

Long-range organization in the ammonium propionate intercalation complexes of kaolinite

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Abstract

Intercalation complexes have been prepared from kaolinite and ammonium propionate in a stepwise procedure, by using hydrazine displaced by ammonium acetate in order to form a 14 Å complex. At this stage the interlayer bonding energy drops to a minimum. Ammonium propionate intercalation complexes showing very sharp 001 reflections can then be obtained under well-specified hydration conditions.

Starting with a single complex, during a process of dehydration a series of complexes is produced which have *d* spacings ranging from 12–25 Å depending upon the state of hydration and the arrangement and particular species of ions among the clay layers. Characterization studies by infrared suggest the path of reaction which leads from one complex to another. The data from chemical analyses coupled with experimental results obtained from differential scanning calorimetry suggest the structural role of the water.

The several models proposed indicate that spacing transitions between the various complexes result from the formation of water bridges between ammonium propionate molecules, the anchoring to the internal OH layer being achieved by hydrogen bonding with the carboxyl group. The intercalated propionate solution may be considered as forming a quasi-liquid crystal organized within the kaolinite interlamellar space.

Introduction

Many kinds of polar molecules intercalate within the interlamellar space of kaolinite. So far, however, attention has been mainly directed either toward the modification of the kaolinite structure provoked by such an intercalation process or toward the arrangement of the intercalating molecules with respect to the kaolinite layers. Much less consideration has been given to the properties of the bidimensional fluid contained between the parallel planes of the intercalated kaolinite surfaces. From this viewpoint, intercalation complexes (intercalates) made from fatty-acid salts are of particular interest, since a large expansion along the *c* axis can be obtained when these salts enter the interlamellar space along with water. Such intercalates can be considered as made from a bidimensional salt solution confined in a geometrically well-defined space.

Weiss and Schäffer (1963) and Weiss *et al.* (1966) have described a 14 and 17 Å intercalate obtained by reacting ammonium or potassium acetate with kaolinite [(001) = 7.15–7.20 Å]. There is thus an increase of the interlayer distance by either seven or ten

Å as a result of the intercalation of an aqueous concentrated solution of these salts. Weiss *et al.* (1966) also indicate that the use of potassium propionate instead of potassium acetate leads to an intercalate with a (001) spacing of 11.2 Å. Deeds *et al.* (1966) have observed a 21 Å intercalate resulting from adsorption of water by a 14 Å dickite–potassium acetate complex.

This paper describes intercalates of ammonium propionate (AP) with (001) spacings as large as 25.5 Å, and considers the properties of the bidimensional fluid between the kaolinite layers. AP complexes with large interlayer spacings have been obtained by operating in a stepwise manner. The hydrazine of the well-known kaolinite–hydrazine intercalate is replaced by a concentrated solution of ammonium acetate which in turn is replaced by a concentrated ammonium propionate solution. The reason for this sequential operation may be understood by the following considerations. Giese (private communication, 1977) has calculated that there is only a small energy change associated with separation of kaolinite layers beyond 10 Å. The 3 Å separa-

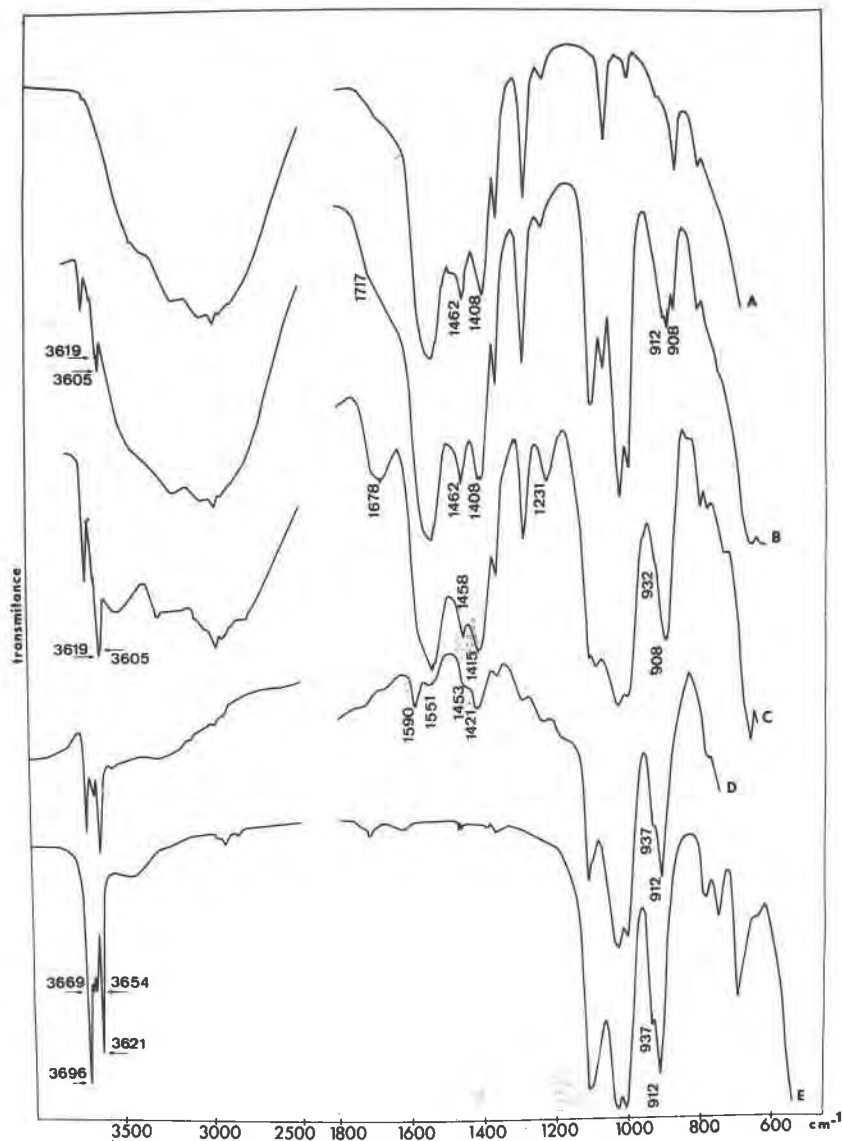


Fig. 1. The IR spectrum of ammonium propionate and its complexes: (A) ammonium propionate (aqueous solution); (B) 25.5A complex; (C) 23.0A complex; (D) 19A complex; (E) Georgia kaolinite (Georgia U.S.A.).

tion of the hydrazine complex is about 30 kcal/mole away from the point where the energy curve levels off, so that energy is required both to displace the hydrazine and to separate the layers. To minimize the energy needed for displacement intercalations, an intercalate of large interlayer spacing is required. There are no known reagents which directly separate the kaolinite layers by more than 10A.

Experimental

The kaolinite-hydrazine complex was prepared as described by Ledoux and White (1966). After recov-

ery by centrifugation, the intercalate was not dried, but was washed immediately with five successive portions of an aqueous saturated solution of ammonium acetate. The resulting 14A product was then immediately washed four times with a saturated aqueous ammonium propionate solution (~1 mole AP/1 mole H₂O). Each washing consisted of dispersing the intercalate in three times its volume of solution for two to three minutes. After centrifugation, the supernatant liquid was discarded and the clay dispersed in a fresh quantity of solution.

Ammonium propionate was prepared by bubbling

Table 1. Basal interplanar spacings, in Å, for some ammonium propionate intercalates

(001)	(002)	(003)	(004)	(005)	(006)	(007)
25.5	12.7	8.4	6.3	5.0	4.2	
23.0	11.4	7.6	5.7	4.5		
19.2	9.6	6.4	4.8	3.8	3.2	2.8
18.2	9.0	6.1	4.5	3.6		
17.3	8.8	5.8	4.4	3.5		

pure ammonia gas into propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$. A saturated aqueous solution was then prepared from the crystalline salt. Because the gradual decomposition of the solution involves NH_3 loss, a small amount of gaseous NH_3 was passed into the solution before each use. An IR spectrum of the solution exposed to air showed a free acid carbonyl band at 1720 cm^{-1} (Fig. 1A) which disappeared upon the addition of NH_3 .

Complexes with spacings of 19Å or less were washed only once with isopropanol before IR measurements were made, because continued washing led to collapse of the complexes. The 25 and 22Å intercalates are not stable in isopropanol. Dry nitrogen, ambient air, or ammonia gas could be circulated around the sample while the X-ray diffractogram was recorded.

A paper-grade Georgia kaolinite and kaolinites from Cornwall (U.K.), Charente and Allier (France) have been used in the present study without noticeably different results.

Results

X-ray diffraction

The intercalate prepared by the addition of ammonium propionate to the 14Å ammonium acetate complex has a (001) spacing of 25.5Å with five higher orders occurring at 12.7, 8.4, 6.3, 5.0, and 4.2Å (Table 1). The peaks are sharp (Fig. 2A). Weaker additional reflections occur in the X-ray trace at 18.2, 9.0, 6.1, and 4.5Å. The (001) kaolinite residual peak is rather weak with a spacing of 7.2Å: about 90 percent of the clay is in the form of a propionate complex.

The reaction product is a mixture of complexes which can have various states of hydration as well as various configurations of molecules between the clay layers, as is demonstrated by the following observations. When the clay mixture is exposed to air for 2 hours, the peaks due to the 25.5Å complex increase in

area by 25 percent, and the peaks due to the 18.2Å complex become weaker. In fact, after one hour the second- and third-order peaks of the 18.2Å complex cannot be seen. The diffractogram of pure 25.5Å complex is shown in Figure 2F.

The 25.5Å complex, upon drying under dry nitrogen a few minutes, collapses to 23.0Å with higher orders at 11.4, 7.6, 5.7, and 4.5Å (Fig. 2B, Table 1). A very weak peak appears at 18.4Å. Both the first- and second-order peaks of the original kaolinite remain very weak. When held for one hour under nitrogen, the clay mixture changes very little except for the development of a very weak second-order peak for the 18.4Å complex. If at this point the nitrogen is replaced by ammonia gas, a mixture of a 23 and 18Å intercalates is obtained (Fig. 2D), the strongest peak being at 18.0Å.

The kaolinite (001) and (002) peaks are weakly developed at 7.3 and 3.6Å. A very weak 14.8Å shoulder changes into a weak maximum after 34 minutes. After 40 minutes of exposure to ammonia, the spectrum has simplified. The strong peak at 22.7Å has collapsed to a vague shoulder at 22.1Å. The 18.0Å peak has intensified and sharpened, although the various orders have the same intensity as previously. A weak kaolinite peak has appeared at 7.1Å.

If the goniometer is set at a constant position corresponding to 25.5Å and dry nitrogen is passed over the complex, one can observe that the collapse of the peak is linear with respect to the square root of the time. The collapse of the 23.0Å complex upon addition of NH_3 behaves similarly. If the 25.5Å complex is exposed *directly* to NH_3 , the transformation into the 18Å intercalate occurs without noticeable transitions through the 23Å complex intermediate. Upon exposing the 18Å complex to air, the 25.5Å peak is regenerated. It was possible to repeat the cycle three times.

Other hydrates of the propionate complex have been prepared simply by allowing the 25Å complex to remain in a desiccator over P_2O_5 for varying times. A 19.2Å complex (Fig. 2C) with a second-order peak at 9.6Å (see Table 1 for higher orders) was produced by leaving the starting complex overnight in the P_2O_5 desiccator. After one week, the complex further collapsed to 17.3Å with higher orders at 8.8, 5.8, 4.4, and 3.5Å (Fig. 2E). After standing for 24 hours under dry nitrogen, the 17.3Å complex developed a peak at 14.5Å, which collapsed to 12.3Å after another 12 hours.

The procedures for obtaining the various complexes are summarized in Figure 3.

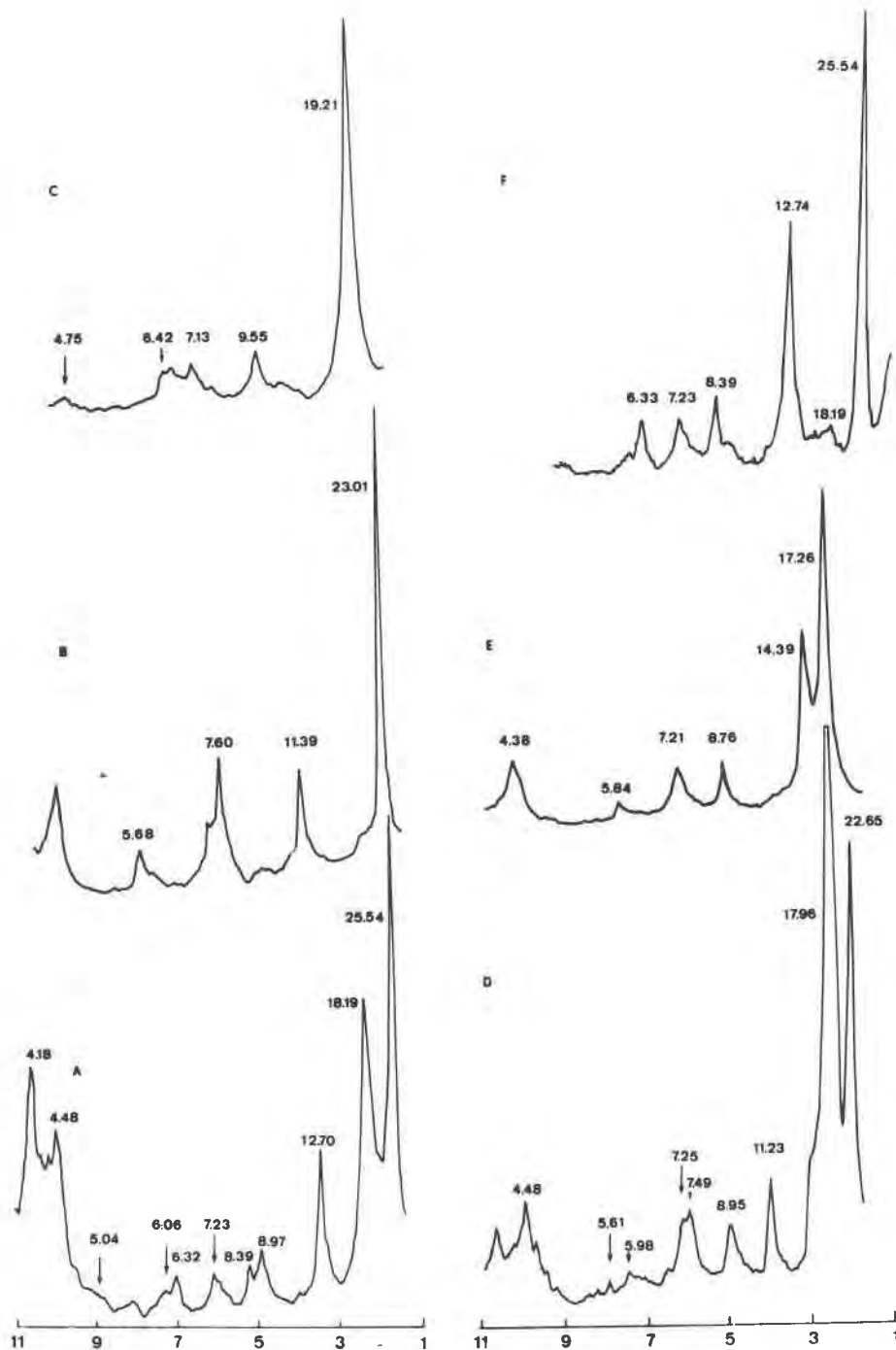


Fig. 2. X-ray diffractograms of ammonium-propionate complexes: (A) 25 + 18A complexes; (B) 23.0A complex; (C) 19.2A complex; (D) 22.7A complex; (E) 17.3A complex; (F) 25A complex. Axis in degrees θ .

Infrared spectroscopy

The IR spectra of the starting kaolinite, of the AP-saturated aqueous solution, and of some of the intercalates are displayed in Figure 1A. They have been

obtained by spreading a thin layer of the corresponding slurry on Irtran windows. Table 2 gives the assignment of the most important IR bands. The IR spectrum of the 25.5A complex exhibits five $\nu(\text{OH})$

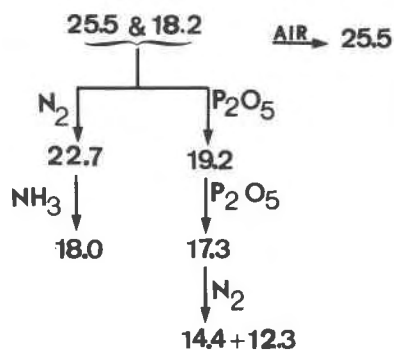


Fig. 3. The decomposition scheme for obtaining the family of ammonium-propionate intercalates (spacing in Å).

stretching bands at 3698, 3668 (shoulder), 3650 (shoulder), 3619 (shoulder), and 3605 cm^{-1} (Fig. 1B). This spectrum is very different from that of the starting material, which shows the first three absorption bands but in different ratios of absorbance (Fig. 1E). The Al-OH bending bands which appear at 937 and 912 cm^{-1} in the unexpanded clay shift to 912 and 908 cm^{-1} in the complex. The remaining bands in the spectra of the 25.5A complex correspond to the unexpanded clay (Fig. 1E) or to an ammonium propionate solution (Fig. 1A).

In the 23.0A complex, prepared by desiccation of the 25.5A complex under N_2 (Fig. 1C), a change in the relative intensities of the OH bands is observed. The shoulders at 3668 and 3650 cm^{-1} become slightly more intense, and the absorption maximum at 3605 cm^{-1} has weakened slightly. A certain amount of water contributing to the broad absorption around 1640 cm^{-1} and to the high frequency region has been

Table 2. Infrared assignments for the ammonium propionate (AP) intercalates

Kaolinite	AP	25.54 Å	22.65 Å	19 Å	
3696 a	3698	3698	3694	} v OH of unperturbed kaolinite lattice	
3669 a	3668	3668	-		
3654 a	3650	3650	3652		
3621 a	3619	3619	3621		
		3605	3605	} Perturbed v OH of the expanded kaolinite	
		3520	3548		
		1717	3298	v OH of AP	
				v - C=O	
			1678	v - C=O hydrogen bonded	
	1551	1551	1590	} v - CO ₂ ⁻ asymmetric : AP	
	1462	1462	1551		
	1408	1408	1453	} δ CH ₃ and CH ₂	
	1367	1367	1421		
	1293	1293	1296	} v - CO ₂ ⁻ symmetric and	
			1231	} δ - NH ⁺ in NH ₄ ⁺ (b)	
	937	912	937	} δ OH of the unexpanded kaolinite.	
	912	908	912		

(a) Ledoux and White (1964), Pampuch and Ptak (1970).
(b) Rao (1963).

lost, and a very definite peak at 3520 cm^{-1} due to perturbed OH vibration of the kaolinite lattice has now appeared. Significantly, the shoulder at 1717 cm^{-1} in the 25.5A complex has been replaced by a strong band at 1678 cm^{-1} (Fig. 1C).

The IR spectrum of the 19.2A complex produced by desiccating the 25.5A complex for several days indicates that much of the ammonium propionate and water have been removed from between the clay layers (Fig. 1D). Only the four OH vibrations of the original kaolinite are present. Although the 3669 cm^{-1} absorption peak is hardly detectable, the 3654 cm^{-1} absorption peak is well developed. A small peak at 3548 cm^{-1} can be attributed to perturbed OH. The Al-OH vibrations in the 19A complex appear at the normal kaolinite positions.

Chemical analyses

The results of elemental chemical analysis of the 17.3, 18.0, and 19.2A complexes are shown in Table 3. Complexes with (001) spacings larger than 19.2A were too unstable to be analyzed in a conventional manner.

The amounts of propionic acid and ammonia were determined independently in the 25.5A complex. Ammonia was analyzed by the Kjeldahl technique, whereas propionic acid content was measured by back titration. The results can be summarized as follows. In the thick expanded clay slurry, propionic acid molecules are combined with ammonia molecules in the expected 1:1 stoichiometry for AP, *i.e.*, the same ratio as in the saturated solution. The amount of free acid, if any, is within the experimental error of the analytical technique.

In 100 g of slurry there are 51.5 g of ammonium propionate, 18.8 g of water, and 30 g of kaolinite. The ammonium propionate:water molecular ratio is thus

Table 3. Chemical analysis and surface area parameters for ammonium propionate intercalates

Product	Analysis	Moles salt/gram of clay x 10 ⁻³	Area of molecule (σ), Å ²	Surface area (S _i), m ²	Moles acid* / moles clay
17 Å	C = 7.04 H = 2.24	1.95	63	739	1.01
18 Å	C = 7.89 H = 2.51	2.19	63	828	1.13
19 Å	C = 8.91 H = 2.92	2.46	63	935	1.27

*One "mole" of clay is the molecular weight of the unit cell, Al₂O₃·2SiO₂·2H₂O

0.56:1.03 in the slurry as compared with 1:1 in the AP starting solution. Dilution may be produced by the water present in the original ammonium acetate intercalate and by absorption of atmospheric moisture.

The same analyses were performed on a sample of the 25.5A intercalate washed with isopropanol several times in order to remove excess AP. This washing provokes the partial collapse of the 25.5A intercalate into intercalate(s) with smaller spacings. In this case 100 g of slurry contains 22 g of ammonium propionate and 32 g of kaolinite. Again, the amount of free propionic acid is within the analytical error. The amount of water here cannot be determined with accuracy because the slurry still contains isopropanol.

The volume of AP solution in the slurry may appear very large at first sight. It should not be forgotten, however, that in the 25.5A intercalate the internal pore volume amounts to about 22 cm³ for the 30 g of clay contained in 100 g of slurry. This figure is obtained by multiplying the internal surface, 400 m²/g, by 18.5A. Since the density of an AP-water solution of molar ratio 1:1 is 1.07 g/ml, out of the 70 g of solution about 24 g of solution are within the layers of the clay. Another fraction is on the clay external surfaces and within pores between particles, and the remainder is present as a free AP solution.

Discussion

The ammonium propionate (AP) intercalate prepared from the 14A ammonium acetate intermediate has a (001) spacing of 25.5A, over three and a half times the (001) spacing of pure kaolinite. This complex is rather labile and its decomposition leads to a family of complexes with a variety of (001) spacings ranging from 12.3 to 22.6A. Decomposition of the complex, which occurs spontaneously in air, can be accelerated by placing the sample in a stream of dry nitrogen or NH₃. The decomposition, therefore, is actually a degassing process in which water vapor and/or NH₃ gas are lost. Indeed, the basal spacings observed, 12.3, 14.5, 17.3, 19.2, 23.0, and 25.5A, differ by 2–3A, roughly the diameter of NH₃ or water molecules. Which complex is obtained depends on the dehydrating agent and drying process. Figure 3 summarizes the manner in which the various complexes are obtained. The collapse from 25.5 to 23.0A in an atmosphere of N₂ and the collapse from 23.0 to 18.1A are probably both due mainly to dehydration, although some NH₃ is lost as evidenced by IR (see further). The treatment by gaseous NH₃ provokes dehydration and as expected reduces the decomposition of AP into propionic acid. Indeed the 25.5A

complex cannot be formed by treatment of the 23.0A intercalate with NH₃. The interchange is reversible as is seen by the regeneration of the larger spacing complex when the 18A intercalate is removed from an NH₃ atmosphere.

Although AP cannot be ruled out as the species which is lost in the 23 to 18A change, it is unlikely that a molecule of molecular weight = 91, hydrogen-bonded to the clay layers, would be labile enough to be involved in the mass transfer implied here. Furthermore, NH₃ is a dehydrating agent and would desorb water in preference to the AP.

The stepwise collapse from 25.5 to 23.0A and of 23 to 18A probably occurs by a diffusion process, because the variation of peak intensity versus \sqrt{t} gives a relatively straight line. The hypothesis that the collapse from 25.5 to 23.0A is due only to the loss of water or NH₃ is strengthened by the almost identical IR spectra of the two complexes.

The changes which take place over several days during desiccation of the 25.5A complex over P₂O₅ are known with less certainty. However, it is probable that the loss of NH₃ plays some role, because the propionate salt slowly decomposes with time. It is difficult to compare the collapse of the 25.5A complex by dehydration with N₂ or NH₃ and by dehydration over P₂O₅, because the difference in time scale may indicate a different mechanism of decomposition. In the first case, on a time scale of minutes, it would seem water is the most important species lost, for the reasons already discussed. In the second case, on a time scale of hours, the decomposition of the AP becomes important and can be followed by IR.

The decomposition of the intercalated AP solution and the interaction of the reaction products with the clay, as followed by IR, will now be considered.

The perturbation of the OH region is much the same in the spectra of the 25.5A and the 23.0A complexes (Figs. 1B and 1C), and it indicates a strong interaction between the organic molecule and the surface. A strong peak at 3520 cm⁻¹, which is masked in the spectrum of the 25.5A complex by a large amount of aqueous AP, is revealed in the spectrum of the partially dehydrated 23.0A complex. This feature could result from kaolinite OH bands being shifted to lower frequencies by H-bond interaction. The origin of the band at 3605 cm⁻¹ will be discussed in a following paper.

In the 19.2A complex (Fig. 1D) an even smaller perturbation of OH than in the two previous complexes suggests a weaker interaction with the propionate. Accordingly, the amount of organic compound adsorbed must be smaller. A weak peak at

3548 cm^{-1} could be due to OH involved in H-bonding.

The content of intercalated AP solution diminishes somewhat from the 25.5A to the 23.0A complex and drastically so in proceeding to the 19.2A complex. The shoulder at 1717 cm^{-1} for the 25.5A complex shifts to a broad band at 1678 cm^{-1} for the 23.0A product, whereas a new band at 1590 cm^{-1} appears for the 19.2A complex.

The decomposition of intercalated AP can be interpreted. The 1717 cm^{-1} shoulder is due to the C=O stretching of a saturated aliphatic acid dimer (Table 2). For the 25.5A complex, this corresponds to some dimeric propionic acid, which could only have come from a partial decomposition of the ammonium propionate into propionic acid (see the chemical analysis). For the 23.0A complex, the 1678 cm^{-1} band corresponds to C=O stretching of an internally hydrogen-bonded carboxylic acid. Because such bonding is not observed in pure propionic acid, the acid must be hydrogen-bonded to the inner hydroxyls of the clay. The band at 1590 cm^{-1} might be due to some form of free carboxylate anion (Table 2). The bands which are normally associated with the carboxylate anion (see Table 2) are present in the 19.2A complex, in agreement with the chemical analysis performed on the slurry. Also the NH_4^+ deformation vibration mode at about 1410 cm^{-1} is always masked.

In summary the various AP intercalates with characteristic (001) spacings also have characteristic chemical features. Of particular importance is the presence of the band at 1678 cm^{-1} , indicating that there are acid molecules attached to the surface OH of the kaolinite lattice in equilibrium with carboxylate anions. The chemical analyses obtained after washing the 17–19A complexes with isopropanol suggest that AP is retained on an appreciable fraction of the interlamellar surface.

Even though about 10 percent of the material remains unexpanded, the surface area available to AP is at least 800 m^2/gm , equal to the maximum surface area in a smectite structure in which a bimolecular layer is intercalated. This estimate may be high because it may count excess AP mixed with the expanded clay, but on the other hand it may be low because it assumes that AP molecules lie parallel to the layers. If the molecules were tilted to allow closer packing, the surface area covered per molecule would be less.

Structural arrangement of the intercalated species

The X-ray diffractograms of the complexes that show very sharp peaks and numerous orders of reflection suggest that there is an ordered structure for

the interlayer species. Since a saturated AP solution gives no X-ray diffraction, the structuring of the solution between the clay layers is the result of interaction with the clay-surface.

In proposing a structure for the solution in the interlamellar space and a model of how it is formed, a number of factors must be considered. First, although the nature of the interlayer species for several complexes can be inferred from IR spectra, the actual structure or arrangement of molecules is not known. Second, the complexes with (001) $<25\text{A}$ were formed by decomposition. Synthesis of these complexes is not the reverse of decomposition, for synthesis requires only water and AP, whereas free acid and NH_3 are also involved in decomposition.

The IR data make it possible to distinguish two limiting interlayer compositions: that of the 25.5 and 19.2A complexes, plus an intermediate composition for the 23.0A complex. Hypotheses for the formation and molecular arrangement of the interlayer species of the 25.5A complex will first be presented, because IR spectra indicate that only H_2O and AP must be accounted for. The other two intercalates, which contain additional species, will then be discussed briefly in terms of the decomposition of AP.

For the 25.5A complex, either (1) the bulk solution enters between the layer and subsequently becomes ordered under the influence of the clay surfaces, or (2) the overall interlayer structure is built up stepwise from a disordered bidimensional layer formed from partially solvated AP.

In the first case, the action is like a wetting process in which the AP solution enters between the expanded layers and displaces the intercalated acetate, the propionate bonding more strongly to the clay than the acetate because of a stronger inductive effect from the longer 3-carbon chain. The formation of hydrogen bonds with the clay surface orders the entering solution, because hydrogen bonds are directional and therefore allow only certain molecular configurations. This theory has difficulty explaining why the clay opens to about 26A, if one assumes the solution enters into the 7A interlayer space of the 14A ammonium acetate complex. Perhaps the solution enters "in bulk" to form an 18A thick interlayer. A similar suggestion was made by Norrish (1954), who found in the Li-montmorillonite-LiCl- H_2O system that the clay layers separate in 8–10A steps corresponding to various organized structures of water. Remember that the 25.5A complex does not form from the hydrazine complex, which has an interlayer separation of 3A.

In the second case, it is assumed that the layers

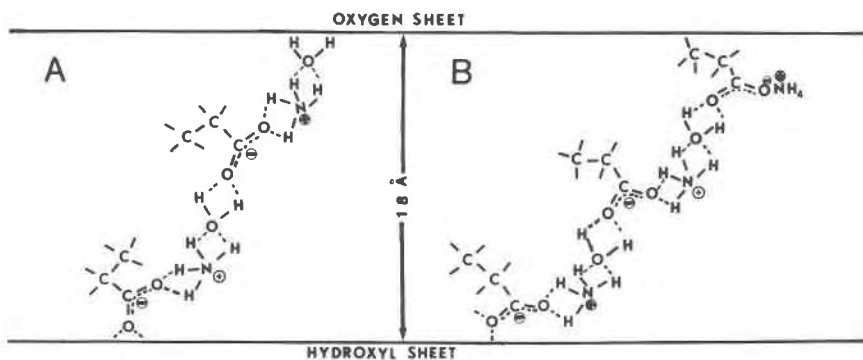


Fig. 4. Models of the interlayer species for the ammonium propionate complex. (A) Two-member chain. (B) Three-member chain.

separate in a stepwise manner. AP, because of the inductive effect mentioned above, displaces ammonium acetate by preferential hydrogen-bonding to the clay. This process is aided by the competition for water of hydration between the cation and anion. A bidimensional structure is formed in which the C=O group is hydrogen-bonded to the hydroxyl surface of the clay. The AP molecule could enter in a parallel orientation among the clay layers to form a monolayer, and subsequently reorient perpendicular to the

surface to lessen crowding as more molecules enter (Weiss, 1963). (This mechanism of formation is likely for the ammonium acetate complex, because the molecule can only wedge between the clay layers by entering parallel to the *ab* plane.) Alternatively, the AP molecule may enter directly in an almost perpendicular orientation, for the layers are already spread about 7Å by the ammonium acetate. A monolayer of perpendicular AP molecules would lead to a *d* spacing of 16–17Å. Expansion along the *c* axis occurs when NH_4^+ cations and water molecules bridge oxygen groups in two or three propionate anions to form 2- and 3-member chains (Fig. 4A,B). Three-member chains would fit into an 18Å interlayer space if they were slightly bent at the hydrogen-bond bridge points. The model of Figure 4B has the carbonyl group interacting with the OH sheet through only one orbital. The 3-member chain is thus tilted so it fits in the 18Å interlayer space with no bending of the hydrogen-bond bridges.

Dehydration and auto-decomposition of the 25.5Å complex produces intercalates of smaller *d* spacing.

An important observation is that shrinkage of the fully-expanded 25.5Å complex takes place when unionized carboxyl groups appear in the interlamellar space. It is conceivable that the unionized propionic acid molecules either (a) bond to form a dimer or (b) are hydrogen-bonded to the surface and to an AP molecule (Fig. 5A). This new type of molecular arrangement could hinder formation of the aggregates of AP and water shown in Figure 4A, B.

Other factors such as the concentration of AP and NH_3 also play an important role in determining what complex is formed. For instance, it has been observed that when the AP solution is undersaturated only a ~ 17 or ~ 23 Å complex is formed.

Increasing the concentration of free NH_3 in the AP solution limits the layer separation first to ~ 23 Å,

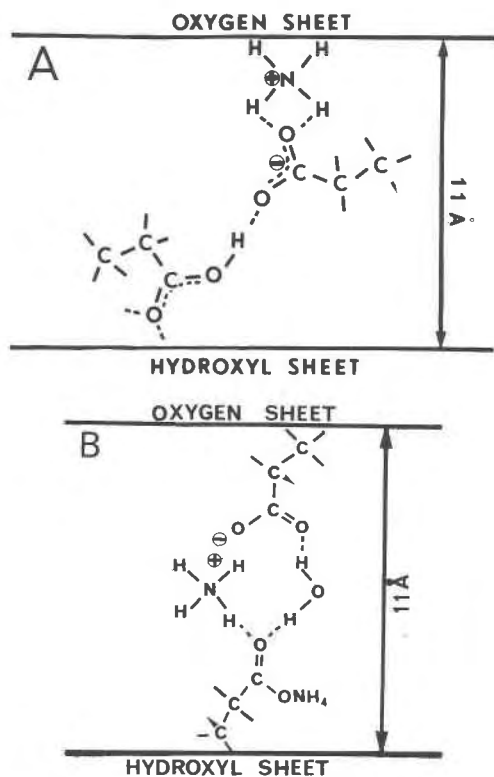


Fig. 5. Models of the interlayer species for the ammonium-propionate complex. (A) and (B) Two-member chains of 11Å length.

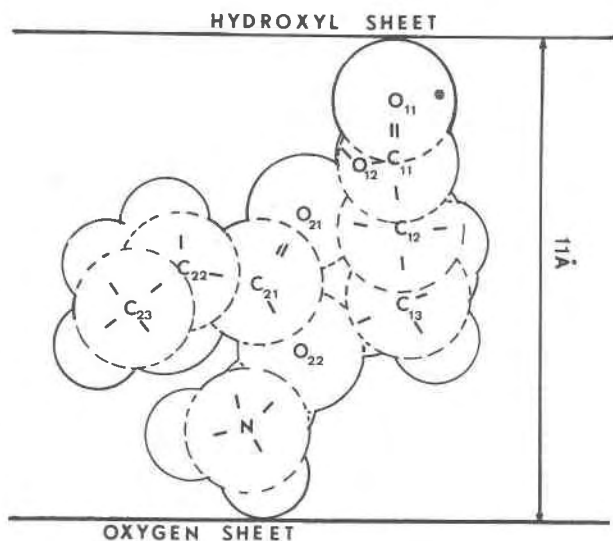


Fig. 6. Projection on the c axis of the interlayer species shown in Fig. 5A. The distances (in Å) from the oxygen plane are as follows: N: 15.26; O₂₂: 12.99; C₂₃: 11.79; C₁₃: 11.34; C₂₁: 10.99; C₂₂: 10.74; C₁₂: 9.44; O₂₁: 8.94; C₁₁: 8.49; O₁₂: 8.39; O₁₁: 6.69; OH: 4.37.

then to 17–18Å at very high concentrations. This effect is the result of competition between NH₃ and H₂O. Water is a necessary bridging molecule for the formation of propionate chains with two or three members.

In summary, several models based on the ammonium propionate–water structure can be proposed: (a) An ammonium propionate molecule could orient perpendicular to the clay surface because of hydrogen bonding of the kaolinite OH to the oxygen electron pair of AP (Fig. 4A, B). Water coordinated to NH₄⁺ would form a discontinuous layer at 7–8Å from the surface of the clay. The interaction of a new layer of AP with the coordinated water would yield the 25.5Å complex. (b) This model (Fig 5A) treats the complex that exists after partial decomposition of AP has occurred. Here the oxygen surface of the clay is hydrogen-bonded to the NH₄⁺ group of the AP, while the hydroxyl surface of the clay is hydrogen-bonded to propionic acid. The aliphatic chains are inter-sheaved in parallel rows, as proposed for other clay complexes by Weiss *et al.* (1963). This model requires one propionic acid molecule for each ammonium propionate molecule. (c) AP forms a dimer with an H₂O bridge between the two carbonyl oxygens (Fig. 5B). Placing the organic molecules perpendicular to the clay would explain the 18 or 17Å spacing, but not the perturbation of the OH, for the methyl groups would be facing the OH and O surface of the clay. Increasing the number of water molecules associated

with the dimer would increase the d spacing. If the dimer were to lie parallel between the clay layers, both the 14Å complex and the OH perturbation could be accounted for.

In order to determine which of the above models is correct, a Fourier projection along the c axis was attempted. The postulated interlamellar model, chosen in view of the molecular configurations of H₂O, NH₃, and propionic acid and the available 11Å interlamellar space, was a chain formed from propionic acid and ammonium propionate according to Figure 5A.

Of the numerous ways to construct a chain from these two molecules, the one chosen was based on a hypothesis of Weiss (1963), in which the NH₄⁺ ion is placed next to the oxygen plane of the clay. The carbonyl groups of the acid are hydrogen-bonded to the hydroxyl plane of the kaolinite. A cross-section of the dimer is shown in Figure 6. Confirmation of this model could in theory be made by using X-ray diffraction data to construct electron-density projections. Unfortunately, the calculations have shown that more than 20 basal reflections would be needed to obtain a correct Fourier projection.

Thermal properties of the 25.5 and 18.0Å intercalates

An independent method for studying the nature of the swelling liquid is low-temperature thermal analysis. Thermal methods are appropriate because measurement of the glass transition temperature in the free and confined solutions might indicate the constraints imposed by the surface of the swelled kaolinite. A differential scanning calorimeter, DSC, was used for this study. The slope of the baseline of the DSC curve records the difference in specific heat between a chemically-inert reference material and the sample. Deflections and discontinuities in slope are produced by transitions in the sample and extend in either direction from the baseline, depending on whether they are endothermic or exothermic. A first-order transition produces a peak, the peak area being proportional to the energy involved in this transition. A second-order transition, such as a glass transition, involves a discontinuous change in the specific heat and yields a step or discontinuity in the DSC trace. Crystallization, on the other hand, produces an exothermic peak without a significant change in the baseline.

It should be noted that on cooling, a number of materials do not crystallize completely, the extent of crystallization depending on a number of factors, such as the rate of cooling and the salt concentration for electrolyte solutions.

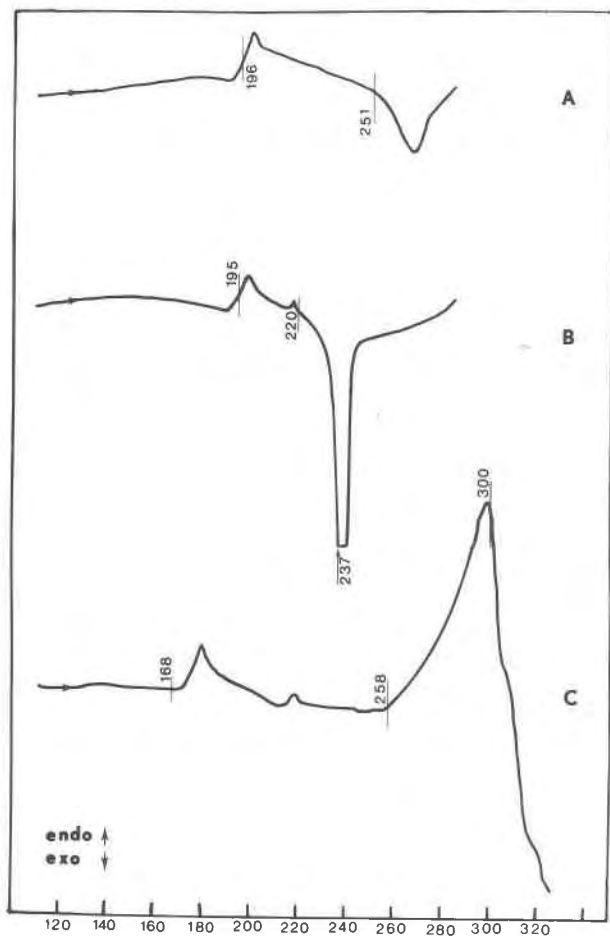


Fig. 7. Heating curves for a saturated aqueous solution of ammonium propionate; heating rate: 10°K/min. A, B, C: sequence of three heating-cooling cycles. The DSC traces on cooling are not shown. Axis in °K.

Procedure

Samples of 7–15 mg of either an approximately equimolar ammonium propionate and H₂O solution or of kaolinite–ammonium propionate complex were sealed in aluminum sample holders and cooled to about 100°K at the rate of 5°K per minute. The DSC curve was then recorded as the sample was heated at 10°K per minute from 100° to 290°K. The 23.0A and 18.0A complexes were studied because they are relatively stable.

Results

The AP concentrated solution (Fig. 7) was taken through three successive cooling and heating cycles. In the first two cycles a glass transition was observed at about 196°K, followed by an exothermic peak starting at about 251°K in the first cycle and at about

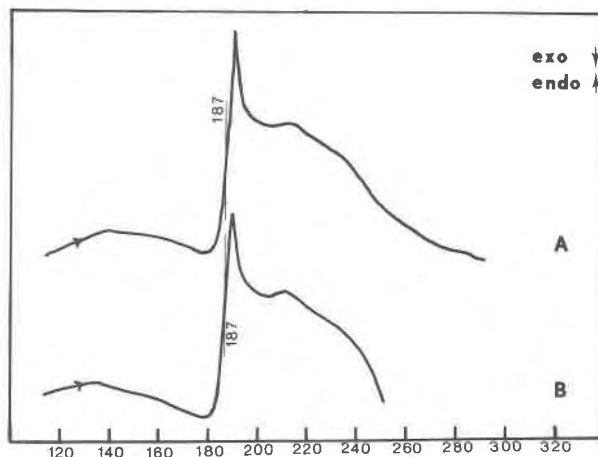


Fig. 8. Successive heating curves for the 23.0A ammonium-propionate complex for a heating rate of 10°K/min. Axis in °K.

220°K in the second. The exothermic peak probably represents a cold crystallization process. The rapidly cooled sample supercools to a glass. On heating a cold crystallization follows the glass transition, because increased thermal energy increases molecular mobility.

During the third cycle two main endothermic effects were observed, starting at about 168°K and at 258°K. The latter is probably due to the melting of ice formed earlier when the solution separated into an ammonium propionate fraction and a less-concentrated aqueous fraction. The first endothermic peak could result from a glass transition affecting the former fraction. Small endothermic peaks are also observed at 220°K in the second and third heating curves.

A well-defined glass transition is observed for the 23.0A AP complex (Fig. 8) at 187°K, but it is not followed by an exothermic peak, as for the free solution. It can thus be concluded that there is no cold crystallization. The decrease of ~ 10°K in the glass-transition temperature may result from the constraints exerted on the solution by the solid surfaces of the interlamellar space. The glass transition observed for the 18A AP complex at about 184°K is followed by an exothermic peak starting at about 204°K and by an endotherm starting at about 250°K. (Fig. 9). This behavior is closer to that of the AP solution (see Fig. 7B) than that observed for the 23A complex.

Discussion

The low-temperature DSC study of the 23 and 18A complexes raises two points meriting discussion. An-

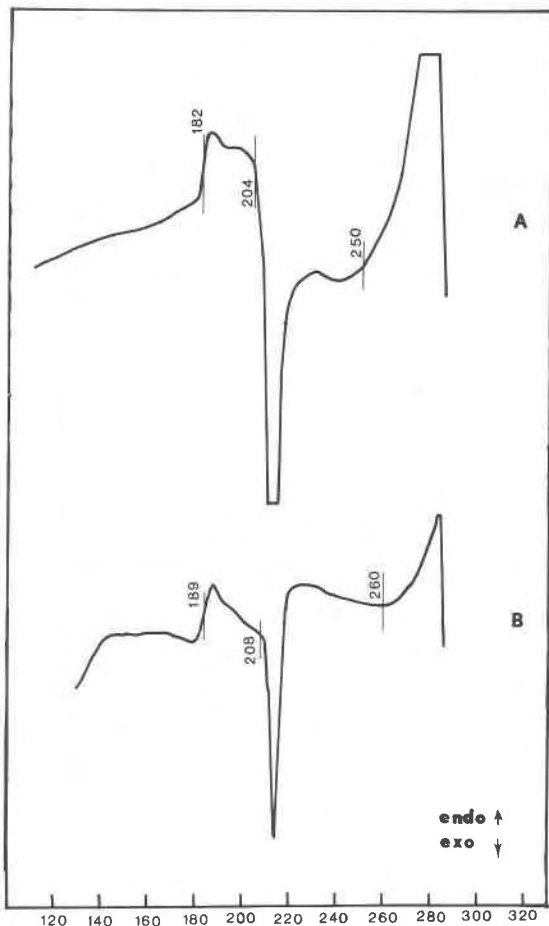


Fig. 9. Successive heating curves for the 18.0A ammonium-propionate complex for a heating rate of 10°K/min. Axis in °K.

gell and Sare (1970) observed that cold crystallization generally occurs above the glass transition (T_g) and suggested that any solution near its glass transition is in a metastable condition with respect to some crystalline phase or combination of phases. This is exactly what is observed during successive cooling and heating cycles of an AP concentrated solution (Fig. 7), which lead finally to a complete separation of water and salt (Fig. 7C). The behavior of the 18A complex is similar, with the glass transition ($\sim 187^\circ\text{K}$) followed first by cold crystallization and then by an endothermic peak due to the melting of water ($\sim 270^\circ\text{K}$).

In the 23A complex, however, the metastable state following the glass transition extends up to 250–260°K, without being followed by cold crystallization when tested under similar kinetic conditions (rate of cooling or heating) as the AP solution and the 18A complex. The difference between the two complexes

is a clear indication that the structures of the intercalated AP solutions have a different stability.

There are at least two explanations for the different thermodynamic stability of the metastable state obtained after glass transition in the 23A complex. In the 18A complex the AP solution is probably more concentrated than in the 23A complex, therefore the osmotic potential gradient towards the external phase is probably higher. Also, as shown by the IR data, the ratio AP/propionic acid (hydrogen-bonded to the surface) is higher in the 23A complex. This may influence, in particular, the stability of the interlayer phase.

Another interesting aspect is the temperature at which glass transition occurs. With respect to the concentrated salt solution, T_g decreases by about 10°K in the intercalated state. Angell and Sare (1970) have shown that T_g depends not only on the concentration but also on the nature of the anions. In the intercalate, surface effects could have the same effect as anions in solution. Surface effects may be considered, for instance, to be hydrogen-bonding of the carboxylate anion to surface hydroxyls instead of to water. Compare Figures 4A and B to Figures 5A and B.

Conclusions

By reacting the ammonium acetate-kaolinite intercalate with a 1:1 ammonium propionate-water solution, a new intercalation complex is obtained characterized by a basal spacing of 25.5Å and a high degree of ordering along the c axis. By drying this intercalate under various conditions, other complexes equally well ordered but with smaller basal spacings are observed. The (001) spacing decreases by steps of 2–3Å, corresponding to the removal of water and/or ammonium bridges. The ratio ammonium propionate/propionic acid/water within the interlamellar space controls the domain of stability of these various intercalates, probably because it changes the kind of hydrogen bonding between the intercalated molecular species with the surface and among themselves.

The modification of the nature of the intercalating solution in going from higher to lower spacing intercalates is evidenced by the evolution of the infrared spectra.

Low-temperature scanning calorimetry shows that the intercalating solution undergoes a glass transition temperature between 180° and 190°K. The glass transition is followed by a cold crystallization process in intercalates with lower (001) spacings.

Because the interaction energy between individual

clay platelets separated by distances above 10A becomes very weak, the 25.5A ammonium intercalate is an interesting starting material for the preparation of new materials containing delaminated kaolinite, as it will be shown in a future publication.

The successful use of the stepwise process to intercalate molecules which produce a separation of 10A or more is an excellent experimental verification of the theoretical calculations of Giese (1974).

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