

TRIS(ACETYLACETONATO)SILICON(IV) BINDING TO MONTMORILLONITE AND HYDROLYSIS TO INTERLAYER SILICIC ACID

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Abstract—The reactions of the tris(acetylacetonato)silicon(IV) cation ($\text{Si}(\text{acac})_3^+$) with Na^+ -, Mg^{2+} -, and Co^{2+} -exchange forms of hectorite and montmorillonite have been investigated to understand better the formation process of clays pillared by silicic acid. In acetone as the solvating medium, $\text{Si}(\text{acac})_3^+$ binds to the Na^+ - and Mg^{2+} -clays with the desorption of only a small fraction (~5%) of the initial exchange cation, suggesting that the complex binds as the ion pair $[\text{Si}(\text{acac})_3^+][\text{Cl}^-]$. With the Co^{2+} -clays, however, the exchange cation is desorbed quantitatively, and $\text{Si}(\text{acac})_3^+$ binding is accompanied by the formation of an acetone-solvated CoCl_2 solution complex which helps to drive the ion-exchange reaction. Thus, Co^{2+} -smectites react with $\text{Si}(\text{acac})_3^+$ in acetone to produce homoionic $\text{Si}(\text{acac})_3^+$ intercalates, whereas Na^+ - and Mg^{2+} -smectites produce mixed-ion intercalates. The interlayer hydrolysis of $\text{Si}(\text{acac})_3^+$ to silicic acid in the homoionic $\text{Si}(\text{acac})_3^+$ - and mixed-ion $\text{Na}^+/\text{Si}(\text{acac})_3^+$ - and $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -exchange forms of montmorillonite films is diffusion controlled. In water as the solvating medium, the reaction of $\text{Si}(\text{acac})_3^+$ with Mg^{2+} - or Co^{2+} -montmorillonite results in the desorption of the exchange cations on a time scale which is comparable to that observed for the solution hydrolysis of $\text{Si}(\text{acac})_3^+$. Thus, the precipitation of silicic acid from aqueous solution competes strongly with the formation of interlayer silicic acid. With aqueous Na^+ -montmorillonite dispersions, however, a significant fraction of the exchange cations desorbed rapidly upon $\text{Si}(\text{acac})_3^+$ binding, and the formation of interlayer silicic acid is favored over the precipitation of $\text{Si}(\text{OH})_4$.

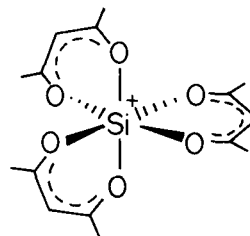
Key Words—Hydrolysis, Montmorillonite, Pillared interlayer complex, $\text{Si}(\text{acac})_3^+$, Silicic acid.

INTRODUCTION

Considerable interest has recently been shown in a class of smectite intercalation compounds which contain interlayer polynuclear-hydroxy cations. These so-called "pillared" (Vaughan and Lussier, 1980) or "cross-linked" (Lahav *et al.*, 1978) clays typically exhibit high porosity and appreciable surface areas for adsorption and possible catalysis (Lussier *et al.*, 1980). Because their pore sizes can be designed to be larger than those of conventional zeolites, they hold considerable promise for the catalytic reactions of large organic molecules (Shabtai *et al.*, 1980). The general approach to the synthesis of pillared clays has been to form the hydroxy metal cations in aqueous solution prior to their exchange into the interlayer region of the clay. Although this approach has been quite successful, it is limited to metal ions with favorable solution hydrolysis chemistry (Brindley and Sempels, 1977; Lahav *et al.*, 1978; Brindley and Yamanaka, 1979; Yamanaka and Brindley, 1979; Yamanaka *et al.*, 1980; Vaughan and Lussier, 1980).

We have explored the *interlayer* hydrolysis reactions

of metal complexes in clays as a means of achieving the intercalation of hydroxy metal species which are not known to form stable hydroxy cations in solution. The viability of this synthetic approach was first demonstrated by the successful intercalation of silicic acid (Endo *et al.*, 1980, 1981). Though silicon is not known to form hydroxy cations in solution, silicic acid can nevertheless be intercalated in smectite by the interlayer hydrolysis of the tris(acetylacetonato)silicon(IV) cation henceforth abbreviated $\text{Si}(\text{acac})_3^+$, shown below:



The purpose of the present work was to examine in greater detail the exchange reactions of $\text{Si}(\text{acac})_3^+$ with Na^+ -, Mg^{2+} -, and Co^{2+} -exchange forms of smectite under aqueous and non-aqueous conditions, and to investigate the hydrolysis of the intercalated complex cation.

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EXPERIMENTAL METHODS

Materials

Hectorite was obtained from the Baroid Division of NL Industries, and montmorillonite was obtained from the American Colloid Company. Homoionic Na⁺, Mg²⁺, and Co²⁺-exchange forms of the minerals were prepared from the <2- μ m fractions by equilibration of 1 wt. % suspensions in saturated aqueous solutions of the appropriate metal chloride salts. The clays were freed of excess salts by dialysis and then lyophilized (van Olphen, 1977). Analysis of ammonium acetate extracts of the homoionic montmorillonites by flame emission spectrophotometry (Na⁺-clay) or by atomic absorption spectrophotometry (Mg²⁺- and Co²⁺-clays) indicated the cation-exchange capacities (CEC) to be 0.84, 0.85, and 0.75 meq/g for the Na⁺, Mg²⁺, and Co²⁺-exchange forms, respectively. Oriented clay films suitable for X-ray powder diffraction (XRD) and infrared (IR) studies were prepared by allowing aqueous suspensions containing 70 mg clay/30 ml water to evaporate under ambient conditions onto an area of 23 cm².

Si(acac)₃⁺ was prepared as the hydrogen dichloride anion salt by reaction of SiCl₄ with 2,4-pentanedione according to the method of Riley *et al.* (1963). The prepared salt was stored under vacuum.

Adsorption measurements

In experiments involving the adsorption of Si(acac)₃⁺ by clay, approximately 250 mg of each homoionic smectite was allowed to solvate in 500 ml of water at 4°C or in acetone at 25°C for at least 24 hr. A 50-ml aliquot of the supernatant was removed and reserved as an analytical blank. Known amounts of Si(acac)₃⁺ were dissolved in 500 ml of solvent and 50 ml of solution was reserved for use as a reference. The remaining 450 ml of Si(acac)₃⁺ solution was then added to the 450 ml of clay-solvent suspension. Small aliquots were removed from the reaction mixture periodically and immediately analyzed. The amount of Na⁺, Mg²⁺, and Co²⁺ released into solution upon Si(acac)₃⁺ binding was determined by atomic absorption spectrophotometry.

Si(acac)₃⁺ hydrolysis

The hydrolysis of Si(acac)₃⁺ in aqueous solution was determined spectrophotometrically. The complex cation exhibits a maximum absorption at 290 nm, whereas free acetylacetone has a maximum at 273 nm. The ratios of the concentration of complex present at a given time to the concentration present initially were determined by fitting the peak position and absorption maximum in the 290–273-nm region using an iterative technique.

Hydrolysis rates for Si(acac)₃⁺ in oriented clay films were obtained by observing the changes in the absor-

Table 1. Hydrolysis of Si(acac)₃⁺ in water.

Temp. (°C)	k (hr ⁻¹)	t _{1/2} (hr)	r ¹
37	0.96	0.72	.998
35	0.79	0.87	.969
4	0.027	26.0	.998

¹ Regression coefficient for a fit of the hydrolysis data to a pseudo first-order rate law.

bance of the 1390-cm⁻¹ IR band of the complex. The 1630-cm⁻¹ band of adsorbed water was also monitored. The exchange of Si(acac)₃⁺ into the clay films was performed in acetone to minimize solution hydrolysis. The films were then immersed in H₂O or exposed to H₂O vapor to initiate hydrolysis at 25°C. Liquid water was allowed to evaporate from the immersed films by placing the film in the IR source beam prior to obtaining the spectrum.

Physical measurements

UV-visible spectra were recorded on a Beckman DK-2A scanning, double-beam recording spectrophotometer. IR spectra were obtained on a Beckman IR7 scanning, double-beam IR spectrophotometer. A Philips X-ray diffractometer equipped with CuK α radiation was used to determine d(001) spacings. Na⁺, Mg²⁺, and Co²⁺ analysis were performed with a Perkin-Elmer 503 double-beam atomic absorption spectrophotometer equipped with a deuterium-arc background corrector.

RESULTS AND DISCUSSION

Solution hydrolysis

Si(acac)₃⁺ hydrolyzes in water to give silicic acid and free acetylacetone as illustrated in Eq. (1).



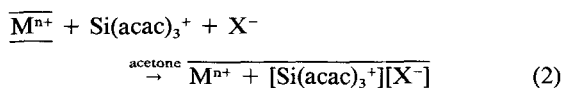
Dhar *et al.* (1959) found that at constant pH the hydrolysis rate is pseudo first-order in Si(acac)₃⁺ complex. Our results confirm the pseudo first-order reaction kinetics. Table 1 provides values for the pseudo first-order rate constant (k) and reaction half-life (t_{1/2}) at 37°, 35°, and 4°C. The temperature dependence of the reaction can be explained by an Arrhenius activation energy of ~18 kcal/mole.

Adsorption of Si(acac)₃⁺

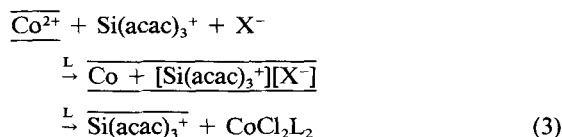
The hydrolysis of Si(acac)₃⁺ was much slower in acetone than in water. In fact, the complex was sufficiently stable in acetone to permit binding to the surface of smectites without significant degradation to silicic acid. Thus, the reaction of freeze-dried samples Na⁺, Mg²⁺, and Co²⁺-montmorillonite (or hectorite) over a 48-hr period with 2 CEC equivalents of Si(acac)₃⁺ in acetone

at an initial concentration of 4.6×10^{-4} M resulted in intercalated clays that exhibited d(001) spacings of 17 Å under air-dried conditions.

It is remarkable that only small amounts (~5%) of the exchange cations in Na^+ - and Mg^{2+} -montmorillonite were desorbed from the clay surface upon binding of the silicon complex. This result suggests that $\text{Si}(\text{acac})_3^+$ binding does not occur by an ion-exchange mechanism. Because electrical neutrality must be maintained upon $\text{Si}(\text{acac})_3^+$ binding, the complex presumably adsorbed to the clay layers by ion-pair formation, as illustrated in Eq. (2), wherein the solid lines define the intercalated species and X^- is the Cl^- counterion.



In marked contrast to the Na^+ and Mg^{2+} systems, the Co^{2+} -exchanged clays quantitatively released the exchange cation to solution upon $\text{Si}(\text{acac})_3^+$ binding, as expected for an ion-exchange mechanism. The exchange mechanism for the Co^{2+} -clays appears to have been facilitated by the formation of blue, acetone-solvated CoCl_2 . Eventually, the blue color of the solvated interlayer Co^{2+} complex discharged into the solution. Thus, $\text{Si}(\text{acac})_3^+$ most likely bound initially as an ion pair as with the Na^+ and Mg^{2+} systems, but subsequent complex formation of Co^{2+} , Cl^- , and acetone in the interlayers led to the formation of a neutral $\text{CoCl}_2 \cdot \text{L}_2$ species ($\text{L} = \text{acetone}$) which desorbed to solution. The formation of the latter complex provided an additional driving force for ion exchange. In contrast, Na^+ and Mg^{2+} did not form analogous species in acetone. The proposed reaction sequence for the Co^{2+} -clays is summarized in Eq. (3):



The IR spectra of $\text{Si}(\text{acac})_3^+$ bound to oriented film samples of Na^+ - and Mg^{2+} -montmorillonite contain well-defined bands at 1320, 1350, 1390, 1540, and 1555 cm^{-1} . Similar bands were observed for homoionic $\text{Si}(\text{acac})_3^+$ -montmorillonite obtained by exchange reaction with the Co^{2+} form of the mineral. The spectra agree well with the spectrum reported previously by Thompson (1969) for the complex cation.

Inasmuch as ion solvation forces in water are stronger than those in acetone, aqueous $\text{Si}(\text{acac})_3^+$ should not bind to clay interlayers by ion pairing with the retention of the initial exchange cations. Thus, the reaction of $\text{Si}(\text{acac})_3^+$ with Na^+ -, Mg^{2+} -, and Co^{2+} -montmorillonites was examined in water at 4°C . At this temperature the solution hydrolysis rate ($t_{1/2} = 26 \text{ hr}$) was sufficiently

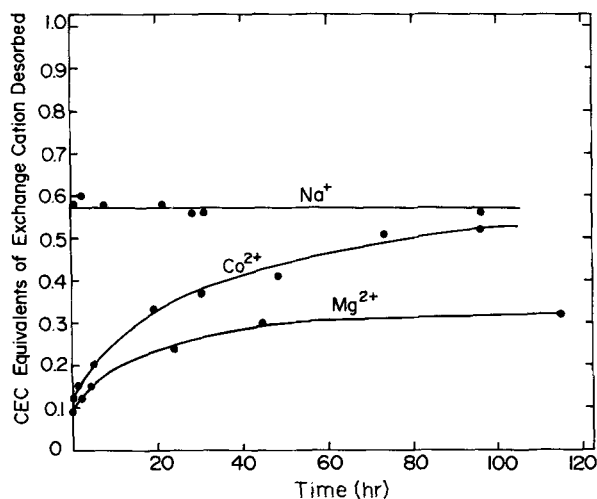


Figure 1. The desorption of Na^+ , Mg^{2+} , and Co^{2+} from montmorillonite upon reaction at 4°C with 2.0 CEC equivalents of $\text{Si}(\text{acac})_3^+$ in aqueous solution at an initial concentration of 4.6×10^{-4} M.

low to monitor conveniently the desorption of the exchange cations initially present in the clay surface. Figure 1 shows the results for the desorption of Na^+ , Mg^{2+} , and Co^{2+} from the surface of montmorillonite when 2 CEC equivalents of $\text{Si}(\text{acac})_3^+$ at an initial concentration of 4.6×10^{-4} M interacted with the three different exchange forms of the mineral. Curves of similar shape were obtained when 1.0 CEC equivalent of $\text{Si}(\text{acac})_3^+$ reacted with the clays under analogous conditions.

As can be seen from Figure 1, Mg^{2+} and Co^{2+} were released very slowly from the surface of montmorillonite in the presence of aqueous $\text{Si}(\text{acac})_3^+$. In fact, the desorption of the two divalent ions occurred on a time scale comparable to the solution hydrolysis of $\text{Si}(\text{acac})_3^+$. After an equilibration time of 100 hr, the solution hydrolysis of $\text{Si}(\text{acac})_3^+$ went through approximately four reaction half-lives, yet only a fraction of the initial Mg^{2+} - and Co^{2+} -exchange cations were desorbed into solution. The desorption of the divalent cations, of course, may have been partially caused by exchange with H^+ formed in the solution hydrolysis of $\text{Si}(\text{acac})_3^+$ (cf. Eq. (1)), as well as by exchange with $\text{Si}(\text{acac})_3^+$. In either case, the solution hydrolysis of $\text{Si}(\text{acac})_3^+$ appears to compete favorably with the ion-exchange reaction. Consequently, more silicic acid was formed from $\text{Si}(\text{acac})_3^+$ by precipitation from aqueous solution than was formed in the clay interlayers.

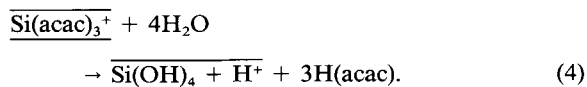
In marked contrast to Mg^{2+} - and Co^{2+} -montmorillonite, the Na^+ -exchange form of the mineral rapidly desorbed ~0.6 CEC equivalents of Na^+ upon reaction of aqueous $\text{Si}(\text{acac})_3^+$. No further Na^+ was released, suggesting a slow subsequent diffusion of the complex

into the interlayers. The rapid initial release of Na^+ suggests that $\text{Si}(\text{acac})_3^+$ rapidly exchanged for the monovalent ion in the dispersed clay. Thus, Na^+ -montmorillonite was favored over the divalent exchange forms of the mineral as a means of incorporating $\text{Si}(\text{acac})_3^+$ into the interlayer region under aqueous conditions. Subsequently the interlayer $\text{Si}(\text{acac})_3^+$ hydrolyzed to interlayer silicic acid as was previously reported (Endo *et al.*, 1980, 1981).

The tendency of aqueous $\text{Si}(\text{acac})_3^+$ to replace Na^+ in preference to Mg^{2+} and Co^{2+} on the exchange sites of smectite may be the result of kinetic factors rather than thermodynamic effects. Initially, the Na^+ clay was fully dispersed in water with all of the basal surfaces exposed to solution and available for ion exchange. The collapse of the interlayers upon partial exchange of the surface Na^+ ions (~ 0.6 CEC equivalents) caused the clay layers to flocculate and entrap unexchanged Na^+ . In contrast, the interlayers of the divalent exchange forms of smectite were swollen by only ~ 10 – 12 Å and access to the exchange sites was much more restricted. Under the latter conditions solution hydrolysis was capable of competing with ion exchange.

Interlayer hydrolysis

Homoionic $\text{Si}(\text{acac})_3^+$ -montmorillonite, as obtained by ion exchange of $\text{Si}(\text{acac})_3^+$ in acetone with Co^{2+} -montmorillonite (cf. Eq. (3)), along with the mixed-ion $\text{Na}^+/\text{Si}(\text{acac})_3^+$ - and $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -forms of the mineral, hydrolyzed slowly at 25°C when they were exposed to water vapor or immersed in liquid water. Hydrolysis rates were determined from the decrease in the absorbance of the 1390-cm^{-1} band of the complex. The decrease in the intensity of the 1390-cm^{-1} band was accompanied by an increase in the 1630-cm^{-1} band for adsorbed water. No physically adsorbed acetylacetone was observed during the course of the hydrolysis reaction, suggesting that the free ligand was rapidly lost to solution. This latter observation is consistent with the earlier observations of Parfitt and Mortland (1968) who found that $\text{H}(\text{acac})$ is readily displaced by water in clay interlayers. Thus, the hydrolysis reaction may be written as shown in Eq. (4):



The extent of $\text{Si}(\text{acac})_3^+$ hydrolysis in oriented film samples of homoionic $\text{Si}(\text{acac})_3^+$ -montmorillonite and mixed-ion $\text{Na}^+/\text{Si}(\text{acac})_3^+$ - and $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -montmorillonite was dependent on the square root of time. Plots of the absorbance for the 1390-cm^{-1} band of $\text{Si}(\text{acac})_3^+$ vs. $t^{1/2}$ gave straight lines with the regression coefficients and relative slopes given in Table 2. The $t^{1/2}$ dependence suggests that the hydrolysis rate was limited by the Fickian diffusion of water into the in-

Table 2. Regression coefficients and relative slopes for plots of absorbance (1390 cm^{-1}) vs. $t^{1/2}$ for the hydrolysis of intercalated $\text{Si}(\text{acac})_3^+$.¹

Exchange cations	Regression coefficients	Relative slopes
$\text{Na}^+/\text{Si}(\text{acac})_3^+$.966	1.42
$\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$.986	1.00
$\text{Si}(\text{acac})_3^+$.997	1.43

¹ Hydrolysis was carried out at 25°C by immersing oriented film samples of the clays in liquid water.

terlamellar region. Fickian diffusion has been observed for adsorption in many types of porous solids, including glassy polymers (Berens, 1978) and zeolites (Barrer, 1978).

The hydrolysis of $\text{Si}(\text{acac})_3^+$ was approximately two orders of magnitude slower in the intercalated state than in homogeneous aqueous solution. Under intercalated conditions, the restricted interlayer environment apparently limited migration of water to the $\text{Si}(\text{acac})_3^+$ sites, and the reaction became diffusion controlled. Although the $d(001)$ spacings were initially the same (~ 17 Å) for the $\text{Na}^+/\text{Si}(\text{acac})_3^+$ -, $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -, and $\text{Si}(\text{acac})_3^+$ -montmorillonites, the hydrolysis was significantly slower for the $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ system, as judged from the relative slopes in Table 2. The slower reaction in this latter system may reflect a more constrained or better ordered interlayer environment relative to the mixed $\text{Na}^+/\text{Si}(\text{acac})_3^+$ and homoionic $\text{Si}(\text{acac})_3^+$ systems. Regardless of the differences in hydrolysis rates, all three exchange-cation systems exhibited the same $d(001)$ spacings upon complete hydrolysis (~ 15.5 Å), suggesting that comparable amounts of hydrated silicic acid were incorporated into the interlayer regions.

CONCLUSIONS

The results of the present study suggest that Co^{2+} -smectites are preferred over Na^+ - and Mg^{2+} -smectites as a means of obtaining homoionic $\text{Si}(\text{acac})_3^+$ -exchange forms of the minerals when acetone is the solvating medium. The use of Co^{2+} on the exchange sites and of acetone as solvent minimizes the tendency toward interlayer $\text{Si}(\text{acac})_3^+/\text{Cl}^-$ ion pairing by facilitating the formation of CoCl_2 -acetone complexes which readily desorb from the clay interlayers and help to drive the ion-exchange reaction. The exchange reactions of Co^{2+} smectites in acetone may be useful as a means of intercalating halide salts of other hydrolytically sensitive cations which tend to form ion pairs in clay interlayers under non-aqueous solvation conditions.

The intercalated $\text{Si}(\text{acac})_3^+$ in homoionic $\text{Si}(\text{acac})_3^+$ -montmorillonite and in mixed-ion $\text{Na}^+/\text{Si}(\text{acac})_3^+$ - and $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -montmorillonite may be converted to

interlayer silicic acid upon hydrolysis in water. The hydrolysis reaction is diffusion controlled, even when Na^+ and Mg^{2+} co-occupy the interlayers. When water is the solvating medium, $\text{Si}(\text{acac})_3^+$ readily displaces Na^+ ions from the dispersed forms of the clay. Thus, interlayer binding and subsequent hydrolysis of the cation to silicic acid can be achieved with little or no competing solution hydrolysis of the cation. The divalent exchange forms of the minerals, however, bind aqueous $\text{Si}(\text{acac})_3^+$ slowly and, consequently, hydrolysis of $\text{Si}(\text{acac})_3^+$ in solution competes strongly with the interlayer binding of the complex cation.

Though the above conclusions are based on results obtained under conditions of concentration and temperature which permitted the necessary spectroscopic and analytical measurements of the binding and hydrolysis reactions of $\text{Si}(\text{acac})_3^+$, they help to define the optimum circumstances for synthesizing clays interlayered with silicic acid.

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Резюме—Реакции катиона три(ацетилацетонато)силикона(IV) ($\text{Si}(\text{acac})_3^+$) с Na^+ , Mg^{2+} , и Co^{2+} -обменными формами гекторита и монтмориллонита исследовались для лучшего понимания процесса формирования глин поддерживаемых кремневой кислотой. При использовании ацетона как растворителя, $\text{Si}(\text{acac})_3^+$ связывается с Na^+ - и Mg^{2+} -глинами, причем только небольшая часть (~5%) начального обменного катиона является десорбированной, указывая на то, что комплекс связан в виде пара ионов $[\text{Si}(\text{acac})_3^+][\text{Cl}^-]$. В случае Co^{2+} -глин, однако, обменный катион десорбируется количественно, и связь $\text{Si}(\text{acac})_3^+$ сопутствует формированию растворенного ацетоном комплекса CoCl_2 в растворе, который помогает течению ионо-обменной реакции. Результатом реакции Co^{2+} -смектитов с $\text{Si}(\text{acac})_3^+$ в присутствии ацетона являются однородные интеркалаты $\text{Si}(\text{acac})_3^+$ а реакции Na^+ - и Mg^{2+} -смектитов—смешано-ионные интеркалаты. Межслойный гидролиз $\text{Si}(\text{acac})_3^+$ на кремневую кислоту в однородных $\text{Si}(\text{acac})_3^+$ и смешано-ионных $\text{Na}^+/\text{Si}(\text{acac})_3^+$ - и $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -обменных формах фильмов монтмориллонита является диффузионно контролируемым. Результатом реакции $\text{Si}(\text{acac})_3^+$ с Mg^{2+} или Co^{2+} в присутствии воды является десорбция обменных катионов по времени сравнима со временем наблюдаемым для гидролиза $\text{Si}(\text{acac})_3^+$ в растворе. Таким образом, осаждение кремневой кислоты из водного раствора конкурирует сильно с формированием межслойной кремневой кислоты. В случае водной дисперсии Na^+ -монтмориллонита, однако, значительная часть обменных катионов быстро десорбируется на связи $\text{Si}(\text{acac})_3^+$, и формирование межслойной кремневой кислоты преобладает над осаждением $\text{Si}(\text{OH})_4$. [E.G.]

Resümee—Um den Bildungsprozess von Tonen mit Kieselsäureeinlagerungen besser zu verstehen, wurden die Reaktionen des Tris(acetylacetonato)silicon(IV)-Kations ($\text{Si}(\text{acac})_3^+$) mit Na^+ -, Mg^{2+} -, und Co^{2+} -ausgetauschten Formen von Hektorit und Montmorillonit untersucht. $\text{Si}(\text{acac})_3^+$ bindet sich in Aceton als Lösungsmittel an die Na^+ - und Mg^{2+} -Tone unter der Desorption eines nur geringen Anteils (~5%) der ursprünglichen Austausch-kationen. Dies deutet darauf hin, daß sich der Komplex wie das Ionenpaar $[\text{Si}(\text{acac})_3^+][\text{Cl}^-]$ bindet. Im Fall der Co^{2+} -Tone wird das Austausch-kation jedoch quantitativ desorbiert, und die $\text{Si}(\text{acac})_3^+$ -Bindung erfolgt durch die Bildung eines Aceton-gelösten CoCl_2 -Lösungskomplexes, der die Ionenaustauschreaktion vorantreibt. Daher führt die Reaktion von Co^{2+} -Smektiten mit $\text{Si}(\text{acac})_3^+$ in Aceton zur Bildung von homoionischen $\text{Si}(\text{acac})_3^+$ -Einschaltungen, während die Reaktion mit Na^+ - und Mg^{2+} -Smektiten zur Bildung von Einlagerungen mit verschiedenen Ionen führt. Die Zwischenschicht-hydrolyse von $\text{Si}(\text{acac})_3^+$ zu Kieselsäure in den homoionischen $\text{Si}(\text{acac})_3^+$ - und in den gemischten $\text{Na}/\text{Si}(\text{acac})_3^+$ - und $\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ -Austauschformen der Montmorillonitfilme wird durch Diffusion kontrolliert. Wenn Wasser das Lösungsmittel ist, so führt die Reaktion von $\text{Si}(\text{acac})_3^+$ mit Mg^{2+} - oder Co^{2+} -Montmorilloniten zur Desorption der Austausch-kationen mit einer Geschwindigkeit, die mit der vergleichbar ist, die man für die Lösungshydrolyse von $\text{Si}(\text{acac})_3^+$ beobachtet hat. Daher wetteifert die Ausfällung von Kieselsäure aus wässriger Lösung mit der Bildung von Zwischenschichtkieselsäure. Im Fall von wässrigen Na^+ -Montmorillonit-Suspensionen desorbiert jedoch ein beachtlicher Anteil der Austausch-kationen sehr schnell gleich nach der $\text{Si}(\text{acac})_3^+$ -Bindung, und die Bildung von Zwischenschichtkieselsäure wird im Vergleich zur Ausfällung von $\text{Si}(\text{OH})_4$ gefördert. [U.W.]

Résumé—Les réactions du cation tris(acétylacetonato)silicon(IV) ($\text{Si}(\text{acac})_3^+$) avec des formes d'échange- Na^+ , $-\text{Mg}^{2+}$, et $-\text{Co}^{2+}$, d'hectorite et de montmorillonite ont été investiguées pour mieux comprendre le procédé de formation d'argiles à acide silicique à piliers. Dans l'acétone comme moyen solvant, $\text{Si}(\text{acac})_3^+$ se lie aux argiles Na^+ et Mg^{2+} avec la désorption d'une petite fraction seulement (~5%) du cation d'échange initial, suggérant que le complexe se lie en tant que pair d'ions $[\text{Si}(\text{acac})_3^+][\text{Cl}^-]$. Avec les argiles Co^{2+} , cependant, le cation d'échange est désorbé quantitativement, et la liaison de $\text{Si}(\text{acac})_3^+$ est accompagnée de la formation d'un complexe CoCl_2 en solution, solvate dans l'acétone, qui aide à pousser la réaction d'échange d'ions. Les smectites- Co^{2+} réagissent ainsi avec $\text{Si}(\text{acac})_3^+$ dans l'acétone pour produire des intercalates homoioniques $\text{Si}(\text{acac})_3^+$, tandis que les smectites- Na^+ et Mg^{2+} produisent des intercalates à ions mélangés. L'hydrolyse interfolaire de $\text{Si}(\text{acac})_3^+$ en acide silicique dans les formes d'échange- $\text{Si}(\text{acac})_3^+$ homoionique, et $-\text{Na}/\text{Si}(\text{acac})_3^+$ à ions mélangés, et $-\text{Mg}^{2+}/\text{Si}(\text{acac})_3^+$ de films de montmorillonite est contrôlée par la diffusion. Dans l'eau comme moyen solvant, la réaction de $\text{Si}(\text{acac})_3^+$ avec la montmorillonite- Mg^{2+} ou $-\text{Co}^{2+}$ résulte en la désorption des cations d'échange sur une échelle de temps qui est comparable à celle observée pour l'hydrolyse de solution de $\text{Si}(\text{acac})_3^+$. La précipitation d'acide silicique à partir de solution aqueuse est ainsi en forte compétition avec la formation d'acide silicique interfolaire. Avec les dispersions aqueuses de montmorillonite- Na^+ , cependant, une fraction significative des cations d'échange désorbe rapidement lors de la liaison de $\text{Si}(\text{acac})_3^+$ et la formation d'acide silicique interfolaire est favorisée par rapport à la précipitation de $\text{Si}(\text{OH})_4$. [D.J.]