STABILITY OF *n*-BUTYLAMMONIUM VERMICULITE IN POWDER AND FLAKE FORMS

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Abstract—Interaction between *n*-butylammonium (BA) chloride and vermiculite from Santa Olalla (Spain) has been studied in large flake (5 × 5 × 0.1 mm) or ground powder (≤80 μm) samples. The differences in adsorption and decomposition of BA ions in both particle sizes have been established. In the interlamellar space, the BA ion remains unaltered in powder samples, but is degraded in flakes. The experimental results suggest decomposition of the BA in the interlamellar space of vermiculite flakes by breaking of the C-N bond. The degradation of BA takes place over a short period. The variety with BA in the interlamellar space is transformed into a new one, due to the degradation of alkylammonium. The transformation occurs through an interstratified phase formed between BA-vermiculite and NH_4-vermiculite, and finally a phase appears in which only ammonium is present in the interlamellar space. Due to the many industrial applications of alkylammonium-clays, determination of the stability of alkylammonium in the interlamellar space of clay minerals is of great importance.

Key Words—Adsorption, Degradation, Interaction, Intercalation Complex, Interstratified Phase, *n*-Butylammonium, Organo-Vermiculite, Particle Size, Vermiculite.

INTRODUCTION

Although the theoretical and practical importance of organo-clays was pointed out almost 30 years ago, there has been an increased interest in these materials as sorbents and catalysts in the last few years. The hydrophilic nature of clay minerals can be changed to organophilic by treatment with organic cations that replace the natural inorganic ions by cation exchange. These organo-clays, especially alkylammonium-clays, have many industrial applications, and recently they have been used as sorbents of a great variety of organic pollutants (Mortland et al. 1986; Boyd et al. 1988; Vimondlaboudigue et al. 1996).

Many studies of alkylammonium-silicate complexes have been published. Intercalated montmorillonite-alkylammonium has been studied, in particular, by Jordan (1949), Weiss (1963) and Walker (1967). Micas and vermiculite complexes have been investigated by Michel and Weiss (1957), Lagaly and Weiss (1969), Ghabru et al. (1989), Vimondlaboudigue and Prost (1995) and others. The geometry and mechanism of interaction between vermiculite and alkylammonium have been studied by Weiss et al. (1958), Johns and Sen Gupta (1967), Serratosa et al. (1970) and González-Carreño et al. (1977). A detailed description of alkylammonium methodology has been provided by Lagaly (1994). When the charge on the 2:1 layer is tetrahedrally located, the combined effect of electrostatic and H-bond interactions determines the keying of the NH_3 groups of alkylammonium ions into the ditrigonal cavities (Martín-Rubí et al. 1974). A recent study of layer charge determination and alkylammonium ion-exchange technique is reported by Mermut

(1993). Mermut (1994) discusses difficulties in layer charge determination of high-charge 2:1 phyllosilicates. The phenomenon of osmotic swelling occurs only with vermiculite. This effect was observed by Garret and Walker (1962) for short chain alkylammonium vermiculite and by Rausell-Colom et al. (1989) for ornithine-vermiculite. The swelling of BA-vermiculite has recently been reported by several workers (Smalley et al. 1989; Crawford et al. 1991; Lee and Solin 1991; Fan et al. 1992; Williams et al. 1994). Lee and Solin (1991) and McCarney and Smalley (1995) have studied swollen samples of *n*-alkylammonium vermiculite by X-ray diffraction (XRD) and electron microscopy.

Decomposition of adsorbed amines and alkylammonium-smectite complexes proceeds above 100 °C, as suggested by others (Weiss and Roloff 1963; Chaussidon and Calvet 1965; Chou and McAtee 1969; Durand et al. 1972). De la Calle et al. (1996) have studied the evolution upon heating of 1-ornithine and of benzylammonium-vermiculite complex. For vermiculite saturated with benzylammonium cations, the stacking sequence is altered by changing benzylammonium to NH_4. Frenkel and Solomon (1977) have observed spontaneous decomposition during storage of montmorillonite with quaternary ammonium ions in nitrogen or oxygen atmospheres at room temperature.

Partial decomposition of the decylammonium cations on vermiculite powder surfaces is also observed at 70 °C, if the complex is treated with nonaqueous solutions or highly acidic solutions (Pérez-Rodríguez et al. 1985; Pérez-Rodríguez et al. 1988). Morillo et al. (1990) have reported the decomposition of alkylammonium cations adsorbed on vermiculite powder
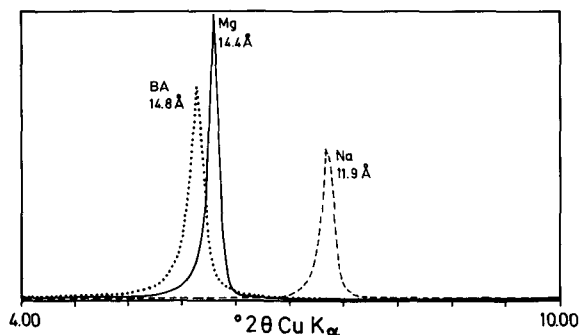
Figure 1. The $d(002)$ diffraction peak of vermiculite ≤ 80 μm saturated with Mg, Na and BA.

under normal conditions of temperature, pressure and humidity after at least 1 y of storage. Alkylammonium cations are partially decomposed into aliphatic chains and the ammonium ions, which remain in the interlamellar space. The reaction between ammonia and clay minerals has been reported by several authors and the adsorption mechanism is fairly well understood (Stone and Wild 1978). The formation and study of interstratified phases in the transformation of Mg to NH_4 vermiculite has been carried out by Ruiz-Conde et al. (1997).

Due to the many industrial applications of alkylammonium-based clays and the new applications of them as adsorbents of organic pollutants, determination of the stability of alkylammonium in the interlamellar space of clay minerals is of great importance, in particular under normal environmental conditions. The goal of this work is to investigate the difference in the adsorption and decomposition of alkylammonium cations in the interlamellar space of vermiculite between powder (≤ 80 μm) and flake samples.

MATERIALS AND METHODS

The vermiculite samples were obtained from the Santa Olalla deposit (Huelva, SW Spain). Its origin, mineralogy and structure have been extensively studied (González-García and García-Ramos 1960; Justo 1984; Justo et al. 1986).

The samples were used in 2 forms: cut flakes ($>5 \times 5 \times 0.1$ mm) and milled powder (≤ 80 μm). Vermiculite powder was obtained using a Retsch Ultra-Centrifugal Mill, model ZSM-1. Both flake and powder samples were treated with saturated NaCl solutions and heated under refluxing conditions. After washing the product with deionized water to eliminate the excess Cl ions, the samples were treated twice with an aqueous 1 mol dm^{-3} BA hydrochloride ($>99\%$, Merck) solution at pH 7 and heated under refluxing conditions during 2 h. The samples were then washed with deionized water to eliminate Cl ions. Flakes previously saturated with Na were also treated with an aqueous BA hydrochloride solution at 70 °C, instead

of at reflux temperature, and for different soaking times (from 5 to 270 min).

The original and reaction products were identified by XRD, using a diffractometer (Siemens Kristalloflex D-501). The infrared (IR) absorption spectra were recorded from 4000 to 400 cm^{-1} using a Nicolet 510-FTIR spectrophotometer. Samples were examined as KBr discs. The C content in the interlamellar space of the vermiculite was measured using a Perkin Elmer elemental analyzer (240-C). Total N was determined using the Kjeldahl method, by digestion of the sample with concentrated H_2SO_4 and a catalyst (Se + K_2SO_4), and displacement of N (as NH_4) with NaOH (50% w/ v) in a vapor stream. The NH_4 ions from the interlamellar space of the vermiculite were determined by displacement with Mg. In both cases the distilled fraction was collected on H_3BO_3 (4% w/v), and the excess was titrated with 0.02 N HCl.

The interstratified phases were studied using the INTER program (Vila and Ruiz-Amil 1988). The program allows the calculation of diffraction effects from given mixtures (XRD intensity function) and compares them with experimentally recorded diffraction curves (Ruiz-Amil et al. 1967; Vila and Ruiz-Amil 1988; Ruiz-Amil et al. 1992). This program was also used to calculate the distribution function of interlayer distances, $W(R)$, by the direct Fourier-transform method (MacEwan et al. 1961). $W(R)$ is defined as the probability of finding a layer at a distance R (in Å). From the peak heights of the curves of the $W(R)$ function, the values of the probability coefficients are calculated by a direct relation, as given by MacEwan et al. (1961); P_A and P_B are the probabilities of the existence of A and B spacing, respectively; P_{AA}, P_{AB}, P_{BA}, P_{BB} are, respectively, the probabilities of A succeeding A, A succeeding B, B succeeding A and B succeeding B, in a given direction through the crystal.

RESULTS

Vermiculite Powder (≤ 80 μm)

Figure 1 shows the $d(002)$ diffraction of the ≤ 80 μm vermiculite powdered sample saturated with Mg, Na and BA ions. The original sample yields a diagram corresponding to a Mg-vermiculite (de la Calle et al. 1988). The Na-vermiculite gives a 2-layer complex with 14.8-Å spacing. At low relative humidity (about 50%) a 1-layer complex is stable with a spacing of 11.9 Å, enabling easy checking of the extent of Mg/ Na exchange. In our experimental conditions this last d-value is obtained. The X-ray diagram of the ≤ 80 μm vermiculite saturated with Na shows a diffraction at 11.9 Å and its rational series that are consistent with a complete exchange of the Mg cation, originally present in the interlamellar space, by Na. The vermiculite saturated in BA shows a 14.8-Å spacing with a rational series of $d(00l)$ reflection that did not change after

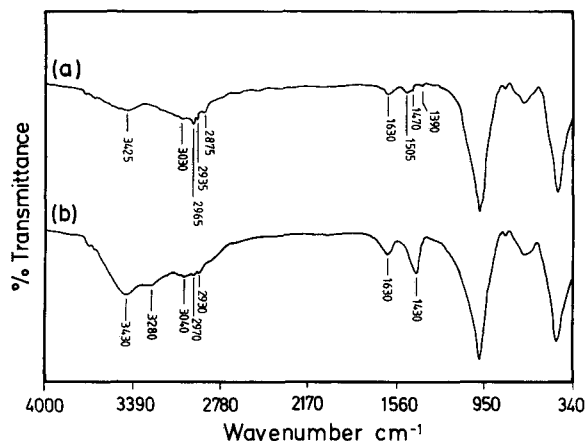Figure 2.   IR spectra of vermiculite ≤ 80 μm saturated with BA (a) and vermiculite flakes saturated with ammonium (b).

Figure 3.   The $d(002)$ diffraction peak of vermiculite flakes saturated with Mg, Na and NH_4.

6 mo of the treatment. These reflections correspond to BA ions in the interlamellar space.

The IR spectra of the original vermiculite and that saturated with Na show characteristic absorption bands of vermiculite with Mg or Na in the interlamellar space in accordance with Farmer (1974). The sample saturated with BA ions (Figure 2a) shows characteristic bands corresponding to the CH_3, CH_2 and $-NH_3^+$ groups. The CH_3 groups give bands at 2965 cm^{-1}, asymmetric C-H stretching; 2875 cm^{-1}, symmetric C-H stretching; 1470 cm^{-1}, asymmetric C-H bending; and 1390 cm^{-1}, symmetric C-H bending. The CH_2 groups produce bands at 2935 cm^{-1}, asymmetric C-H stretching; 2875 cm^{-1}, symmetric C-H stretching; and 1490 cm^{-1}, scissoring. All of these values are in agreement with the study reported by Serratosa et al. (1970).

The $-NH_3^+$ groups give absorption bands at about 3030 cm^{-1}, corresponding to the N-H stretching vibrations; and at 1630 and 1505 cm^{-1}, which are associated with the asymmetrical and symmetrical N-H deformation vibrations, respectively. This last absorption band appears in the region between 1580 and 1500 cm^{-1}. The higher and lower values indicate a strong or weak hydrogen bond, respectively (Serratosa et al. 1970). The absorption band corresponding to the symmetric deformation vibration of the $-NH_3^+$ group in the powder BA-vermiculite sample appears at 1505 cm^{-1}, in agreement with a weak hydrogen bond (Laby and Walker 1970; Serratosa et al. 1970). These absorption bands correspond to the presence of BA intercalated in the interlamellar space. The band at 1630 cm^{-1} also corresponds to the OH deformation of water, because the OH stretching band at 3425 cm^{-1} suggests the presence of some interlamellar water. These XRD and IR results show that the formation of BA-vermiculite complex has been taken place.
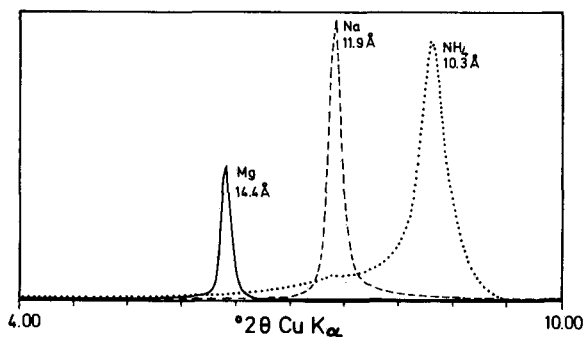
Vermiculite Flakes

Figure 3 shows the $d(002)$ diffraction peak produced by flakes ($>5 \times 5 \times 0.1$ mm) after Mg and Na saturation and treatment with BA. The XRD patterns of vermiculite saturated with Mg and Na ions are similar to those of vermiculite of particle size ≤ 80 μm, as described above. Diffraction maxima appear at 14.4 and 11.9 Å with their rational series corresponding to Mg- and Na-vermiculite, respectively (Reichenbach and Beyer 1994). However, after the treatment with BA, the X-ray diagram pattern observed using flakes is completely different from that obtained using particle size of ≤ 80 μm. The $d(002)$ diffraction peak appears at 10.3 Å together with its rational series corresponding to a vermiculite with interlamellar NH_4.

The IR spectrum of vermiculite saturated in Mg or Na shows the characteristic absorption of this mineral with Mg or Na in the interlamellar space. The spectrum of the flake sample treated with BA (Figure 2b) shows many differences from that observed for the powder sample. The absorption bands at 1430, 3040 and 3280 cm^{-1} are characteristic of the ammonium ion in the interlamellar space in accordance with previous reports of Ahlrichs et al. (1972) and Stone and Wild (1978). Furthermore, weak bands in the 2975–2925 cm^{-1} region of the C-H of CH_3 and CH_2 groups are present in addition to water bands at 3430 and 1630 cm^{-1}.

The NH_4 exchange capacity of the flakes after treatment with BA is 137 cmol kg^{-1} of clay, which is similar to the 140 cmol kg^{-1} reported for the original vermiculite by Justo (1984). Carbon is practically absent from this sample after treatment with BA.

Our data show a great difference between the complexes obtained after alkylammonium treatment of flakes and ≤ 80 μm particles which can be explained in the following way. The NH_4 present in the interlamellar space of vermiculite flakes is produced by decomposition of BA. First the alkylammonium cation is adsorbed between the layers of vermiculite, and later it is decomposed into aliphatic chains and the ammo-
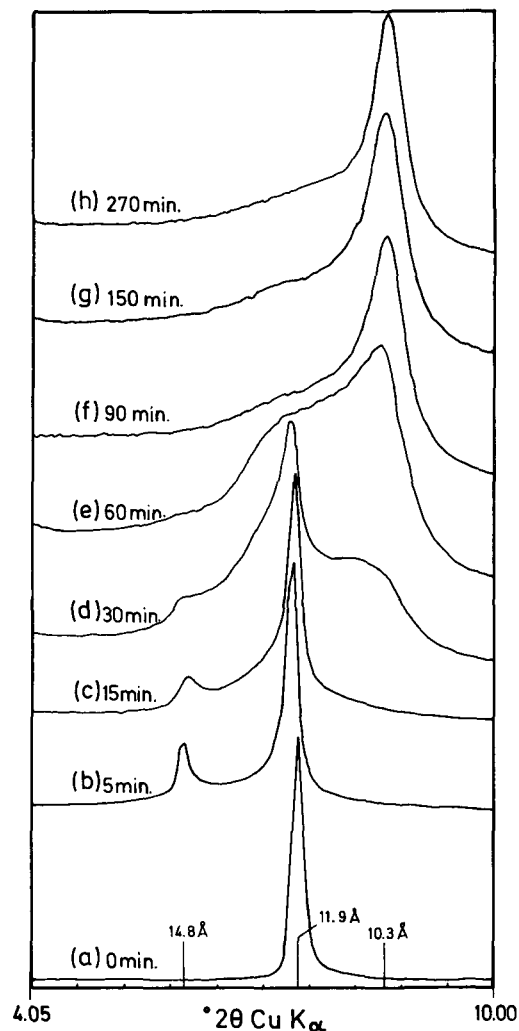
Figure 4. The $d(002)$ diffraction of a vermiculite flake treated with BA for 5–270 min.

nium ion. The former is removed while the latter remains in the interlamellar space as an exchangeable cation. In order to confirm this mechanism, the treatment of vermiculite with BA was carried out at different soaking times and lower temperatures and the products were X-rayed.

Figure 4 shows the $d(002)$ intensity profiles obtained at different times between 5 and 270 min. As the treatment time increases, the intensity of the 11.9-Å diffraction peak decreases, the peaks of the interstratified phase of 10.3 and 14.8 Å appearing. At the beginning of the experiment, the new 14.8-Å phase (BA-vermiculite) is also observed. After 60–90 min of treatment, the 10.3-Å diffraction is predominant. From the XRD results, it can be deduced that a diffraction at 14.8 Å appears first and that this later changes to an interstratified phase of 10.3 and 14.8 Å, and finally to 10.3 Å.

In the X-ray diagram of Na-vermiculite flakes treated with BA solution for 5 min at 70 °C, diffraction maxima appear at 11.9 and 14.8 Å (Figure 4b). These and related peaks were studied using the INTER program (Vila and Ruiz-Amil 1988). The 11.9-Å peak produces a rational series and the $W(R)$ function (Figure 5) corresponds to a segregated phase. The sequence of the interlayer distances for this segregated phase is 11.9 Å (A), 23.8 Å (AA), 35.7 Å (AAA), etc. (Figure 5a). The 14.8-Å peak produces a rational series and the $W(R)$ function corresponds to a second segregated phase. The interlayer distances for this phase are 14.8 Å (A), 29.6 Å (AA), 44.4 Å (AAA) (Figure 5b). From the peak heights in the $W(R)$ functions, the values of P_A (proportion of A layers), P_B (proportion of B layers), P_{AA} (probability of A succeeding A) and P_{BB} (probability of B succeeding B) are obtained. Subsequently, $P_A = 0.99$, $P_{AA} = 0.99$, are found in both cases. These $W(R)$ functions correspond to the Na-vermiculite and BA-vermiculite complex, respectively.

The formation of an interstratified phase is also suggested. This phase may be characterized by a 10.3-Å and 14.8-Å binary interstratification. The peaks occurring on the curve (Figure 5c) can be assigned to interstratified 10.3-Å (A) and 14.8-Å (B) layers. From the $W(R)$ function it is deduced that: $P_A = 0.35$, and $P_{AA} = 0.40$. Figure 5d shows the $W(R)$ function of the sample after 30 min of treatment at 70 °C and a similar interstratified phase is deduced in which $P_A = 0.75$ and $P_{AA} = 0.65$. The $W(R)$ function obtained from the sample after 270 min of treatment at 70 °C corresponds to an interstratification with high values of P_A (0.90) and P_{AA} (0.90) (Figure 5e).

Table 1 shows the evolution of P_A and P_{AA} values for the NH_4-vermiculite phase in the interstratification obtained from the distribution functions of interlayer distances. The existence of an interstratified phase between a phase at 10.3 Å (ammonium-vermiculite) and at 14.8 Å (BA-vermiculite) is indicated. The P_A and P_{AA} values increase with time.

DISCUSSION

The IR spectra of the Na-vermiculite flakes treated with BA at 70 °C show absorption bands corresponding to amine group, aliphatic chains and ammonium ions, besides the characteristic bands of the silicate network. The alkylammonium is present in the interlamellar space at short treatment times, and the bands corresponding to NH_4 between the layers are more and more intense after longer treatment times. Although it is difficult to observe because of the rate of degradation, at short times, the symmetric deformation of the NH_3 group seems to appear at 1565 cm⁻¹, which indicates a stronger hydrogen bond than in powder.

From XRD data, the following mechanism of BA intercalation and degradation can be deduced. Accord-
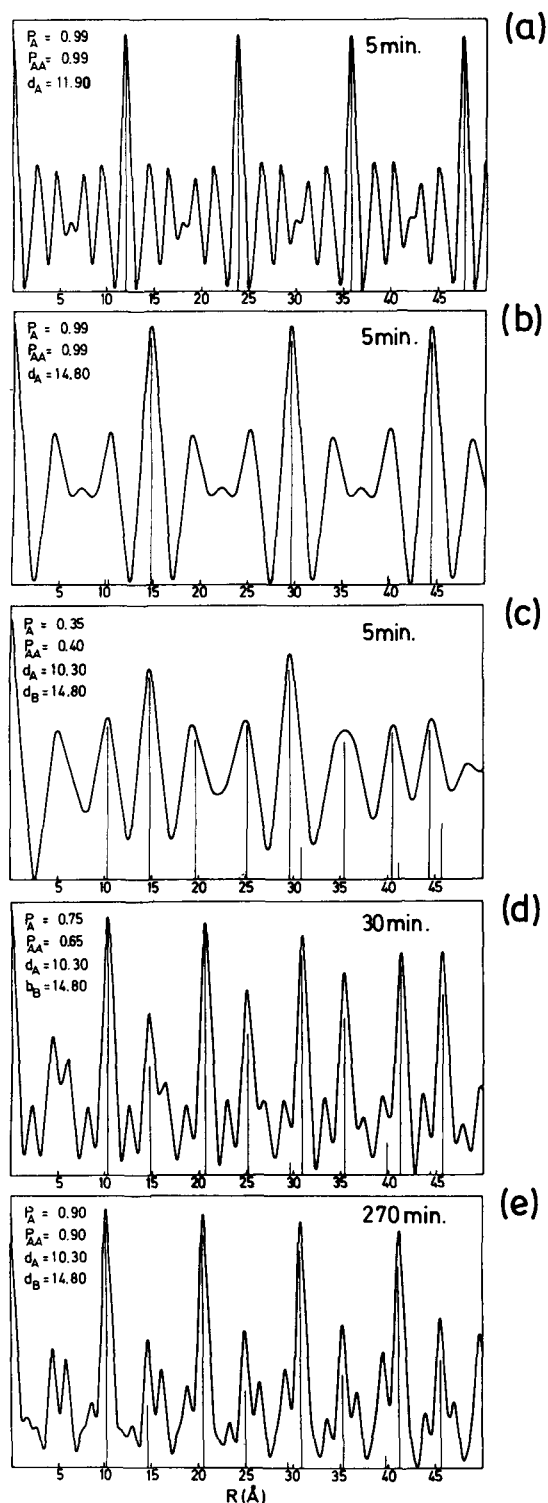
Figure 5. Distribution function of vermiculite flake sample treated for 5 min at 70 °C showing a segregated Na-V phase (a); a segregated *n*-BuNH₃-V phase (b); and a binary interstratification between NH₄-V (A) and *n*-BuNH₃-V (B) phases (c). At 70 °C for 30 min, binary interstratification between NH₄-V (A) and *n*-BuNH₃-V (B) phases appears (d). At 70 °C for 270 min, a binary interstratification between NH₄-V (A) and *n*-BuNH₃-V (B) phases is detected (e).

Table 1. Evolution of P_A and P_{AA} values for the NH₄-vermiculite phase in the interstratification between ammonium-vermiculite and BA-vermiculite.

Time (min)	P_A	P_{AA}
5	0.35	0.40
15	0.50	0.45
30	0.75	0.65
60	0.90	0.90
90	0.85	0.80
150	0.90	0.85
270	0.90	0.90

ing to the $d(00l)$ of 14.8 Å and its rational series, the BA-vermiculite complex is formed. The degradation of BA takes place within a short period. The phase with BA in the interlamellar space is transformed into a new one, due to the degradation of alkylammonium. Interstratification forms between BA-vermiculite and NH₄-vermiculite. Finally, a vermiculite phase appears with only ammonium in the interlamellar space. This transformation implies a sliding of the layers over each other. The ditrigonal surface cavities become face to face, as in the original mica. There are no random translations as in the starting complex (de la Calle et al. 1996).

The experimental results obtained suggest decomposition of the BA in the interlamellar space of vermiculite flakes by breaking of the C-N bond. This is attributed to the high acidity of the small amount of water present in the system, which is strongly dissociated (Mortland et al. 1963; Pérez-Rodríguez et al. 1988). The breaking of the C-N bond is partially favored by the way in which the -NH₃⁺ groups of the BA cations are located on the hexagonal (ditrigonal) holes, and as a result, the interaction between the -NH₃⁺ groups and the negative charge of the clay is strong (Vimondlaboudigue and Prost 1995), and the C-N is weakened. The degradation of the BA ion in flakes is rapid, however; with the ≤80 µm vermiculite powder, the alkylammonium remains unaltered in the interlamellar space for a period of at least several months.

It is noteworthy that the complexes obtained by the treatment of vermiculite flakes or ≤80 µm powder with BA, under the same experimental conditions, are completely different. In the interlamellar space, the BA is degraded when flakes are used but remains unaltered during our experiments when small particles are used. It is difficult to explain this difference, but there are probably 2 reasons. First, the ≤80 µm particles are obtained by grinding, producing breakage in the crystals that are responsible for Fe oxidation and loss of O and OH, decreasing the interlamellar charge. The variation in the interlamellar charge with particle size was shown by Robert et al. (1987). Therefore, the interaction with -NH₃⁺ groups of BA is weaker than in

flakes (as has been confirmed by the position in the symmetric deformation of the NH_3 group). The second reason is that the proportion of water in the interlamellar space of the ≤ 80 μm particles is higher (as a result of a lower lamellar charge and easier diffusion) than in flakes. This produces less acidity in the interlamellar space, making the degradation of BA more difficult. The dissociation of the interlayer water is favored by a high BA/H_2O ratio, in contrast to the dilute aqueous solutions in which the stability constants are measured (Mortland and Raman 1968).

The weaker interaction between $-NH_3^+$ groups and the clay mineral surface and lower (at least partially) acidity in the interlamellar space of ≤ 80 μm particles than in vermiculite flakes may be responsible for the greater stability of alkylammonium in the ≤ 80 μm particles.

CONCLUSIONS

In the interlamellar space, the BA ion remains unaltered in powder samples, but is degraded in flakes. The BA is decomposed in the interlamellar space of vermiculite flakes by breaking of the C-N bond. The degradation of BA takes place over a short period. The phase with BA in the interlamellar space is transformed into a new one, due to the degradation of alkylammonium. The transformation is carried out through an interstratified phase formed between BA-vermiculite and NH_4-vermiculite, and finally a phase appears in which only ammonium is present in the interlamellar space. It is difficult to explain this difference, but there are probably 2 reasons. First, the ≤ 80 μm particles are obtained by grinding, decreasing the interlamellar charge. Second, the proportion of water in the interlamellar space of the ≤ 80 μm particles is higher than in flakes. This produces less acidity in the interlamellar space, making the degradation of BA more difficult.

ACKNOWLEDGMENTS

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