

Clay–Aminopropylsiloxane Compositions

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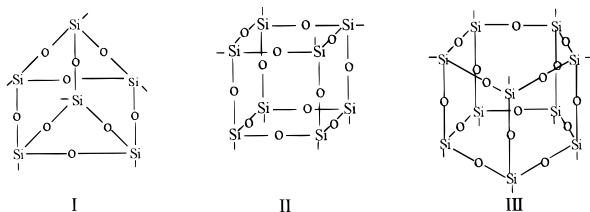
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The intercalation of a cubic octamer derived from the controlled hydrolysis of (3-aminopropyl)triethoxysilane with smectite clays has been studied. The organosilicon cubanes are adsorbed in amounts exceeding the cation exchange capacity of the mineral. The excess quantity is incorporated in the form of physically adsorbed ion pairs, $[(\text{H}_3\text{N}-\text{Pr})_8\text{O}_{12}\text{Si}_8] (\text{OH})_8$. The ion pair formation affects the basal spacings of the clay organosilicon compositions. Removal of the ion-paired cubes by water treatment reduces the d_{001} spacing from 18 to 16 Å. Lower surface areas were found for the unwashed samples indicating stuffing of the galleries by the ion-paired cubes. The orientation of the ion-exchanged and physically adsorbed octameric organosilicates in the interlayer region is deduced from the XRD and infrared results. Calcination of the washed or unwashed phases gives silica pillared structures with d_{001} spacings near 16 Å, with the washed phase showing the higher surface area.

Introduction

Aminofunctional silanes of the type $\text{X}_3\text{Si}(\text{CH}_2)_n\text{Z}$, where X represents an easily hydrolyzed group, e.g., $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$, or $-\text{Cl}$, Z is a pyridyl group for $n = 2$ or $-\text{NH}_2$, $-\text{NR}_2$, and $-\text{NH}(\text{CH}_2)_2\text{NH}_2$ for $n = 3$, are excellent precursors for the synthesis of silica pillared clays.^{1,2} Under controlled conditions of hydrolytic condensation these pillaring precursors are converted to a family of three-dimensional organosilicon oligomers composed of a polyhedral silicon–oxygen skeleton with intermittent siloxane chains that bear the amino functionalized substituent.³ Three typical structures of the polyhedral derivatives are shown below:



The various amino-functionalized oligomeric derivatives cannot be isolated, but gel permeation chromatography for the $\text{Z} = -\text{N}(\text{Et})_2$ member⁴ and ^{29}Si NMR spectroscopic studies for the $\text{Z} = -\text{NH}_2$ member⁵ have shown that the respective octameric species II are predominantly formed in methanolic or ethanolic solu-

tion of the monomers upon addition of water. The cubic silsesquioxanes present certain special features that make them ideal pillaring agents for interactions with smectite clays. First, protonation of the amino groups generates oligomeric cationic species with expendable and bulky organic groups that can be easily inserted into the lamellar zone of the clay and then can be removed by thermal treatment leaving behind silica pillared structures. Second, the cubic geometry of the various amino members offers only one possible orientation for placement in the interlayer zone of the clay. Third, the various aminofunctional silanes possess the ability to bind metal ions (M^{n+}) yielding metal complexes, $[\text{X}_3\text{Si}(\text{CH}_2)_n\text{Z}]_x\text{M}^{n+}$, that are the same as those derived from the related organic ligands without the $\text{X}_3\text{-Si}$ group. This important property makes possible the design and synthesis of metal complexes in which the metal center is coordinated to the functionalized group of the siloxane octamer. The resulting cationic complexes are expected to be excellent pillaring precursors for the synthesis of metal-substituted silica-pillared clays.

These important properties and also the lack of systematic studies describing the interactions of clays with cage-like organosilicate materials prompted us to study in detail the intercalation of sodium montmorillonite with a typical octameric silsesquioxane derived from (3-aminopropyl)triethoxysilane. Particular emphasis was given to the factors that affect the nature of the intercalated products and the pillared structures obtained by subsequent thermal processing.

Experimental Section

Materials and Reactions. The clay used in this work was a montmorillonite obtained from the island of Milos, Greece, with code name Zenith-N (OCMA). The structural formula for Zenith as determined from chemical analysis is:

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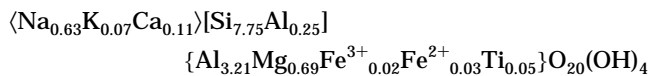
(1) Lewis, R. M.; Ott, K. C.; Van Santen, R. A. U.S. Patent 4510257, 1985.

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and its cation exchange capacity (CEC) measured by the Co-(II) procedure⁷ is 80.2 mequiv/100 clay. The clay was fractionated to <2 μm by gravity sedimentation and purified by standard methods. Sodium-exchanged samples were prepared by immersing the clay into 1 N solution of sodium chloride. Cation exchange was completed by washing and centrifuging four times with dilute solution of NaCl. The samples were finally washed with distilled-deionized water and transfer into dialysis tubes in order to obtain chloride free clays and then dried at room temperature. H^+ -Zenith was prepared by passing a 1% suspension of Na^+ -montmorillonite through a column of hydrogen-saturated Amberlite IR-120 resin.

The organosilane used in this study was (3-aminopropyl)-triethoxysilane, (APTEOS), $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$, from Janssen Chimica, Belgium. The formation of the octameric oligosiloxane from the hydrolytic polycondensation of the monomer occurs after dilution of APTEOS in ethanol-water ($v/v = 14/1$) to give a solution of concentration 0.45 M.⁶ The APTEOS-clay complexes were prepared by reacting a 0.5 wt % clay suspension with aliquots of the above siloxane solution such that the ratio, $R = [\text{APTEOS}]/[\text{clay}]$, was 3. After stirring for 6 h, the clay-organosilane aggregates were washed with water either once or several times, separated by centrifugation and air-dried by spreading on glass plates.

Ion-Exchange Adsorption Isotherm. The ion exchange isotherm for the adsorption of the cubane-like $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ by Na^+ -montmorillonite was obtained by adding the appropriate amount from a hydrolyzed 0.45 M APTEOS solution in ethanol-water ($v/v = 14/1$) to 100 mg of Na^+ -montmorillonite in the form of an aqueous paste and bringing the suspension volume to 30 mL with ethanol. The suspension was stirred for 1 h and then centrifuged at 10 000 rpm. The amount of $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ adsorbed by the clay was calculated after analyzing the supernatant solution for the remained $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ concentration spectrophotometrically. The determination was accomplished by adding to the supernatant solution 5 mL of 0.01 M $\text{Cu}(\text{NO}_3)_2$ in ethanol and measuring the absorbance at 590 nm. For each $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ concentration used to construct the adsorption isotherm, a blank experiment was also conducted for measuring the absorbance of the copper- $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ complex at the same wavelength.

X-ray Diffraction Measurements. X-ray powder diffraction (XRD) data were collected on a D500 Siemens diffractometer using $\text{Cu K}\alpha$ (40 KV, 35 mA) radiation and a secondary beam graphite monochromator. The spectra were recorded in the 2θ range from 2 to 30°, in steps of 0.03° and counting time 1 s/step.

FTIR Spectroscopy. Infrared spectra in the region 400–4000 cm^{-1} were measured with a Nicolet 550 infrared spectrometer equipped with a DTGS detector. Each spectrum was the average of 200 scans collected at 2 cm^{-1} resolution, by means of a SPECAC variable-angle attachment. Samples were in the form of KBr pellets containing ca. 2 wt % sample.

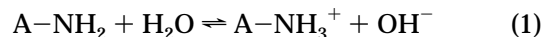
Cyclic Voltammetry. Voltammograms were recorded on a PAR Model 174A polarographic analyzer operated in conjunction with a Model 175 universal programmer. A conventional H-cell was used with a pyrolytic graphite as working electrode (0.25 cm^2), a saturated calomel reference electrode, and a platinum gauze as the counter electrode. APTEOS-clay films were cast onto the freshly cleaved pyrolytic graphite electrodes by allowing 10 μL of an aqueous 1% organosilane-clay suspension to evaporate at room temperature on the electrode surface. The APTEOS-clay suspension was prepared by ultrasonication for 15 min followed by a settling time of 10 min.

Surface Area Measurements. The nitrogen adsorption experiments were carried out employing a Quantachrome

AUTOSORB-1 automatic analyzer and using the volumetric method to calculate the adsorbed amount of nitrogen. The samples were outgassed at 523 K for 48–72 h under high vacuum (10^{-5} mbar) in the outgassing section of the apparatus. Then they were placed in the sample cell station, and the experiment was carried out at 77 K in a constant-level liquid nitrogen bath. Using the software of the analyzer, one can either perform an experiment choosing the appropriate conditions (equilibration time, P/P_0 tolerance, etc.) or analyze the data calculating the surface area and the pore volume with a variety of methods (BET, Langmuir, t -method, etc.).

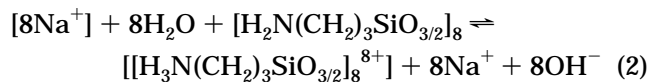
Results and Discussion

Nature of the Oligomeric Organofunctional Siloxanes. Amino-functional alkoxy silanes of the general type $(\text{OR})_3\text{Si}(\text{CH}_2)_3\text{Z}$, $\text{R} = -\text{CH}_3$ or $-\text{C}_2\text{H}_5$ and $\text{Z} = -\text{NH}_2$, $-\text{NR}_2$, or $-\text{NHCH}_2\text{CH}_2\text{NH}_2$, undergo facile hydrolytic condensation, owing to the internal catalytic action of the basic alkylamino groups, to yield a family of three-dimensional organosilicon oligomers of various structures according to the particular conditions of hydrolysis and aging of the solutions. Details of their synthesis, mechanisms of formation and factors affecting the structure, physical and chemical properties have been systematically reviewed.^{3,8} In addition, the conditions for the controlled hydrolysis of 3-aminopropyltriethoxysilane (APTEOS) or the [(*N,N*-diethylamino)propyl]trimethoxysilane to the octameric cubic structure II have also been described.^{4,5} The hydrolytic condensation, which takes place smoothly in a methanol or ethanol- H_2O solution, involves a first preequilibrium reaction in which the terminal amino groups are protonated:



The pK_b value of a hydrolyzed APTEOS solution, hereinafter designated as $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$, was determined by titration of 50 mL of a hydrolyzed 0.045 M APTEOS solution with a 0.1 M HCl solution and found near 6 (data are not shown).

When an ethanolic solution of APTEOS, prepared to contain the octameric unit, was diluted with water and then added to a clay suspension, an immediate flocculation of the clay particles was observed. Apparently, the flocculation was induced by the insertion of the protonated form of the $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ derivative into the clay layers by an ion-exchange reaction. Even though the alkylamino groups of the octamer are weakly basic, $\text{pK}_b \sim 6$, protonation of the cubes in the aqueous environment of the clay platelets is favored by the acidity of the clay surfaces and their affinity to adsorb readily bulky organic or organometallic cations.⁹ Both factors shift the equilibrium reaction 2 to the right, and



intercalation proceeds to completion while the pH of the solution will increase due to the produced OH^- groups. To follow closer the interaction of the clay surfaces with

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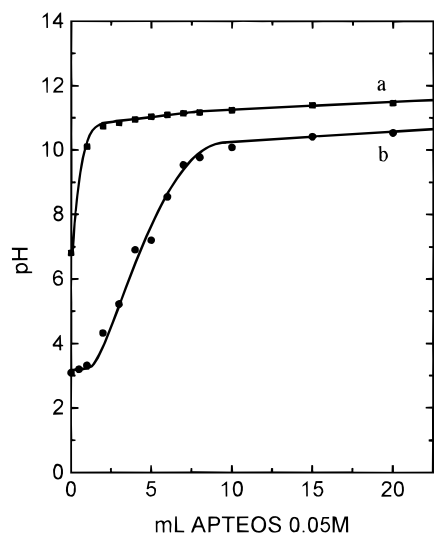


Figure 1. Titration curves of (a) Na^+ -montmorillonite and (b) H^+ -montmorillonite with a hydrolyzed 0.05 M APTEOS solution.

an $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ solution, the following two potentiometric titrations were performed. In the first, a suspension of sodium-montmorillonite, 300 mg in 20 mL of H_2O , was titrated with a hydrolyzed 0.05 M APTEOS solution. The titration results are shown in Figure 1a. At the start of the titration there was a sharp increase in the pH of the reaction mixture resulting from the protonation of the $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ units and their consequent intercalation. After the addition of about 3 mL of $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ solution, the pH of the medium reached the value of 11 and then remained constant. Note that this final pH value is the same as that of a hydrolyzed 0.05 M solution of APTEOS. In the second titration an acid montmorillonite dispersion was titrated with the same hydrolyzed APTEOS solution and the results are illustrated by curve b in Figure 1. We now observe that the pH remained almost constant at the beginning of the titration since the protons at the exchange sites of the clay were engaged in protonation of the adsorbed amino groups of the cubane units. After all protons were tied up, the pH increased steadily and reached the constant value of 10. From the midpoint of the titration curve we can estimate the amount of the $(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8^{8+}$ units introduced into the clay surfaces by a cation-exchange process. This amount corresponds to 84.0 mequiv/100 g of clay, a value very close to the CEC of the clay (80 mequiv/100 g).

Ion Adsorption. The adsorption of the $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ cubes by the clay surfaces was further examined by determining the corresponding uptake curve, shown in Figure 2. The steep rise in the curve at low APTEOS concentrations reflects the high affinity of the clay particles for the $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ cubic units. Furthermore, from the plateau of the curve we find that the amount of the adsorbed APTEOS exceeds considerably the coverage imposed by the cation-exchange capacity of the clay. In fact, it corresponds to about 1.8 times the CEC. Adsorption of amines by clay surfaces in excess of the CEC has been observed for alkylamines¹⁰ and diamines¹¹ and has been attributed to the for-

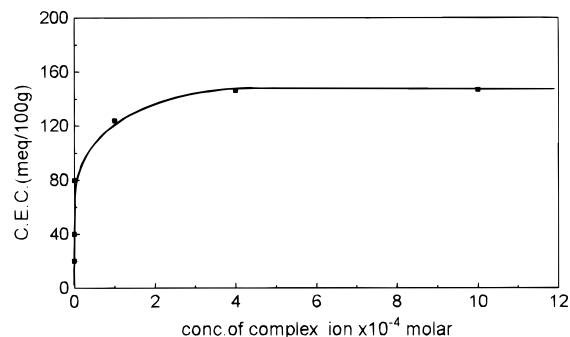


Figure 2. Adsorption isotherm of $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ cubes on Na^+ -montmorillonite.

mation of ammonium-amine associations of the type $[\text{RNH}_2 \cdots \text{H} \cdots \text{H}_2\text{NR}]^+$ in the interlayer zone of the smectite. Such associations could similarly explain the adsorption behavior observed in the present study. However, because the organosilicon cubic octamers are bulky and robust organophilic cations, there is also the possibility of being adsorbed in the form of ion pairs that are derived from the protonation of the organosiloxane units, i.e., $[\text{H}_3\text{N}(\text{CH}_2)_3\text{Si}_8\text{O}_{12}][\text{OH}]_8$. Previously, ion-pair formation has been proposed to explain the incorporation of trisbipyridyl or tris-1,10-phenanthroline metal chelates¹² or quaternary long-chain alkylammonium ions¹³ to clay surface in excess of the CEC. In the ion-pair mechanism the excess metal chelates are loosely held by the surfaces and are easily removed by washing with water.

In an experiment designed to probe the type of aggregation responsible for the excess adsorption of the amino-functionalized organosilicon cubes by the clay surfaces the intercalation of the $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ was performed in a 0.05 M solution of sodium sulfate. The purpose was to demonstrate the presence in the clay layers of sulfates, acting as the counteranion of the ion-paired cubes, by infrared spectroscopy and in addition by the chemical analysis of sulfur to verify the presence of sulfates in the interlayers and to estimate the amount of the physically adsorbed ion-paired cubes. As can be seen in Figure 3 the FTIR spectrum of clay- $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8][\text{SO}_4]_4$ complex, washed once with water (a) shows clearly the asymmetric vibration at 1130 cm^{-1} and the bending at 620 cm^{-1} of the sulfate anion.¹⁴ These vibrations disappear when the clay sample was washed four times with water (b). The remaining bands arise from vibrations of the clay structure. A black experiment was also conducted in order to verify whether the IR absorptions could originate from sulfate ions sorbed by the clay surfaces. The IR spectrum of the clay sample, which was treated with 0.05 M Na_2SO_4 and then rinsed once with water, did not show sulfate absorptions. The chemical analysis results, listed in Table 1, offer additional support for the ion-pair formation. It is seen that washing the clay composition four times with water brings a decrease in the sulfur content from 2.57% to 0.38% implying that

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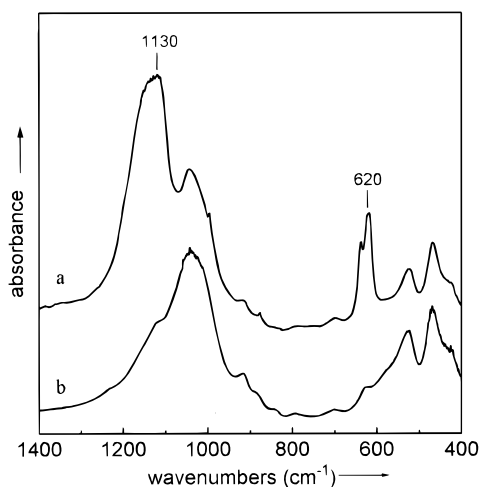


Figure 3. Infrared absorption spectra from a clay- $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8][\text{SO}_4]_4$ complex, washed once (a) and four times with water (b).

Table 1. Effect of Washing on the Chemical Analysis of the Intercalated Products

sample	%C	%H	%N	%S
Na^+ -Zenith+APTEOS- SO_4^{2-} washed $1 \times \text{H}_2\text{O}$	4.24	1.81	1.37	2.30
Na^+ -Zenith+APTEOS- SO_4^{2-} washed $4 \times \text{H}_2\text{O}$	3.03	1.60	1.12	0.38

most of the sulfate anions, incorporated in the form of $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8][\text{SO}_4]_4$ ion pairs, were desorbed from the clay galleries. Similarly the substantial decrease in the carbon content of the clay-silsequioxane product is in line with the loss of siloxane octamers upon water washing. On the basis of the sulfur analysis we can calculate the maximum quantity of the ion-paired $[\text{H}_3\text{N}(\text{CH}_2)_3\text{Si}_8\text{O}_{12}][\text{SO}_4]_4$ cubes incorporated into the clay. This amounts to 0.20 g/g of the clay complex. The conclusion is that the clay surfaces, apart from the electrostatically bound octameric silicate units, can also host additional cubic units in the form of physically adsorbed ion pairs which are easily leached into the aqueous environment by water washing.

X-ray Analysis. The accommodation of ion-paired cubic organosilane units in the clay galleries should be reflected in the X-ray diffraction patterns of the clay-organosilicon compositions. Representative spectra for samples washed once (a) and four times with water (b) are shown in Figure 4. The effect of the washing cycles on the basal $d(001)$ values is shown schematically in Figure 5. The data clearly demonstrate that water treatment of the intercalated samples affects greatly the $d(001)$ values. Successive washing brings a gradual decrease in the interlayer distance from 18.2 to 15.9 Å. Similar decreases in the d spacing with water treatment were also observed by Feller et al.² when montmorillonite was intercalated with the hydrolysis products of 2-(2-trichlorosilyl)ethylpyridine and (3-aminopropyl)-trimethoxysilane. The authors attributed these changes to different phases generated by the intercalation of partially hydrolyzed dimeric or trimeric siloxane units. However, such planar silicate units should give an interlayer separation of about 12.6 Å.¹⁵ The present

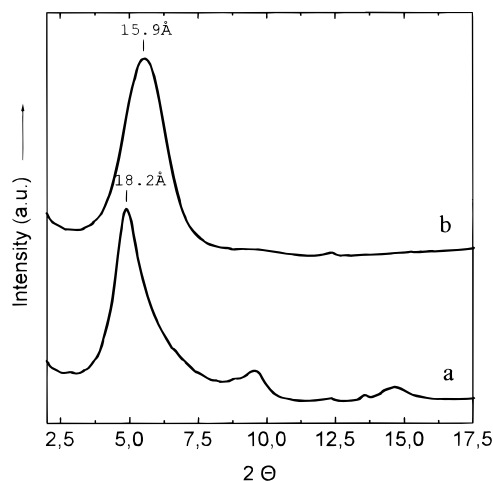


Figure 4. XRD patterns from clay- $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]$ samples, washed once (a) and four times with water (b).

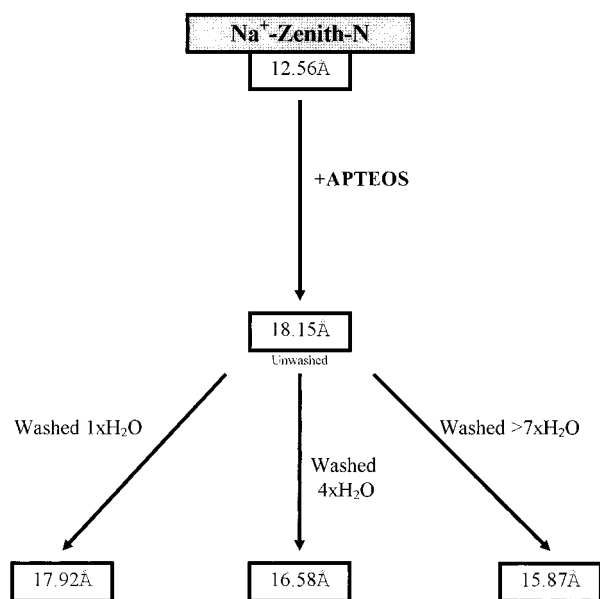


Figure 5. Flowchart of the effect of washing cycles on the basal $d(001)$ values of a clay- $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]$ composition.

XRD results suggest that the preformed cubic silsesquioxanes are introduced as intact units into the clay layers. The cubes are first fixed at the exchange sites of the mineral and then occupy the between space in the form of ion pairs. Equilibration with distilled water frees the ion-paired silicate onium salts from the clay surfaces and causes a decrease in the d spacing to about 16 Å. The d value of 16 Å for the washed sample implies that the flexible alkyl groups of the cubes must adopt a horizontal orientation between the clay surfaces, as seen in Figure 6. In this configuration the distance l between two parallel levels encompassing the alkyl chains is estimated to be 6.6 Å, a value very close to the experimentally observed intersheet separation, $\Delta = 16.0 - 9.6 = 6.4$ Å, 9.6 Å being the thickness of the clay sheet. On the contrary, if the alkylamino chains were directed in an upward position, then the Δ value would be expected to be near to the estimated lateral dimension of 11.2 Å of the cubic octamer.

In the flat orientation of the alkyl chains the distance of 11.2 Å between two diametrically opposite $-\text{NH}_3^+$ end groups is close to the calculated free distance between

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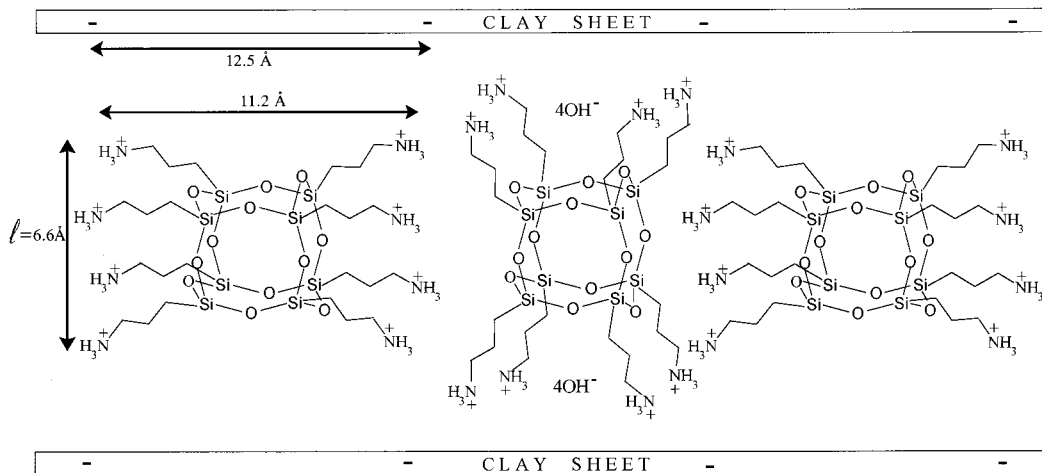


Figure 6. Schematic representation of the arrangement of intercalated $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]$ cubes in Na^+ -montmorillonite.

two negative sites, 12.5 Å, in the clay framework for a montmorillonite with a CEC of 80 mequiv/100 g of clay. Accordingly, a flat orientation of the cubes in the interlayer zone of the mineral offers a good match between the negatively charged sites of the clay surfaces and the positively charged $-\text{NH}_3^+$ groups of the cubes, as shown in Figure 6. As a result of this matching between the opposite charges, a spontaneous assembly of the cubes is anticipated to take place at these positions upon contact of a $(\text{H}_2\text{N}-\text{Pr})_8\text{Si}_8$ solution with a clay dispersion. Furthermore, in this configuration the empty space between the electrostatically bound cubes can be used to provide the necessary hydrophobic environment for hosting additional silicate cubes in the form of ion pairs. In view of the enhanced d spacing, observed for the unwashed samples, we propose that these additional ion-paired cubes have their side alkyl chains directed in an upward position in the interlayer zone, as shown in Figure 6. Fitting of the terminal $-\text{NH}_3^+$ groups into the hexagonal cavities of the clay layers and certain deformation of the alkyl chains could lead to the observed d spacing of 18.5 Å, somehow smaller than the expected distance of 21 Å for a fully extended lateral orientation of the alkyl groups.⁵ This tentative model for the orientation of the silicate cubes in the clay interlayers is further reinforced by infrared evidence as will be discussed later.

After a washed sample was calcined at 500 °C the interlayer distance was slightly decreased from 15.9 to 15.7 Å. This small difference favors further the parallel orientation of the side organic chains in a washed sample. In such a geometry, the removal of the alkyl chains by calcination would hardly affect the d spacing, as was indeed observed. Finally, for the calcined sample the intersheet separation, $\Delta = 15.7 - 9.6 = 6.1$ Å, indicates that the silica pillars comprise two silicon atom layers, since previous studies have shown that one layer of silicon atoms yields a thickness of 3.0 Å.¹⁵

Infrared Spectra. The infrared spectra, shown in Figure 7, were recorded from clay- $(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8^{8+}$ samples that were rinsed once (a) and four times with water (b). In the region 1350–1600 cm^{-1} , spectrum (a) exhibits strong bands around 1560 and 1500 cm^{-1} , associated with the deformation vibrations of the $-\text{NH}_3^+$ groups, and also a number of weaker bands at lower frequencies attributed to bending vibrations of CH_2 and

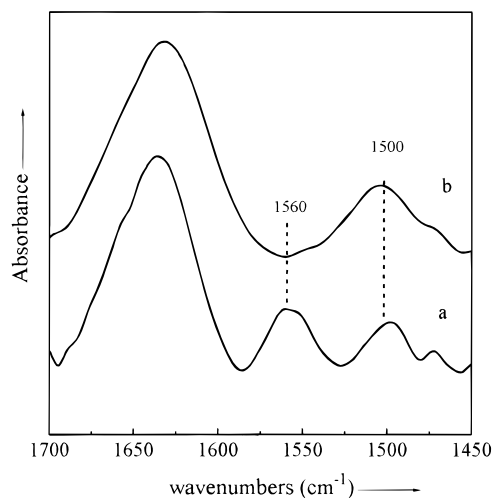


Figure 7. Infrared spectra of clay- $(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8^{8+}$ samples, washed once (a) and four times with water (b).

CH_3 units. The $-\text{NH}_3^+$ deformation vibrations are of particular value in assigning the orientation of an alkylamino group in the lamellar space of a clay. In a previous infrared study of the butylammonium cation intercalated in montmorillonite, the bands at 1560 and 1500 cm^{-1} were assigned to the symmetric deformation vibration of the $-\text{NH}_3^+$ group with different orientation of the aliphatic chains in the interlayer space.¹⁶ Specifically, the lower band at 1500 cm^{-1} was assigned to $-\text{NH}_3^+$ vibrations in which the C_3 axis of the group is oriented parallel to the layers, while the band at 1560 cm^{-1} is a similar vibration but with the C_3 axis inclined to the silicate layers. In accord with these findings, we associate the bands at 1500 and 1560 cm^{-1} in the spectrum of the once-washed sample to the presence of two different conformations of the $-\text{NH}_3^+$ of the silicate cubes in the clay layers. In the first, each alkyl chain of the silicate cube coincides with the C_3 axis of the terminal $-\text{NH}_3^+$ groups, and therefore all chains are parallel to the clay layers. In this conformation the NH_3^+ groups are fixed at the exchange sites of the mineral. The second conformation, associated with the $-\text{NH}_3^+$ deformation at 1560 cm^{-1} , results from an orientation where the aliphatic chains are inclined at a

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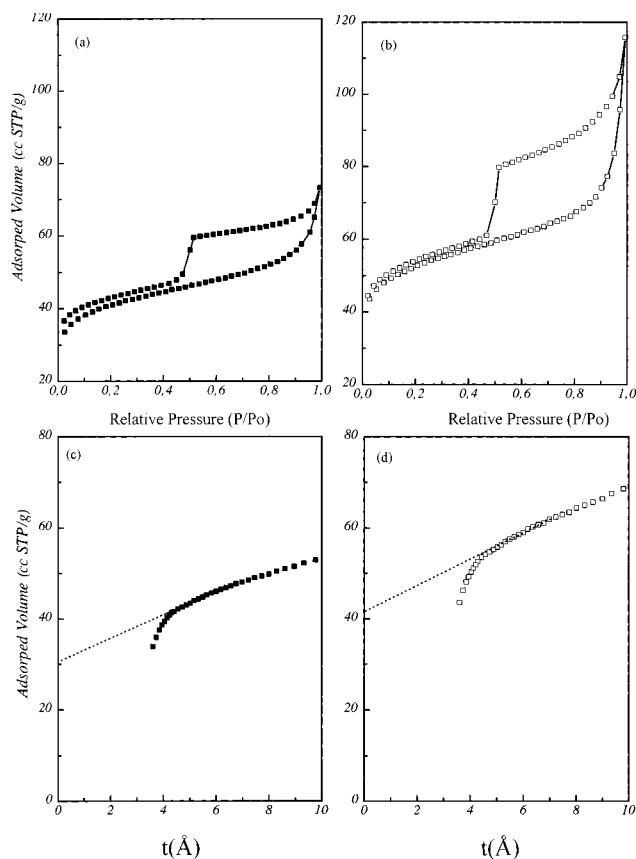


Figure 8. Adsorption–desorption isotherms (upper) and the representative t -plots (lower) from clay– $(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8^{8+}$ samples, washed once (a, c) and four times with water (b, d).

certain angle to the silicate layer. This is the orientation taken up by the physically adsorbed ion-paired cubes hosted in the empty space between the electrostatically bound cubic units (Figure 6). Inspection of spectrum (b), from the washed sample, shows that the band at 1560 cm^{-1} is missing. This is evidence that the band at 1560 cm^{-1} is derived from the ion-paired, washable cubic units. An alternative interpretation of the infrared data could be based on hydrogen-bonding interactions between protonated and partially protonated silsequioxane units. Hydrogen-bonding associations in aqueous media have been reported in the absorption of ethylenediamine by ethylenediammonium montmorillonite.¹⁷ Such associations are manifested in the infrared spectra by two $\text{N}^+-\text{H}\cdots\text{N}$ deformation vibrations, one asymmetric at 1637 cm^{-1} and one symmetric at 1538 cm^{-1} . It is very important that these vibrations did not disappear when the clay suspensions were washed with water. These characteristic vibrations of hydrogen-bonded clusters are not present in either spectrum (a) or (b), the strong band at about 1650 cm^{-1} arises from vibrations of interlayer water. The infrared spectra therefore do not support the formation of hydrogen bonded cubic polymeric associations in the clay interlayers.

Surface Area Measurements. The nitrogen adsorption–desorption isotherms for clay samples first intercalated with the cubic octamer and then calcined at $500\text{ }^\circ\text{C}$ are presented in Figure 8. The isotherm

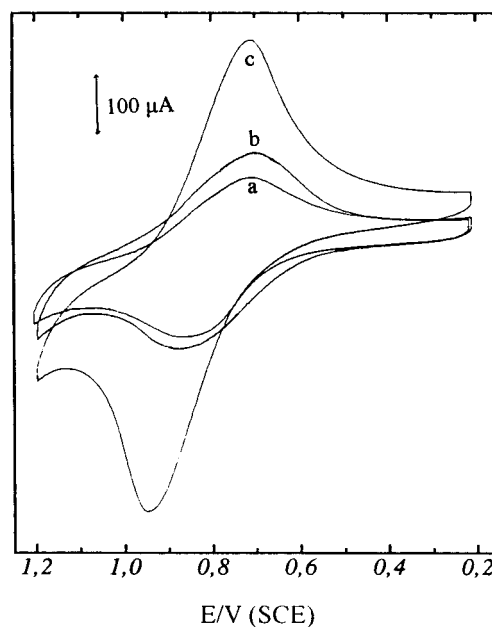


Figure 9. Cyclic voltammograms (100 mV s^{-1}) of K_2IrCl_6 , 1 mM in 0.1 M acetate buffer at $\text{pH} = 4$ on (a) a bare graphite electrode and the same electrode modified with clay–APTEOS compositions, (b) APTEOS loading 1 CEC, and (c) 3 CEC.

designated by (a) stems from the sample once washed and that by (b) from a thoroughly water-washed sample. The adsorption data were treated with the BET equation in the linear part of the isotherm and with the t -plot method. Both samples show a large hysteresis loop illustrative of a mesoporous structure with a contribution from micropores. The corresponding t -plots are also representative of micropores in the presence of mesopores.¹⁸ The BET surface area was $142\text{ m}^2/\text{g}$ for the unwashed and $168\text{ m}^2/\text{g}$ for the washed sample. The washed sample with the higher surface area had a total pore volume of $0.179\text{ cm}^3/\text{g}$ with $0.076\text{ cm}^3/\text{g}$ attributable to micropores, whereas the low surface area once-washed sample had a total pore volume of $0.123\text{ cm}^3/\text{g}$ with the micropores volume being $0.064\text{ cm}^3/\text{g}$. The slit width of the pores, which can be estimated from the lower linear portion of the t -plots (Figure 8c,d) was in the range $0.7\text{--}0.9\text{ nm}$ for both samples. From the higher surface area observed for the washed sample we may conclude that repeated washing of the material causes the evacuation of the micropores from the ion-paired intercalated species that otherwise stuff the empty space of the clay galleries. It is likely that the ion-paired silicate cubes, if remained in the galleries, could generate during calcination aggregates that hinder the entrance of the N_2 molecules into the labyrinth of the pillared structure and thus result in lower values of surface area and porosity for the unwashed clay.

Cyclic Voltammetry. The use of Laponite clay pillared with the cubane-like $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]^{8+}$ octamers for electrode surface modification and the ion-exchange properties of the resulting coatings have been reported.¹⁹ The present electrochemistry results are intended to demonstrate the ability of montmorillonite

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to bind the octameric $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]^{8+}$ cubes not only at its exchange sites but also in the form of physically adsorbed ion-paired $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8](\text{X})_8$ species. The latter can participate in an anion exchange reaction in which X^- is replaced by some other anionic, redox-active species present in solution, e.g., IrCl_6^{2-} . As a result of this exchange the redox-active anions are effectively preconcentrated within the clay coating. Figure 9 compares the cyclic voltammetric response from K_2IrCl_6 , 1 mM solution in 0.1 M acetate buffer at $\text{pH} = 4$, recorded with a bare graphite electrode (a), and with the same electrode modified with a film of sodium montmorillonite loaded with $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8]^{8+}$, 1 CEC (b) and 3 CEC (c). It is easily seen that the IrCl_6^{2-} is concentrated within the clay coating, leading to an enhanced current response compared to the unmodified electrode response, only when the quantity of intercalated octamer exceeds the CEC of the mineral, curve (c). The electrode from experiment (c), i.e., coated with IrCl_6^{2-} -APTEOS-CME, was then transferred to pure electrolyte solution. The current intensity accounted for

about 70% of the previously accumulated electroactive species. Rinsing the electrode in pure water four times and then immersing it again into the electrolyte solution gave a CV very similar to the response from (b). Obviously, this time leaching of the ion-paired $[(\text{H}_3\text{N}-\text{Pr})_8\text{Si}_8][\text{IrCl}_6]_4$ into the aqueous solution deprives the clay coating from most of the electroactive IrCl_6^{2-} anions.

Conclusions

The main conclusion of this work is the high tendency of smectite clays to insert into their surfaces three-dimensional organosilicon oligomers in amounts exceeding the CEC of the mineral, the excess being in the form of physically adsorbed ion pairs. The presence of ion-paired silsesquioxanes in the clay galleries influences the free distance between the layers and the surface area and porosity of the silica-pillared compositions.

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