalates. The smaller footprints of trimethyl and triethyl onium ion head groups ($m = 1, 2$) allowed for comingling of the exchange ions on single-nanolayer tactoids and the formation of phase – segregated organic and sodium ion clays upon stacking of the tactoids. © 1998 Academic Press

INTRODUCTION

The diverse intercalation chemistry of smectite clays (e.g., montmorillonite) has led to several important materials applications. For instance, the incorporation of large polycations between the negatively charged 2:1 aluminosilicate layers gives rise to microporous pillared structures that are useful in catalytic applications (1). Other interesting applications taking advantage of this rich intercalation chemistry include polymer nanocomposites (2) and chemical sensors (3). Organoclays are formed when the hydrated exchangeable clay cations are replaced by long chain alkylammonium ions. The specific properties of an organoclay depend on the particular intercalated surfactant, as well as on the nature of the layered material itself. Important applications of these organoclays stem from their hydrophobic properties (4). Organoclays are used industrially as rheological control agents in paints, greases, and oil-well drilling fluids (5) and as adsorbents for removing organic pollutants from aqueous solutions (6).

Surprisingly few investigations have been reported on mixed organic–inorganic ion exchanged forms of smectite clays. Mixed ion clays have the potential of combining the hydrophilic properties of the native inorganic clay with the hydrophobic qualities of an organo clay. A fundamental understanding of the structure and polar nature of mixed ion clays may lead to materials applications. For example, the ability to mediate the surface polarity of naturally occurring clays by partial ion exchange with onium ion surfactants might be advantageous in trapping pollutant plumes in subterranean environments.

As shown in Fig. 1, several products may form when the inorganic cations of a smectite clay are partially replaced by organic cations. Phase segregation can occur, yielding starting material and newly formed organo clay (Fig. 1a). As indicated in Figs. 1b and 1c, mixing of the two ions at exchange sites can lead to the formation of a single homostructured phase or to two types of heterostructured phases. The mixed ion homostructure (Fig. 1b) has all the interlayers occupied by both the metal ions and the onium ions, whereas the heterostructures (Fig. 1c) have two types of segregated galleries, one inorganic and one organic cation interlayer. The two galleries of the heterostructure may be stacked either in a disordered, interstratified manner or in a regularly alternating fashion. The regular stacking

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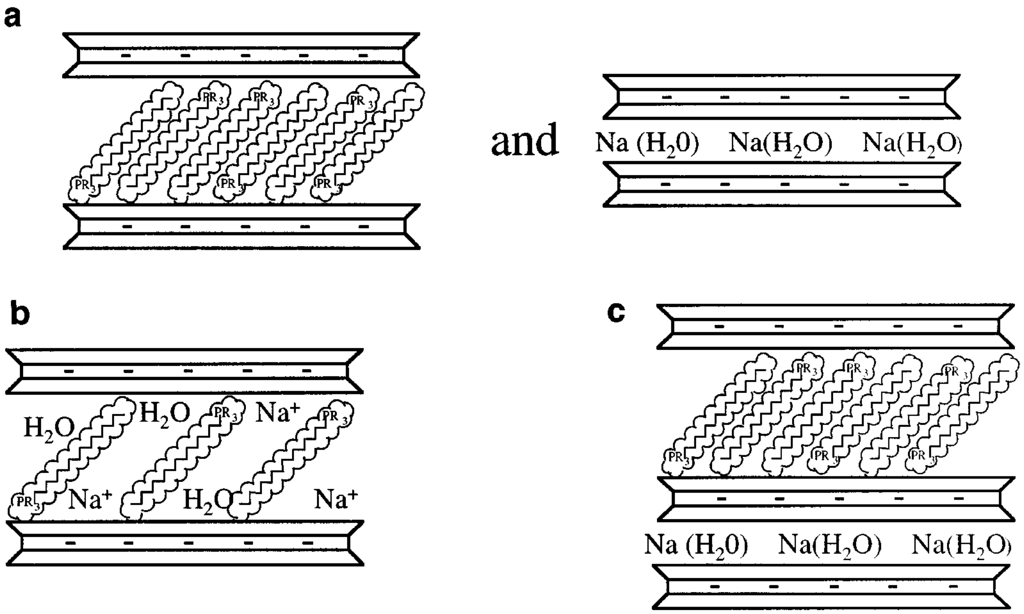

FIG. 1. Three possible structures formed when the exchange sites of smectite clays are occupied with two different cationic species, namely, alkylammonium ions and hydrated sodium ions. (a) denotes the two phase-segregated homoionic parent end member materials. (b) is the mixed ion homostructure with both species intercalated within one gallery, while (c) is the mixed ion heterostructure with the two cations segregated into two interlayers. The stacking pattern of the organic and inorganic galleries may be regular or random.

of the distinguishable organic and inorganic galleries is reminiscent of staging behavior in graphite (7).

In general, homo- and heterostructured mixed ion intercalates of smectite clays are relatively uncommon. Méring and Glaeser (8) first proposed the segregation of Na^+ and Ca^{2+} ions in the galleries of montmorillonite, but there was no evidence for regular heterostructure formation. A homostructured phase containing inorganic cations and a minor fraction of short chain alkylammonium cations has been reported for partially exchanged montmorillonites (9, 10). However, a disordered heterostructure formed when comparable amounts of organic and inorganic cations occupied the exchange sites. A mixed ion homostructure also was observed when the organic cation was hexadecyltrimethylammonium (11). Rectorite is an example of a clay mineral with staged galleries (12). However, only one of the interlayers is readily accessible for ion exchange. Also, the clay-related potassium niobate $K_4Nb_6O_{17} \cdot nH_2O$ has distinguishable interlayer regions, with both galleries showing intercalation chemistry (13). Staging-like behavior has also been achieved for a swelling fluoromica through an irreversible process that fixes small interlayer cations like lithium in vacant octahedral positions in the silicate layers (14). Mixed inorganic–organic onium ion heterostructures have been recently reported for a swelling fluoromica (15), but the exchange process used to form these compositions also gave mixtures of regularly and randomly interstratified heterostructures as coproducts.

We recently reported three complementary pathways for the formation of regularly alternating mixed inorganic–onium ion fluorohectorite heterostructures (16). We also demonstrated different intercalation properties for the staged interlayer regions and were able to synthesize a derivative that compared favorably to the rare mineral rectorite. In the present work, we have investigated the intercalation process that leads to the formation of fluorohectorite heterostructures. In particular, we have elucidated the role of the onium ion geometry in the synthesis of regularly ordered heterostructures.

EXPERIMENTAL METHODS

Clay Preparation

A synthetic, high charge density lithium–fluorohectorite, $Li_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$, (Corning, Inc.), was converted to the sodium form by exchange with 0.1 M NaCl. Homoionic alkylammonium ion derivatives were obtained from Li^+–FH by ion exchange reactions with the bromine salts of the desired onium ions. A two-fold excess of surfactant cations was utilized to ensure complete exchange. All organoclays were washed with a 50/50 (v/v) water/ethanol mixture until no change in the X-ray diffraction pattern was observed for the air-dried materials.

Surfactant Synthesis

Two series of quaternary ammonium bromide surfactants with varying chain lengths and head group sizes were synthesized from the corresponding 1-alkylbromides and trialkylamines, (Aldrich) (17, 18). For the $C_{16}H_{33}N(C_mH_{(2m+1)})_3Br$ series, the ionic head group size m was varied from 1 to 5, while the surfactant alkyl chain length was kept constant at 16 carbon units. The $C_nH_{(2n+1)}NBu_3Br$ surfactant series changed the alkyl chain length n in two-carbon unit intervals from 4 to 22 while keeping the tri-*n*-butyl head group fixed. In all preparations a slight excess of trialkylamine was used. The reactants were dissolved in ethanol and refluxed for 3 days before the ethanol was removed by rotary evaporation. The products were recovered in either solidified or oil form, depending on the surfactant chain length. The solids were recrystalized twice from ethylacetate/pentane, whereas the oils were washed several times with pentane.

Heterostructure Preparation

All heterostructured clays were prepared in a simple one-step procedure by the direct addition of a half an exchange equivalent of surfactant cations to a Na^+ clay suspension. In a typical preparation 0.30 g sodium–fluorohectorite clay was exfoliated in about 100 mL of deionized water prior to surfactant addition. The suspension was stirred after surfactant addition for at least 48 h at ambient temperature or at 80°C, in the case of the sparingly water soluble tri-*n*-pentyl terminated surfactant. All the heterostructures were washed free of excess salt and air dried.

Product Characterization

X-ray diffraction, XRD, patterns were recorded on a Rigaku rotaflex diffractometer equipped with Ni-filtered Cu$K\alpha$ radiation. All of the clay samples were analyzed as preferentially ordered films. A Cahn 121 TG thermogravimetric analyzer was used to determine the surfactant content of the clay samples. The samples were heated at 5°C per minute up to 800°C.

RESULTS AND DISCUSSION

Previously, we developed three different synthetic strategies (16) to produce staged 1 : 1 Na^+ : onium ion fluorohectorite heterostructures. Figure 2 illustrates these three pathways for the case where the onium ion is $C_{16}H_{33}PBu_3^+$. The mixed ion heterostructures presented in this paper contain alkylammonium ions instead of alkylphosphonium ions. Pathway I, which represents the pathway used in the present work, embodies the direct addition of a quantity of surfactant cations to obtain a reaction mixture in which the overall ratio of onium to sodium ions was 0.5 : 1.0. Pathway II is the reverse approach, wherein a homoionic organoclay is treated with a concentrated NaCl solution to produce the heterostructured products. This procedure proved to be more susceptible to the creation of heterostructures with layer stacking defects, as judged by the broadening of the 00*l* XRD reflections. Pathway III in Fig. 2 involves the reaction of equal molar quantities of the two end member homoionic clays in a water suspension. Pathway III is more cumbersome than pathway I because it involves the preparation of two homoionic clays. However, it does lead to the formation of the same heterostructured products as the route I pathway. For these reasons pathway I was preferred over the other two pathways represented in Fig. 2.

Onium Ion Chain Length Effect

Our clay heterostructures are defined as intercalates that contain equal amounts of onium and sodium ions staged into regularly alternating galleries. The unit-cell dimensions along the layer stacking direction is expected to correspond to the sum of the basal spacings for the Na^+–FH and the organoclay end members. The effect of ammonium chain length on heterostructure formation was studied first. The alkyl chain length of a $[C_nH_{(2n+1)}NBu_3]^+$ surfactant was increased in two-carbon atom units ($n = 4$–20) while keeping the tri-*n*-butyl head group fixed. The XRD profiles for the 1 : 1 Na^+ alkylammonium reaction products are shown in Fig. 3. The basal spacings for both the homoionic organoclay end members and the 1 : 1 Na^+-ammonium reaction products are given in Table 1. The short chain onium ions with $n = 4$ and 6 formed little or no heterostructured product, in part, because the sodium competed more favorably for exchange sites of the clay than the onium ions. Consequently, the XRD patterns of the products contain primarily the 12.4 and 6.2 Å reflections characteristic of Na^+–FH. For $n = 8$ and 10, the onium ions begin to displace increasingly more sodium from the exchange sites and some heterostructured product, along with unexchanged Na^+–FH is identified in the XRD pattern. At $n \geq 12$, the replacement of sodium by onium ions is quantitative and well developed 1 : 1 staged heterostructures are formed. For chain lengths in the range $n = 8$–22, the observed difference in basal spacings between the organoclay and heterostructured products remain fairly constant and very near the expected 12.4 Å spacing of Na^+–FH.

The above interpretation of the XRD results is supported by thermogravimetric analysis (TGA) of the reaction products (see Fig. 4). The calculated and observed TGA weight loss for the products obtained from the $[C_nH_{(2n+1)}NBu_3]^+$ surfactant series is summarized in Table 2 for the products obtained when Na^+–FH is exposed to half an exchange equivalent of surfactant cations. The decomposition of the C_{22} surfactant occurs in stages (not shown). On the basis of

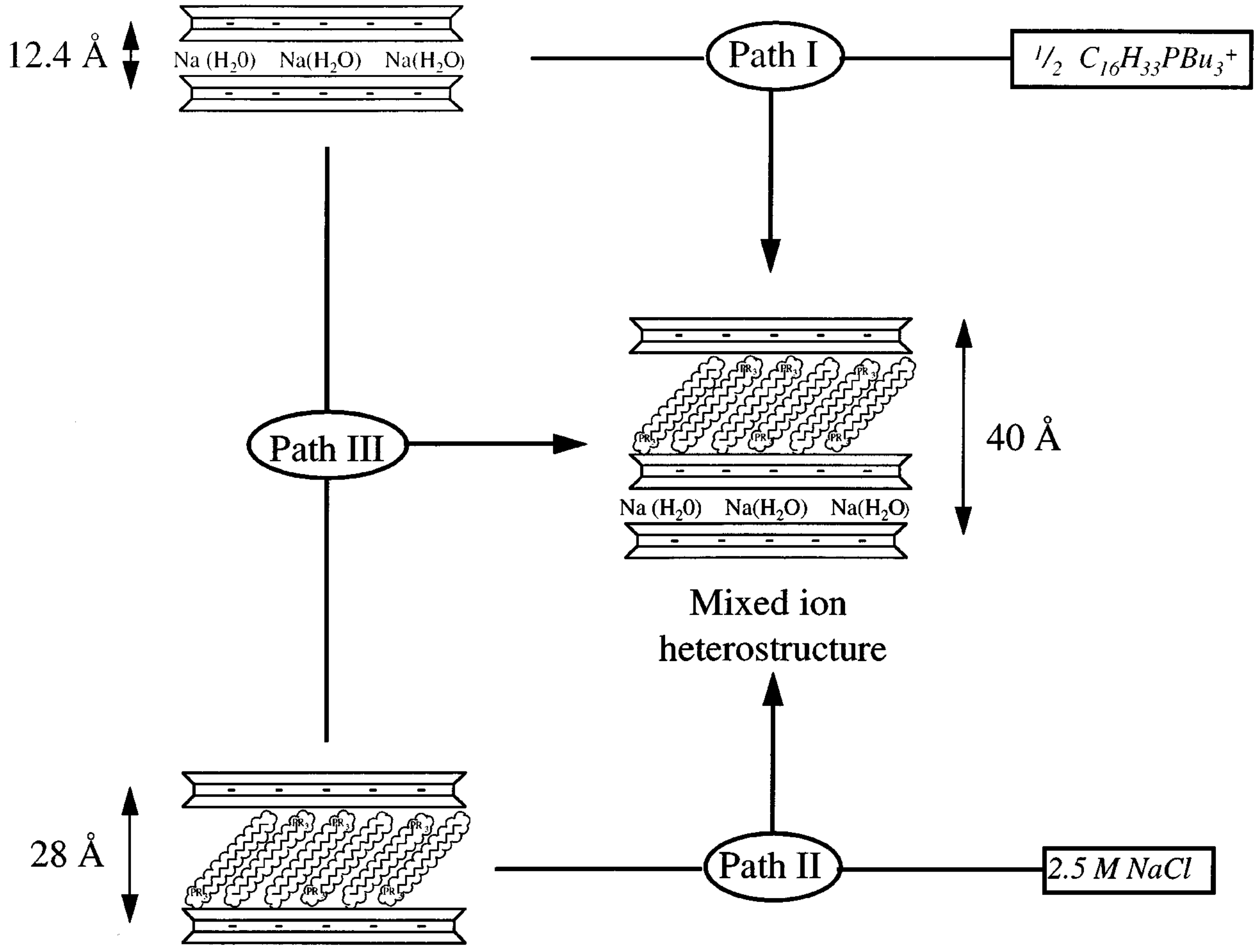

FIG. 2. Three synthetic approaches to mixed ion heterostructures with regularly alternating galleries. Pathway I involves the addition of half a cation exchange equivalent of surfactant. Route II concerns the treatment of an organo clay with a strong NaCl solution while method III simply recombines the two homoionic end member clays.

the observed weight loss in the region 125–550°C, about 20% of the supplied onium ions are exchanged into the clay galleries when $n = 4$ and 6. However, quantitative uptake of the surfactant cations and staged heterostructure formation occurs when C_{12} or longer chain surfactants are used in the exchange process. The onium ions with C_8 and C_{10} chain lengths define a transitional region corresponding to 12–36% onium exchange. In this transitional field there is an onset on heterostructure formation as evidenced by the development of heterostructured related diffraction peaks (see Fig. 3).

On the basis of the results, the extent to which staged heterostructures are formed depends on the onium content. We refer to the relationship between staged heterostructure formation and onium ion stoichiometry as the *surfactant chain effect*. The C_4 and C_6 onium ions are too hydrophilic to quantitatively displace sodium from exchange sites. No heterostructured intercalate can be formed under these equilibrium conditions because there is little or no onium binding. The onium ion simply does not compete effectively with sodium in the exchange process. Most of the aqueous onium ions are thus lost upon washing and drying of the products. Increasing the chain length to C_8 leads to some heterostructure formation but the onium ion exchanged product is still in equilibrium with a substantial amount of Na^+–FH. The shoulder on the Na^+–FH peak near 13 Å corresponds to a mixed ion homostructured material that has both cationic species mixed within the same interlayers. This same type of product also is evident in the C_6 exchange system.

The surfactant chain effect starts to dominate at C_{10} and is fully operative for the C_{12} onium ion as a result of the longer surfactant alkyl chains. A mixed ion homostructure is absent in the C_{10} case, even though the equilibrium has shifted further in favor of mixed cation intercalates due to the increased onium content. Increasing the onium ion

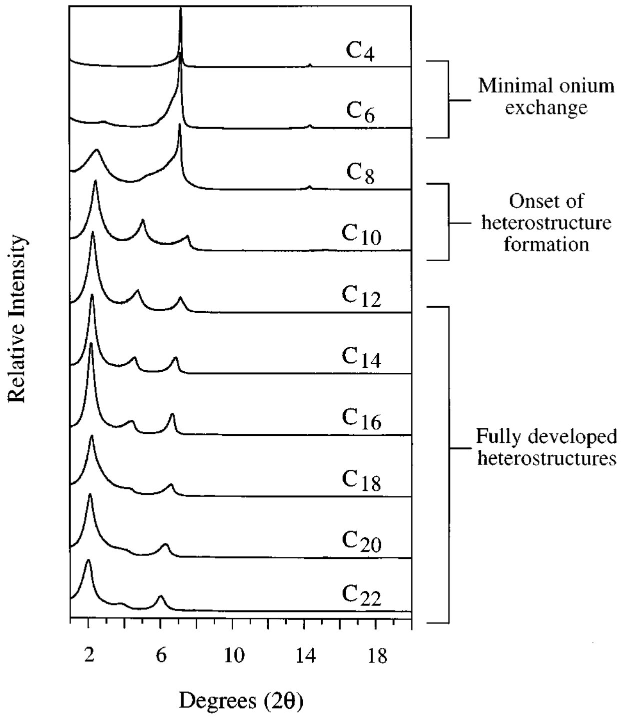

FIG. 3. XRD patterns (Cu$K\alpha$) of intercalates formed by reaction of a Na^+–FH suspension and 0.5 equivalents of $[C_nH_{(2n+1)}NBu_3]^+$ onium ions. The surfactant alkyl chain length was varied in two-carbon units over the range $n = 4$–22 while the tri-n-butyl head group was kept constant.

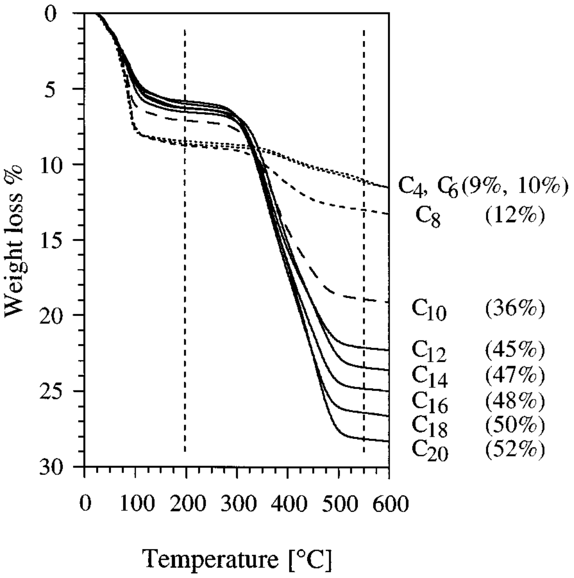

FIG. 4. TGA curves for the mixed intercalates depicted in Fig. 3 with $n = 4$–20. Three separate areas corresponding to surfactant content are indicated. The weight loss below 200°C corresponds to the release of gallery water. Decomposition of the organic onium is indicated by the weight loss in the region 200°–550°C.

chain length beyond C_{10} results in a practically quantitative surfactant uptake, as evidenced by TGA. However, these C_{12} and longer onium ions differ somewhat in the fidelity of alternating onium and sodium ion intercalation, as judged by variations in the widths of the 00l reflections. The highest ordered air-dried heterostructure products with the smallest peak widths are obtained for the C_{14} and C_{16} surfactant chain lengths.

When the surfactant is added to the aqueous clay suspension, all exchange sites are available for reaction. XRD studies of the reaction products as a function of time indicate that some fully exchanged organoclay, as well as the

TABLE 1
Comparison of X-Ray Basal Spacings for Q^+- and Mixed Ion Na^+, Q^+-Fluorohectorites,[a] Where Q^+ is $C_nH_{(2n+1)}NBu_3^+$

Carbon chain length, n	Q^+-FH [Å]	Na^+, Q^+-FHHS [Å]	Difference [Å]
22	29.7	43.7	14.0
20	28.6	41.7	13.1
18	28.4	40.4	12.0
16	26.9	39.4	12.5
14	25.9	38.2	12.3
12	25.1	37.8	12.7
10	23.0	35.3	12.3
8	22.1	34.0	11.9
6	15.8	—	—
4	15.7	—	—

[a] All products were prepared by ion exchange reaction of Na^+–FH with $C_nH_{(2n+1)}NBu_3^+$, abbreviated Q^+.

TABLE 2
TGA Determination of the Exchange Ion Compositions for 1:1 Na^+, Q^+-Fluorohectorites,[a] Where Q^+ is $C_nH_{(2n+1)}NBu_3^+$

Carbon chain length, n	Expected organic weight loss[b], wt.%	Observed organic weight loss[c], wt.%	Q^+ : Na^+ ratio in the mixed ion product
20	22.0	22.9	52:48
18	20.9	21.0	50:50
16	19.9	19.3	48:52
14	18.8	17.8	47:53
12	17.6	16.0	45:55
10	16.5	12.0	36:64
8	15.3	3.7	12:88
6	14.0	2.5	9:91
4	12.8	2.5	10:90

[a] All products were formed by the ion exchange reaction of Na^+-fluorohectorite with 0.5 equivalents of $C_{16}H_{33}NBu_3^+$, abbreviated Q^+.

[b] Expected weight lost for a water-free (dehydrated) mixed ion clay containing 1:1 Na:Q^+.

[c] Observed weight loss due to loss of Q^+.

mixed ion heterostructure, is initially formed at the initial stages of surfactant addition. This homoionic organoclay phase reacts further with the Na^+–FH component on aging of the reaction slurry. Thus, the actual exchange pathway involves a combination of pathways I and III of Fig. 2. Surfactants with longer tails, as in the case for $n > 18$, slow down this onium ion reshuffling process between homoionic end member structures, because of increased van der Waals interactions between surfactant tails and a decreased onium ion water solubility. Hence, longer equilibration times are needed for the surfactants with longest chain lengths.

Plots of the observed *d*-spacing as a function of the alkyl chain length for both the homoionic $[C_nH_{(2n+1)}NBu_3]^+$ organoclays (circles) and the staged 1 : 1 $[C_nH_{(2n+1)}NBu_3]^+/Na^+$ heterostructures (squares) are shown in Fig. 5. The dashed line in the figure is the spacing expected for a mixed ion homostructure in which the onium and sodium ions cooccupy every gallery. The surfactant alkyl chain in such a homostructure was assumed to have a 90° angle with respect to the clay layer surface. The basal spacing was calculated by the relationship $15.7\ Å + n \cdot 1.265\ Å$, where 15.7 Å is the thickness of the clay layer (9.6 Å) plus the van der Waals thickness of a NBu_3 head group (6.1 Å), and where *n* is the number of carbon units in the alkyl chain (19). The slopes of the lines defined by the observed spacings for both the homoionic organo clays and the mixed ion heterostructures are in good agreement with each other. The surfactant alkyl chains in both structures each have inclined angles of 33° and 36°, respectively, with respect to the layer surface.

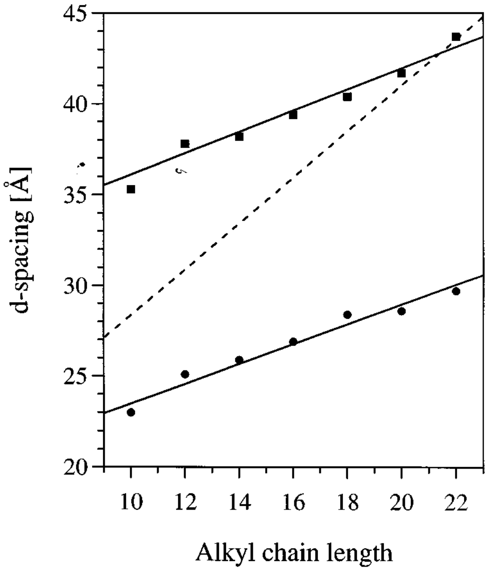

FIG. 5. Dependence of XRD basal spacings on the alkyl chain length *n* for homoionic $C_nH_{(2n+1)}NBu_3^+$–fluorohectorites (circles) and mixed ion Na^+, $C_nH_{(2n+1)}NBu_3^+$–heterostructures (squares). The dashed line corresponds to the calculated basal spacings for mixed ion homostructures in which the two cationic species cooccupy the interlayer galleries.

A best fit of the line for the homoionic organoclays gives an intercept at 18.0 Å. In comparison, an intercept at 30.3 Å is obtained for a best line drawn through the basal spacings for the staged heterostructured materials (*d*-spacings of the C_8 and C_{10} transitional structures excluded). The 12.3 Å difference in intercept for the two lines is the value expected for a heterostructure in which the onium and sodium ions are staged in regularly alternating galleries. The line for the mixed ion heterostructure and the expected line for the mixed ion homostructure intersect around 43 Å. At this particular basal spacing no distinction can be made between heterostructure and a homostructure. However, the observed spacing for every other point precludes a mixed ion homostructure.

In summary, the tail length of the onium ion surfactant determines the extent of sodium ion replacement upon the addition of half an equivalent of the surfactant. Small onium ions are too hydrophilic to displace sodium quantitatively. A quantitative onium loading is obtained only when the surfactant becomes more hydrophobic at surfactant chain lengths of $n \geq 12$.

Head Group Size Effect

In a second set of intercalation experiments we investigated the effect of the surfactant head group size on heterostructure formation. The $[CnH_{(2n+1)}N(C_mH_{(2m+1)})_3]^+$ head group size *m* was increased one carbon unit at a time from Me, Et, *n*-Pr, *n*-Bu, to *n*-Pe, while the chain length was fixed at $n = 16$. This chain length ensures a quantitative onium ion uptake on the partial displacement of the sodium ions. Diffraction profiles for the intercalation products are given in Fig. 6. In contrast to the staged $C_{16}H_{33}NBu_3^+/Na^+$ heterostructure, phase segregated organo clay and sodium clay products were obtained when Na^+–FH was equilibrated with half an exchange equivalent of trimethyl terminated quaternary ammonium surfactant ($m = 1$). The first-order (27.3 Å) and second-order (13.7 Å) peaks for $C_{16}H_{33}NMe_3^+$–FH and the 12.4 Å Na^+–FH peak are well developed. Thus, the small size of the surfactant head group causes the two cationic species to segregate into discrete galleries during the exchange reaction. The nature of the reaction products becomes more complex when a triethyl terminated surfactant ($m = 2$) is used. All possible products, homoionic parent end members, and a mixed ion heterostructured intercalate are found as products. The XRD shows predominantly the segregated 27.2 Å $C_{16}H_{33}NEt_3^+$–FH and 12.4 Å Na^+–FH phases, but also a small amount of a heterostructured phase, as evidenced by the diffraction shoulder around 39 Å. The cationic species are thus evidently segregated into distinct interlayers. When the head group size is increased to

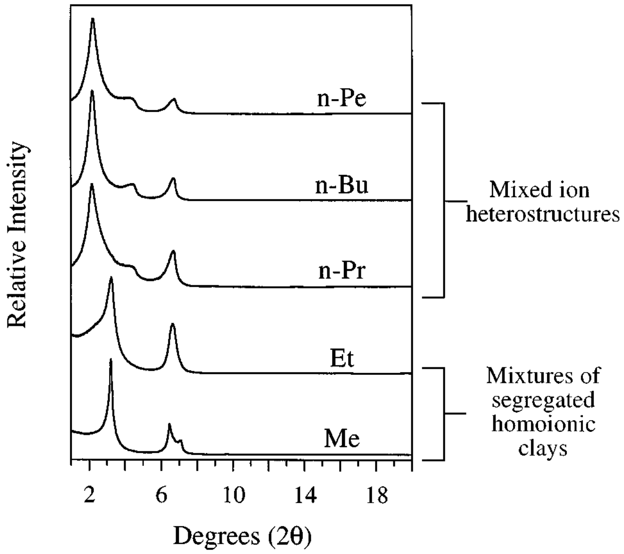

FIG. 6. XRD patterns (Cu$K\alpha$) of materials obtained when a Na^+–FH suspension is treated with half an equivalent of $[C_{16}H_{33}N(C_mH_{(2m+1)})_3]^+$ surfactant. The head group size was increased in one-carbon units from $m = 1$–5 to form an expanding series that included Me, Et, *n*-Pr, *n*-Bu, and *n*-Pe groups.

TABLE 3
Surfactant Head Group Size and X-Ray Basal Spacings (d_{00l}) for Homoionic Q^+ Fluorohectorite[a] and 1:1 Mixed Na^+ Q^+ Fluorohectorite Heterostructures,[b] Where Q^+ is $C_{16}H_{33}NR_3^+$

		d_{00l}, [Å]	
Surfactant head group, *R*	Surfactant head group size [$Å^2$][c]	Q^+-FH	Na^+, Q^+-FHHS
Me	34	27.3	—
Et	56	27.2	—
n-Pr	78	27.0	39.5
n-Bu	101	26.9	39.4
n-Pe	123	26.4	38.9

[a] Abbreviated Q^+-FH.

[b] Abbreviated Q^+, Na^+-FHHS.

[c] For comparison, the charge density of fluorohectorite is 1 electron charge per 84 $Å^2$.

n-Pr, *n*-Bu, and *n*-Pe ($m \geq 3$), the equilibrium clearly shifts exclusively toward a staged mixed-ion heterostructure.

Clearly, the size of the surfactant head group is a key factor in determining heterostructure formation. When the head group size is large relative to the charge density of the layered host, there is insufficient space to accommodate hydrated Na^+ ion between groups. We refer to the relationship between head group size and layer charge density as the *head group footprint effect*. The fluorohectorite layer charge density is calculated to be one electron per 84 $Å^2$ based on an orthogonal $Li_{1.12}[Mg_{4.88}Li_{1.12}]Si_8O_{20}F_4$ unit cell (20). The surfactant ionic head group areas, as estimated based on the van der Waals radii, are given in Table 3. This table also includes the basal spacings for all five homoionic organoclays and the *d*-spacings for the three 1:1 mixed ion heterostructures. The surface area per unit of charge is matched by the area of the head group (i.e., the "footprint") only for the tri-*n*-propyl and larger surfactant head group sizes (i.e., $m \geq 3$). The larger tri-*n*-butyl and tri-*n*-pentyl surfactants can fold back upon themselves, thereby covering the basal surface area. A completely hydrophobic clay surface thus arises for $m \geq 3$. The lack of free space between onium ions precludes the cooccupancy of both cationic species within the same gallery. The hydrated sodium ions are now forced to take position on the hydrophilic side of the clay layer.

Previously reported neutron scattering and NMR studies have shown that alkali metal exchange forms of smectite clays in stirred aqueous suspension form tactoids containing 1–3 nanolayers (21–23). The number of nanolayers per tactoid depends on the nature of the exchange cation and the shear rate (23). The formation of staged Na^+–onium ion heterostructures can be understood in terms of an equilibrium between tactoids containing one and two nanolayers. As illustrated in Fig. 7, when half an equivalent of a $C_nH_{(2n+1)}NR_3^+$ onium ion contains an alkyl chain with $n > 10$, the hydrophobic chain effect will cause quantitative displacement of half the Na^+ from the basal surfaces of both types of tactoids. However, the position of the equilibrium between the two tactoid forms will depend on the size of the NR_3 head group. For R = propyl, butyl, or pentyl, the head group footprint effect causes preferential displacement of Na^+ from the gallery region defined by the two-layer tactoid. This two-layer structure optimizes the hydrophobic interactions between onium ions while keeping the external surfaces hydrophilic for solvation by water. Consequently, the tactoid equilibrium is shifted to the two-nanolayer structure. Drying the tactoids leads to a regularly ordered heterostructure.

Conversely, for small head groups, R = methyl or ethyl, there is no head group effect and the Na^+ ions are randomly displaced from the basal surfaces. In order to optimize the hydrophilic character of the basal surfaces, for solvation by water the tactoid equilibrium is shifted toward the single nanolayer tactoid (cf. Fig. 7). Drying the suspension forms initially a hydrated homogeneous mixed ion intercalate. However, further removal of the gallery water results in segregation of the organic and inorganic ions within the galleries and the formation of layer stacking patterns characteristic of the phase segregated end members.

Finally, we note that tactoids containing three nanolayers may be unstable in Na^+–fluorohectorite suspensions. We were unable to form 1:2 Na^+: onium ion heterostructure.

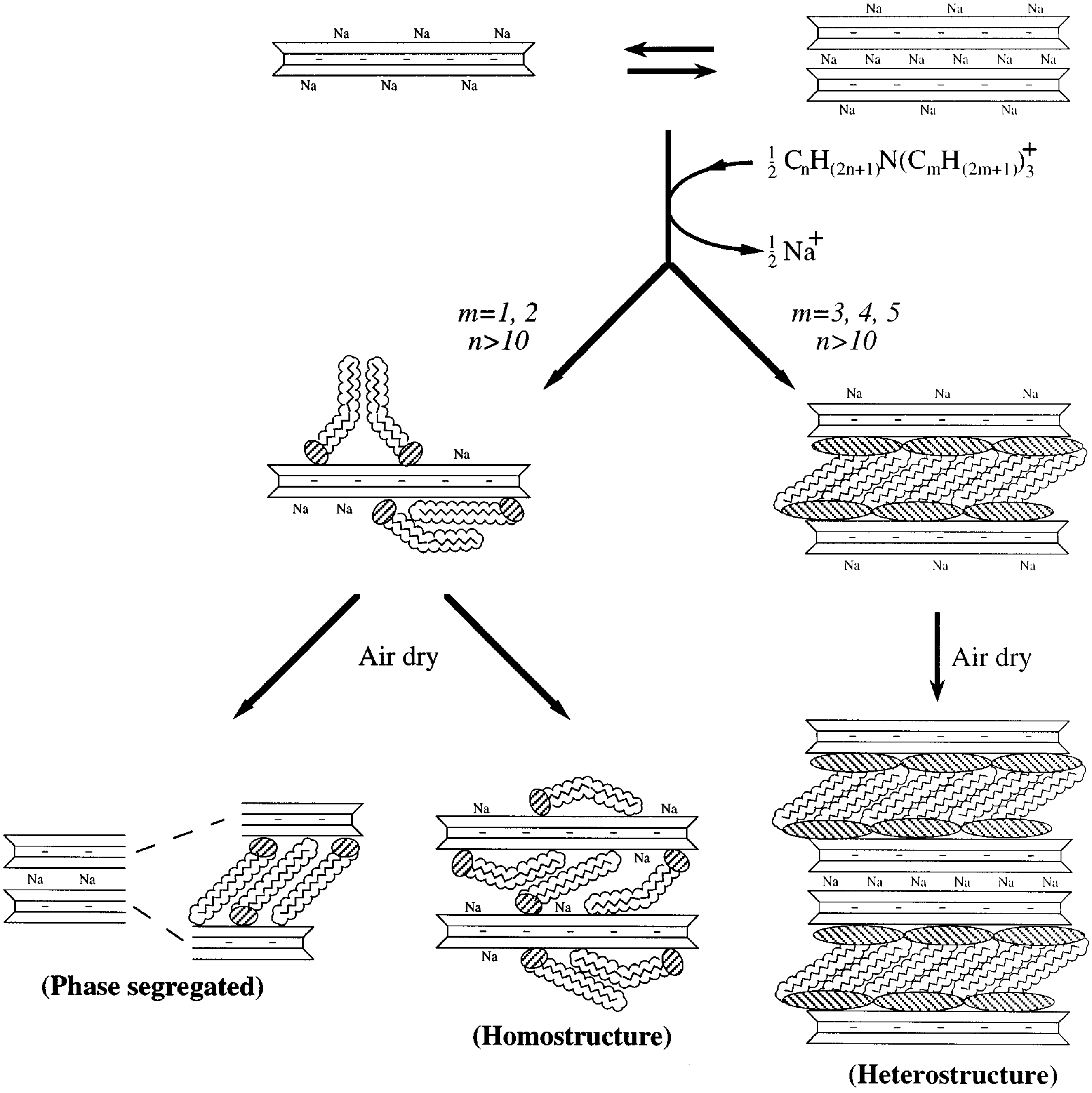

FIG. 7. Summary of the reaction pathway leading to heterostructured, homostructured, and phase segregated mixed ion intercalates formed by replacing 50% of the exchange cations in Na^+–fluorohectorite with $C_nH_{(2n+1)}N(C_mH_{(2m+1)})_3^+$ cations ($n \geq 10$; $m = 1$–5).

Instead, a 1:1 staged heterostructure and an organo clay were formed.

CONCLUDING REMARKS

We have elucidated the processes leading to the formation of staged fluorohectorite heterostructure containing regularly alternating interlayers of inorganic (Na^+) and organic (alkylammonium) cations. First, the alkyl chain of the onium ion must be sufficiently long ($n > 10$ carbon atoms) to quantitatively displace half of the Na^+ ions through a hydrophobic binding effect. Second, the head group footprint must be sufficiently large ($m \geq 3$ carbon atoms) to exclude binding of Na^+ between onium ions.

These conditions favor the formation of bipolar two-nanolayer tactoids in aqueous suspension with hydrophobic onium ions intercalated between the layers and hydrophilic Na^+ ions on the external surfaces. These dispersed bipolar tactoids should be ideally suited for the adsorption of organic molecules from aqueous solution. Heterostructures are formed when the bipolar tactoids are removed from suspension and dried.

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