

THE INTERACTION BETWEEN ROUNDUP (GLYPHOSATE) AND MONTMORILLONITE. PART II. ION EXCHANGE AND SORPTION OF *ISO*-PROPYLAMMONIUM BY MONTMORILLONITE

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(Received 7 December 1977)

Abstract—The adsorption mechanism of *iso*-propylammonium (PAH^+), the cationic component of Roundup, by various homoionic montmorillonites and the structures of the associations obtained in the interlayer space were investigated, using infrared, X-ray, and carbon analysis methods. Adsorption from aqueous and ethanol solutions of Roundup was studied. The infrared spectra were compared with those obtained by the treatment of montmorillonites with ethanol and CCl_4 solutions of the free *iso*-propylamine (PA). The adsorption of PA from ethanol gives rise to protonation of the amine. PA sorbed from CCl_4 solution forms an ammonium-amine association. Adsorption of PAH^+ from alcohol solution of Roundup occurs by the mechanism of cation exchange. With transition metal exchangeable cations, PAH^+ is sorbed in excess, forming hydrogen bonds between NH_3^+ groups and hydroxyls resulting from dissociation of water molecules. The process of adsorption of PAH^+ from aqueous solutions of Roundup depends on the concentration of the solution. If montmorillonite is reacted with 0.5% solution of Roundup, PAH^+ is adsorbed by exchanging metal cations and the adsorption capacity of the clay does not exceed the c.e.c. If the montmorillonite is reacted with 5.0% solution of Roundup, the PAH^+ exchanges protons originating from the hydrolysis of the interlayer water. Protons which are transferred from the interlayer space to the water solution are accepted by the anion component of Roundup. The amounts of PAH^+ adsorbed from concentrated Roundup solutions are much higher than the cation exchange capacity of montmorillonite. Hydrogen bonds are formed between the ammonium and water or hydroxyl groups on the interlayer space. With the trivalent exchange ions Al and Fe, which tend to polymerize in the interlayer space, excess sorption gives rise to hydrogen bonding of NH_3^+ to oxygen of the polymer.

Key Words—Adsorption, Exchange, Glyphosate, Herbicide, *Is*o-propylammonium, Montmorillonite.

INTRODUCTION

The interaction between the anionic component of Roundup and montmorillonite was described in Part I of the present series (Shoval and Yariv, 1978). The present paper deals with the interactions between montmorillonite and the cationic component of Roundup, namely the *iso*-propylammonium cation (PAH^+).

Amines sorbed in the interlayer space of montmorillonite may exist either in the form of positively charged ammonium ions or as neutral amine molecules. The interactions occurring in the interlayer space during the sorption of the amines can be summarized as follows:

1. For ammonium ions which serve as proton donors:
 - a. hydration through the formation of hydrogen bonds between the ammonium ion and water molecules;
 - b. hydrogen bond formation between NH and O atoms from the oxygen plane of the silicate layer;
 - c. hydrogen bond formation between NH and hydroxyls obtained by the reversible dissociation of water molecules in the interlayer space under the influence of the metallic cation; and
 - d. hydrogen bond formation between NH and oxygens of polymeric AlOH and FeOH complexes.

2. For amine molecules which serve as proton donors:
 - a. hydrogen bond formation with water bonded to the oxygen plane of the silicate layer;
 - b. hydrogen bond formation with hydroxyls; and
 - c. hydrogen bond formation with atoms of the oxygen plane.
3. For amine molecules which serve as donors of electron pair:
 - a. formation of ammonium ions by proton acceptance from water molecules;
 - b. interaction with ammonium ion and the formation of ammonium-amine;
 - c. coordination to metallic cations; and
 - d. hydration through the formation of hydrogen bonds between the amine and water molecules.

Many investigators have shown that under various conditions the adsorption of amines by montmorillonites may highly exceed the cation exchange capacity of the clay, a phenomenon known as "excess adsorption," but no satisfactory explanation has been given to this phenomenon. Vansant and Uytterhoeven (1973) attributed the excess adsorption of weak bases to the inclusion of ammonium salts. Yariv and Heller-Kallai (1975) attributed it to the formation of ammonium-amine associations in the interlayer space.

The present communication deals with the adsorption of PAH^+ by montmorillonites from solutions of Roundup, $(\text{PAH})_3\text{G}$. The structures of the various as-

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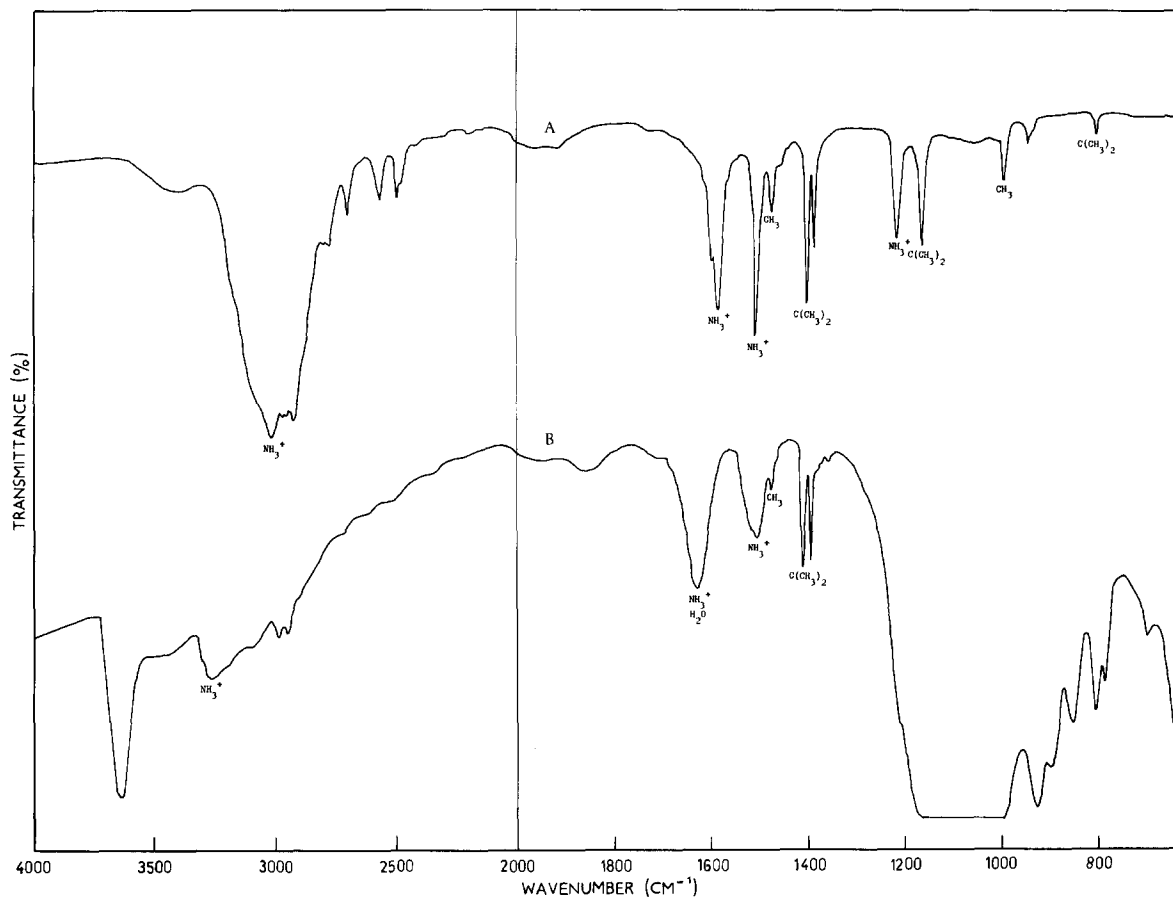


Fig. 1. Infrared spectra of (A) *iso*-propylammonium chloride (in KBr disk) and (B) *iso*-propylammonium montmorillonite (self-supporting film).

sociations in which PA is involved and which are obtained in the interlayer space are investigated, and adsorption mechanism is proposed and an explanation is suggested for the excess adsorption.

To clarify the reaction mechanism which takes place during the adsorption of the cationic component of Roundup by montmorillonite and to interpret the various infrared spectra the spectrum of (PAH)-montmorillonite prepared from 0.1 N aqueous solution of (PAH)Cl was studied. The spectrum of PA sorbed by the various homoionic montmorillonites from solutions of pure amine in ethanol and in CCl_4 was also studied.

EXPERIMENTAL

Roundup was supplied by Monsanto and was purified by extracting impurities with CCl_4 . *Iso*-propylamine and *iso*-propylammonium chloride were supplied by BDH. The homoionic montmorillonites used in the present study and their preparation were previously described (Yariv et al., 1968). They were stored in the form of ~1.5% aqueous suspensions. A homoionic sample of *iso*-propylammonium montmorillonite was

prepared by repeated saturation of a sample of Wyoming bentonite with 0.1 N solution of (PAH)Cl. It was then washed 3 times with distilled water, at which time no Cl was detected.

Adsorption from aqueous solutions

Aliquots of the suspensions, containing 50-mg portions of clay, were placed in glass tubes, 10 ml of Roundup solutions with varying concentrations up to 5 wt % were then added and the suspension was well stirred for a few minutes. After 24 hr, or after 2 weeks, the solution was separated and the clay fraction was washed 3 times with distilled water. The clay was made into a self-supporting film by allowing it to settle out from the aqueous suspension of ~1.5% on a section of polyethylene and air drying.

Adsorption from ethanol and CCl_4 solutions

Air-dried self-supporting films (prepared by drying 4 ml of ~1.5% aqueous clay suspension on a section of polyethylene) were immersed in 10 ml of 5% ethanol solutions of Roundup or of *iso*-propylamine and in 5% CCl_4 solution of *iso*-propylamine. The film was sepa-

Table 1. NH_3^+ symmetric deformation frequencies (in cm^{-1}) of (PAH)-montmorillonite obtained during the adsorption of PA from organic solvents.

| Exchange cation | From CCl_4 solution | | From ethanol solution |
|-----------------|------------------------------|--------|-----------------------|
| H | 1507 | 1492 | 1498 |
| Li | 1508sh | 1491 | 1500 |
| Na | 1507 | 1492sh | 1500 |
| K | 1506 | 1496sh | 1500 |
| Cs | 1505sh | 1492 | 1502 |
| NH_4 | 1505sh | 1491 | 1501 |
| Mg | 1507sh | 1490 | 1499 |
| Ca | 1509sh | 1495 | 1499 |
| Ba | 1506sh | 1491 | 1486 |
| Al | 1510sh | 1492 | 1500 |
| Fe | 1510sh | 1492 | 1498 |
| Ag | 1510sh | 1492 | — |
| Mn | 1506sh | 1492 | 1500 |
| Co | 1507 | 1492sh | 1502 |
| Ni | 1505sh | 1490 | 1497 |
| Cu | 1509 | 1491sh | 1501 |
| Zn | 1507sh | 1492 | 1499 |
| Cd | 1509sh | 1492 | 1499 |
| Hg | 1505sh | 1491 | 1501 |

sh—shoulder.

rated from the solution after 24 hr, or after 2 weeks, and washed by immersion in the pure organic solvent.

Carbon content, infrared, and X-ray powder diffraction measurements

The carbon content of the clay samples was estimated with a Leco Carbon Analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 237. X-ray powder diffraction patterns of oriented aggregates were recorded on a Seifert Iso-Debyeflex IIIA diffractometer.

RESULTS AND INTERPRETATION

Iso-propylammonium montmorillonite

The carbon analysis showed that PAH^+ -capacity of montmorillonite is 84 meq/100 g, which is in the normal range for ion-exchange capacity of the Wyoming bentonite. The c -spacings for films which were air-dried, dried for 1 week over saturated $\text{Mg}(\text{NO}_3)_2$ solution, and dehydrated under vacuum at 200°C are 13.2, 13.1, and 12.9 Å, respectively. The infrared spectra of (PAH)-montmorillonite and of (PAH)Cl are shown in Figure 1.

The spectrum of (PAH)-montmorillonite differs from that of the (PAH)Cl. The most striking differences are in the location of the absorption bands of the NH_3^+ group. These frequencies are dependent on whether or not the clay is hydrated. They are at 3255, 1620, and 1498 cm^{-1} in the spectrum of air-dried (PAH)-montmorillonite; 3230, 1610, and 1492 cm^{-1} in the spectrum of (PAH)-montmorillonite dried under vacuum at 200°C

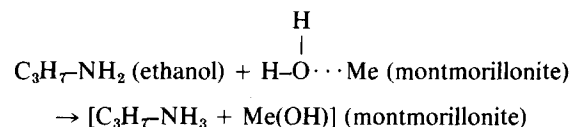
and at 3030, 1580, and 1503 cm^{-1} in the spectrum of (PAH)Cl. It is therefore concluded that the NH_3^+ group forms hydrogen bonds with water molecules in the interlayer space of the clay.

Adsorption of iso-propylamine from ethanol solution

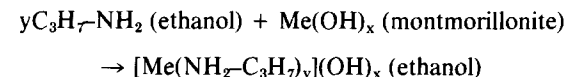
Adsorption of the amine by the montmorillonites studied here (excluding Ag-montmorillonite) gives rise to spectra similar to that of (PAH)-montmorillonite indicating that the amine is protonated in the interlayer space. The symmetric bending vibration absorbs at $1498\text{--}1503\text{ cm}^{-1}$ (Table 1), indicating that the organic ion is hydrated. After dehydration under vacuum at 200°C this band shifts to $1490\text{--}1492\text{ cm}^{-1}$. The effect of the exchangeable cation on the wave number of the NH_3^+ band is very small because a great portion of the exchangeable metal cation has been extracted by the PA alcohol solution (the presence of metal cations in the alcohol supernatant was confirmed by various qualitative tests).

The reaction can be summarized as follows:

1. The first stage:



2. The second stage:



where Me is the metal cation and x and y are, respectively, the oxidation state and the coordination number of the metal cation.

The spectrum obtained with Ag-montmorillonite shows that this clay adsorbs free amine (Figure 2) indicating that a complex of the type $[\text{Ag}\cdots\text{NH}_2\text{-C}_3\text{H}_7]^+$ is formed between the silver ion and the amine in the interlayer space. The NH_2 absorption bands appear at 3330 , 3285 , and 1588 cm^{-1} .

Adsorption of iso-propylamine from CCl_4 solution

The spectra of species obtained by the adsorption of PA from CCl_4 solution differ from the spectra of species obtained by the adsorption of PA from alcohol solution. In the first case the spectra show two maxima characteristic for the NH_3^+ symmetric band (Table 1). The first maximum appears at 1492 cm^{-1} and is characteristic for anhydrous ammonium ion. The second maximum appears at 1507 cm^{-1} . New bands appear at 1599 , 3260 , and 3350 cm^{-1} which are characteristic for the presence of free amine. There is a relationship between the intensity of the band at 1507 cm^{-1} and those of the

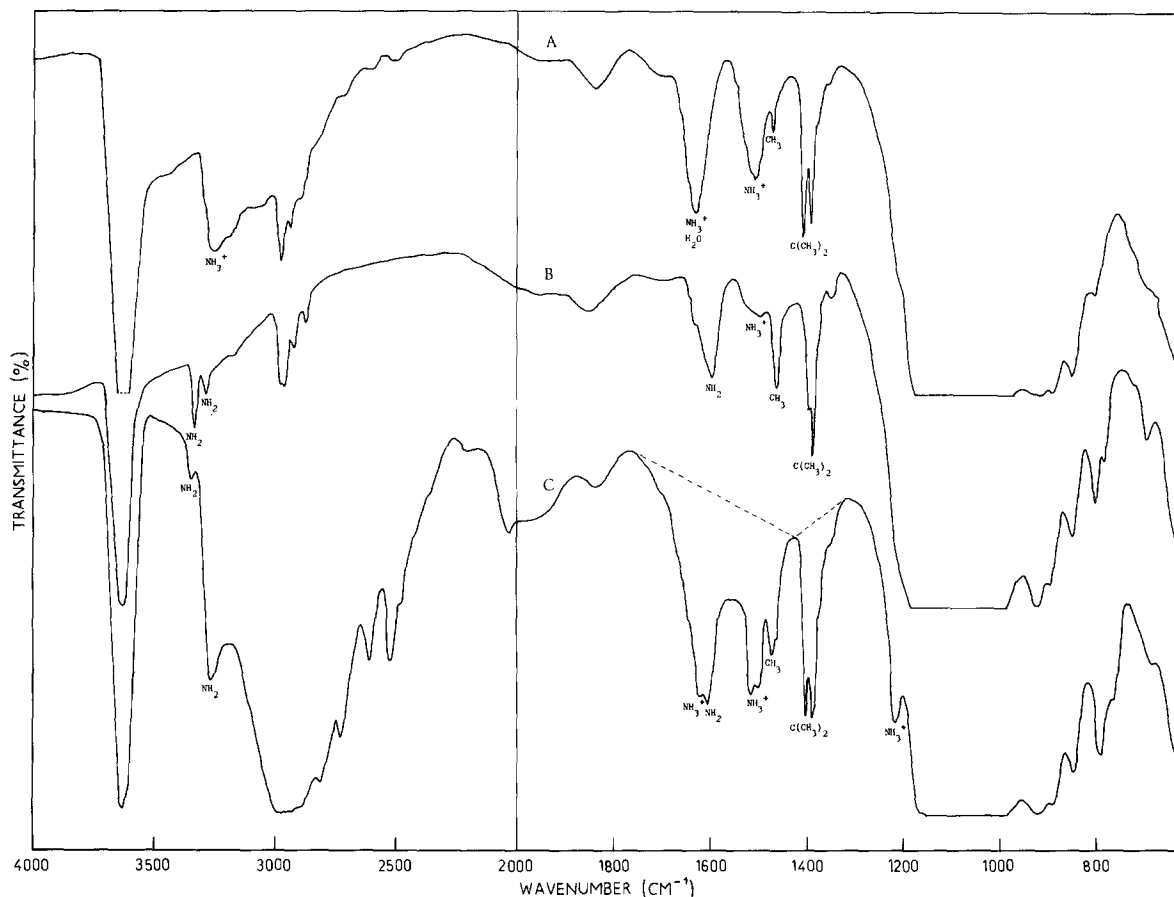


Fig. 2. Infrared spectra of *iso*-propylamine sorbed by (A) Na-montmorillonite from ethanol solution; (B) Ag-montmorillonite from ethanol solution; (C) Na-montmorillonite from CCl_4 solution. Spectrum (A) is characteristic for ammonium montmorillonite. Spectrum (B) is characteristic for free amine coordinated to an exchangeable transition metal cation. Spectrum (C) is characteristic for ammonium-amine-montmorillonite.

NH_2 bands and it is suggested that an ammonium amine complex, such as $(\text{C}_3\text{H}_7\text{-NH}_2 \cdots \text{H}_2\text{O} \cdots \text{H}_3\text{N-C}_3\text{H}_7)^+$ is formed in the interlayer space. The formation of this complex is associated with the elevation of the baseline in the $1430\text{--}1700\text{ cm}^{-1}$ range.

Adsorption of *iso*-propylammonium from an aqueous solution of Roundup

PAH^+ is adsorbed from an aqueous solution of Roundup by the mechanism of ion exchange. The reaction is fast and there are no considerable differences between the amounts sorbed during 1 or 14 days. The amounts of PAH^+ sorbed after 14 days from 0.5 and 5.0% aqueous solutions of Roundup (in meq per 100 g of clay) are given in Table 2.

The capacity of the clay to adsorb PAH^+ from a solution of Roundup of a concentration of 0.5% was equal to ~ 100 meq/100 g clay which is in the range of the cation exchange capacity of montmorillonite. Excluding Cs-montmorillonite, the infrared spectra of these clay samples are similar to that of (PAH)-montmoril-

lonite. The NH_3^+ asymmetric bending band absorbs at 1500 cm^{-1} indicating that the ammonium cation is hydrated in the interlayer space. In Cs-montmorillonite the ion-exchange reaction is not complete and the water structure in the interlayer space is determined solely by the hydrophobic character of the residual Cs rather than by the hydrophilic character of the ammonium head of the organic ion. The NH_3^+ band shifts to 1509 cm^{-1} and it is possible that it forms a hydrogen bond with atoms of the oxygen plane of the silicate sheet.

The capacity of the clay to adsorb PAH^+ from a solution of Roundup of a concentration of 5.0% was 2 and 3 times as much as the cation-exchange capacity of the clay indicating that the adsorption of PAH^+ occurs by a process other than a reversible cation-exchange reaction. The infrared spectra of the various homoionic montmorillonites reveal that the amine is present in the clay in the form of ammonium ion. Spectra of Na-montmorillonite treated with aqueous solutions of Roundup are shown in Figure 3. The frequencies of the characteristic absorption bands of PAH^+ adsorbed by the var-

Table 2. *Iso*-propylammonium (in meq/100 g clay) adsorbed by homoionic montmorillonites from aqueous solution (0.5 and 5%) and ethanol solution (5%) of Roundup.

| Exchange cation | 0.5% aqueous solution | 5% aqueous solution | 5% ethanol solution |
|-----------------|-----------------------|---------------------|---------------------|
| H | 72 | 221 | 154 |
| Li | 78 | 229 | 69 |
| Na | 86 | 253 | 129 |
| K | 100 | 221 | 94 |
| Cs | 78 | 164 | 82 |
| NH ₄ | 80 | 268 | 108 |
| Mg | 69 | 180 | 42 |
| Ca | 69 | 180 | 35 |
| Ba | 94 | 229 | 47 |
| Al | 97 | 201 | 259 |
| Fe | 122 | 170 | 239 |
| Ag | 100 | 238 | 105 |
| Mn | 72 | 220 | 130 |
| Co | 100 | 268 | 166 |
| Ni | 119 | 177 | 234 |
| Cu | 116 | 257 | 268 |
| Zn | 119 | 228 | 159 |
| Cd | 111 | 201 | 155 |
| Hg | 108 | 206 | 109 |

ious homoionic montmorillonites are tabulated in Table 3.

Two types of interaction of the NH₃⁺ group in the interlayer space can be distinguished. With H-, Al-, and Fe-montmorillonite the NH₃⁺ band appears at 1520 cm⁻¹ and is not shifted when the film is heated under vacuum up to 200°C. This is characteristic for hydrogen bond formation between the NH₃⁺ group and oxygen of a polymeric hydroxy iron or aluminum cation complex which is formed in the interlayer space. With all other montmorillonites this band absorbs at 1512 cm⁻¹ and this frequency does not change on dehydration under vacuum. The HOH stretching band which normally absorbs at 3400 cm⁻¹ is weakened and instead a band, characteristic of hydrogen bonded OH group, appears at 3060 cm⁻¹. It is therefore suggested that hydrogen bonds are formed between NH₃⁺ groups and hydroxyl ions in the interlayer space. The intensity of the H₃O⁺ band at 1710–1720 cm⁻¹ increases remarkably with the sorption of PAH⁺ indicating that the dissociation of water in the interlayer space increases with increasing hydrophobic character of the interlayer space.

The *c*-spacings of the homoionic montmorillonites untreated and treated with 5% Roundup solution are given in Table 4. The *c*-spacings of the air-dried films of the treated clays range between 12.9 and 13.3 Å and are an integral series of diffraction. After heating the films at 200°C under vacuum the *c*-spacings drop only slightly to 12.6–13.2 Å. The *c*-spacings of the untreated homoionic montmorillonites, on the other hand, drop to 10.0 Å after being heated under vacuum to 200°C.

Table 3. Characteristic absorption bands (in cm⁻¹) of *iso*-propylammonium adsorbed on homoionic montmorillonites from 5% aqueous solution of Roundup.

| Exchange cation | NH ₃ ⁺ asym. def. | | NH ₃ ⁺ sym. def. | |
|-----------------|---|------|--|------|
| | (2) | (1) | (2) | (3) |
| H | 1620 | 1518 | 1512 | 1500 |
| Li | 1620 | 1512 | 1515 | 1503 |
| Na | 1622 | 1512 | 1512 | 1500 |
| K | 1616 | 1506 | 1507 | 1504 |
| Cs | 1615 | 1513 | 1512 | 1509 |
| NH ₄ | 1615 | 1512 | 1512 | 1498 |
| Mg | 1620 | 1512 | 1510 | 1502 |
| Ca | 1620 | 1513 | 1514 | 1505 |
| Ba | 1615 | 1511 | 1510 | 1500 |
| Al | 1613 | 1520 | 1516 | 1501 |
| Fe | 1612 | 1519 | 1513 | 1501 |
| Ag | 1610 | 1512 | 1515 | 1500 |
| Mn | 1620 | 1512 | 1512 | 1499 |
| Co | 1620 | 1512 | 1511 | 1505 |
| Ni | 1615 | 1511 | 1510 | 1500 |
| Cu | 1610 | 1513 | 1510 | 1502 |
| Zn | 1620 | 1516 | 1512 | 1500 |
| Cd | 1620 | 1512 | 1510 | 1505 |
| Hg | 1615 | 1510 | 1510 | 1503 |

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(1) Air-dried.

(2) Dried under vacuum at 200°C.

(3) Adsorbed from 0.5% solution of Roundup.

This is proof that the ammonium ion is located in the interlayer space preventing its collapse. The ammonium ion together with the hydration water form a monolayer in the interlayer space. The *c*-spacings of the ammonium-treated samples are smaller than those of the untreated samples because PAH⁺ increases the hydrophobic nature of the clay and water is excluded from the interlayer space.

When the adsorption was carried out from a solution of 0.1% the absorption bands of NH₃⁺ shift from 3030, 1580, and 1503 cm⁻¹ (in the spectrum of (PAH)Cl recorded in a KBr disk) to 3250, 1620, and 1492–1495 cm⁻¹ in montmorillonite indicating that the ammonium ion enters into the interlayer space of the mineral. The appearance of NH₃⁺ bending frequency at 1492–1495 cm⁻¹ is characteristic for an anhydrous ammonium ion. This can be explained as follows. Since the amount of PAH⁺ adsorbed by the clay is very small the structure of the interlayer water in montmorillonite is determined by the metal exchange ions. The PAH⁺ which cannot destroy this water structure remains anhydrous.

Adsorption of iso-propylammonium from an alcohol solution of Roundup

The adsorption of PAH⁺ from an ethanol solution of Roundup is very slow compared with the adsorption from aqueous solution. The adsorption after 24 hr is

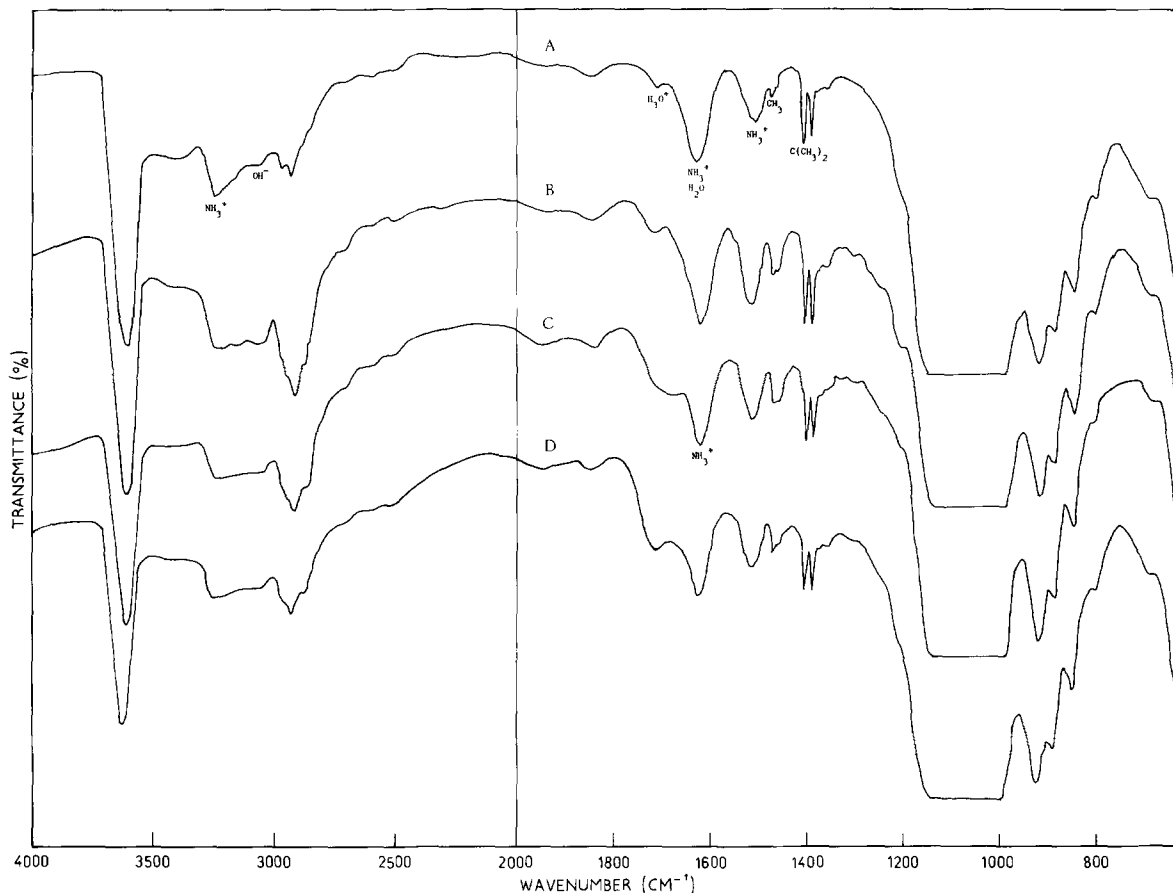


Fig. 3. Infrared spectra of self-supporting films of *iso*-propylammonium montmorillonite prepared by the treatment of Na-montmorillonite with an aqueous solution of Roundup. (A) 0.5%; (B) 5.0%; (C) sample (B) heated at 200°C under vacuum; and (D) sample (C) left 24 hr in air.

very slight, especially with the divalent cation montmorillonites (excluding Cu- and Hg-montmorillonite). The adsorption increased with time and considerable amounts of PAH⁺ were adsorbed by the montmorillonites after 14 days. The adsorption from a methanol solution of Roundup or from an ethanol solution to which a few drops of water has been added, is much faster. The amounts of PAH⁺ adsorbed by the various homoionic montmorillonites within 2 weeks are given in Table 2.

The monovalent cation montmorillonites studied here adsorb PAH⁺ by the mechanism of a reversible cation exchange. The divalent cation montmorillonites (excluding Mn- and Hg-montmorillonite) are only partly susceptible to cation exchange reactions with PAH⁺. The trivalent cation montmorillonites and H-montmorillonite adsorb PAH⁺ in great excess of the cation exchange capacity of the clay.

The frequency of the characteristic infrared absorption bands of PAH⁺ adsorbed on the various homoionic montmorillonites from the 5% ethanol solution are given in Table 5. The NH₃⁺ symmetric bending is affected

by the drying time of the clay film. After 1 hr drying the film still contains considerable amounts of ethanol and the NH₃⁺ band appears at 1510 cm⁻¹. This frequency is characteristic for the solvation of NH₃⁺ by ethanol. After air-drying for 6–8 hr the band is shifted to 1500 cm⁻¹. This frequency is characteristic for the hydrated ammonium ion. Shoulders appear at 1492 (anhydrous ammonium) and 1510 cm⁻¹ (ethanol solvated ammonium). After vacuum drying at 200°C the 1492 cm⁻¹ becomes the dominant absorption band.

From X-ray powder diffraction data (Table 4) it is obvious that the PAH⁺ is adsorbed in the interlayer space. Most montmorillonites (excluding Mg-, Ca-, and Ba-montmorillonite) have *c*-spacings ranging between 12.7–13.9 Å with air-dried films, and between 11.6–13.6 Å with films heated under vacuum at 200°C. Air-dried films of Mg-, Ca-, and Ba-montmorillonites have *c*-spacings of 13.9, 14.0, and 12.6 Å, respectively. When heated under vacuum the *c*-spacings drop to 10.9, 10.6, and 10.7 Å, respectively, and the peaks do not have an integral series of diffraction. This indicates that the distribution of the PAH⁺ in the clays is inhomogeneous.

Table 4. Basal spacings of montmorillonites treated with 5% aqueous and ethanol solutions of Roundup.

| Exchange cation | Untreated clay | | | Treated with aqueous solution | | | Treated with ethanol solution | | |
|-----------------|----------------|--------|-------|-------------------------------|--------|--------|-------------------------------|--------|--------|
| | (1) | (2) | (3) | (1) | (2) | (3) | (1) | (2) | (3) |
| H | 14.6 Å | 14.6 Å | 9.9 Å | 13.3 Å | 13.1 Å | 13.0 Å | 12.7 Å | 13.2 Å | 12.4 Å |
| Li | 12.6 | 12.4 | 9.8 | 13.3 | 13.0 | 12.8 | 12.9 | 13.1 | 12.7 |
| Na | 12.3 | 12.3 | 9.7 | 13.4 | 13.2 | 12.9 | 13.0 | 13.0 | 12.4 |
| K | 12.0 | 11.9 | 9.9 | 13.4 | 12.9 | 12.8 | 13.0 | 12.9 | 12.3 |
| Cs | 12.4 | 12.3 | 11.2 | 12.9 | 12.6 | 12.6 | 12.8 | 12.8 | 12.6 |
| NH ₄ | 12.3 | 12.1 | 10.4 | 13.1 | 12.9 | 12.6 | 13.0 | 13.1 | 13.0 |
| Mg | 14.7 | 14.7 | 10.5 | 13.1 | 12.8 | 12.7 | 13.9 | 14.6 | 10.9 |
| Ca | 15.4 | 15.4 | 9.9 | 13.2 | 13.1 | 12.8 | 14.0 | 14.4 | 10.6 |
| Ba | 12.7 | 12.7 | 11.2 | 13.3 | 13.2 | 12.9 | 12.6 | 12.7 | 10.7 |
| Al | 15.4 | 15.2 | 11.4 | 13.3 | 13.4 | 13.2 | 13.9 | 13.8 | 13.6 |
| Fe | 13.6 | 13.9 | 9.8 | 13.2 | 13.3 | 13.2 | 13.1 | 13.5 | 12.8 |
| Ag | 12.1 | 12.2 | 10.7 | 13.6 | 13.3 | 13.2 | 13.0 | 12.9 | 12.3 |
| Mn | 15.0 | 14.4 | 9.9 | 13.3 | 13.4 | 12.8 | 12.9 | 13.4 | 11.9 |
| Co | 15.0 | 14.7 | 10.0 | 13.1 | 13.2 | 12.8 | 13.0 | 13.2 | 12.5 |
| Ni | 15.2 | 14.7 | 10.2 | 13.1 | 12.8 | 12.7 | 12.9 | 13.4 | 12.8 |
| Cu | 12.5 | 12.4 | 9.9 | 13.0 | 13.2 | 12.7 | 13.5 | 13.5 | 13.0 |
| Zn | 15.1 | 13.7 | 10.2 | 13.1 | 13.3 | 12.7 | 13.2 | 13.0 | 13.0 |
| Cd | 15.3 | 14.8 | 9.9 | 13.1 | 13.0 | 12.9 | 13.1 | 13.8 | 11.6 |
| Hg | 13.0 | 13.2 | 9.6 | 13.2 | 13.2 | 13.1 | 12.9 | 12.9 | 12.1 |

(1) Before heating.

(2) Hydrated at 40% relative humidity 1 week.

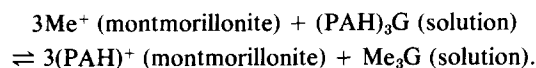
(3) After heating at 200°C under vacuum.

Only some of the interlayer spaces contain PAH⁺ and their *c*-spacings cannot be smaller than 12.0 Å, even under vacuum. Interlayers which do not contain PAH⁺ collapse to a spacing of 10.0 Å as a consequence of the dehydration of the film.

DISCUSSION

The maximum of the NH₃⁺ symmetric bending absorption band at 1490–1520 cm⁻¹ can give useful information on the character of the ammonium ion in the interlayer space. The characteristic maxima of the various forms of association of PAH⁺ are summarized in Scheme 1.

Hydrated ammonium ion is the major association form of the amine obtained when the adsorption takes place from 0.5% aqueous solution of Roundup with all forms of montmorillonite or from the ethanol solution with montmorillonites saturated with the major elements (excluding Al-montmorillonite). In all these cases the adsorption of PAH⁺ takes place by the mechanism of a reversible cation exchange reaction as follows:



The ammonium content in the clay does not exceed its cation exchange capacity.

Anhydrous ammonium ion is the chief PAH⁺ form in the clay for the following cases:

1. When the hydrated ammonium ion is thermally dehydrated under vacuum.

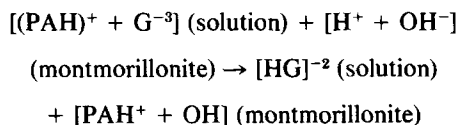
2. When the adsorption is carried out from free amine solutions in organic solvents such as ethanol or CCl₄. When such clay films are dried in the atmosphere the organic solvent molecules are replaced by water molecules and the ammonium ion is hydrated.

3. When the adsorption is carried out from very dilute (0.1%) aqueous solutions of Roundup. The water structure is determined by the exchangeable metal cation and the amount of adsorbed PAH⁺ is too small to break this structure. These results are in agreement with the thermodynamic calculations of Vansant and Uytterhoeven (1972) who showed that an interlayer, in which both metal and ammonium ions are present, is not stable in contrast to an interlayer which contains either metal or ammonium ions solely.

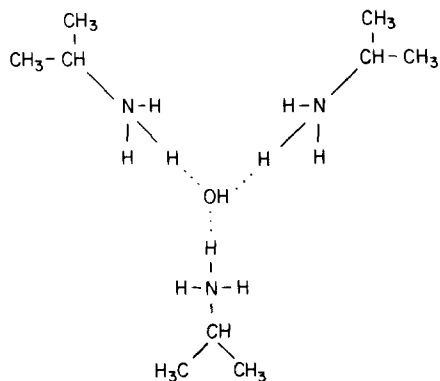
Ammonium-amine is obtained by the treatment of montmorillonites with a CCl₄ solution of PA and is identified by the appearance of perturbed bands characteristic for the ammonium ion and perturbed bands characteristic for an amine. Ammonium-amine associations of aliphatic amines are obtained only in the presence of excess of free amines (Yariv and Heller, 1970; Heller and Yariv, 1970; Yariv et al., 1971). In the present study they were not formed during the interaction of Roundup with any of the montmorillonites.

Hydrogen bonds between ammonium and hydroxyl ions in the clay interlayer of all montmorillonites (excluding Al- and Fe-montmorillonite) are formed during the adsorption of PAH⁺ from a 5% aqueous solution of Roundup. They are also formed with transition metal montmorillonites treated with a 5% ethanol solution of

Roundup. In all these cases the adsorption of the ammonium ion is in great excess of the cation exchange capacity of the clay. When such clays are thermally dehydrated under vacuum the frequency of the absorption bands of NH_3^+ are not shifted and it is therefore concluded that this ammonium-hydroxyl association is anhydrous. H^+ and OH^- ions are produced by the dissociation of interlayer water. Since G^{-3} is a proton acceptor, exchange reaction between ammonium and hydrogen takes place according to:



The association which is obtained when the amine is present in excess is very stable and repeated washings of the clay with distilled water do not remove the excess amine to any considerable extent. (Most investigators who observed sorption of amines in excess of cation exchange capacity of the clay succeeded in removing this excess by repeated washings of the clay with distilled water.) It appears that the OH^- ion is intercalated in a "cage" formed by several amphipathic PAH^+ species. The following structure is suggested:



Since the carbon adjoining the NH_3^+ group is a secondary carbon, the washing out of the OH^- ion by water is sterically hindered.

Polymeric cationic species are formed in Al- and Fe-montmorillonite during the adsorption of organic proton acceptors (Heller-Kallai et al., 1973). In the present study, although the proton acceptor G^{-3} is not adsorbed by the clay from the aqueous solution, it accepts protons donated by the clay and Al and Fe polymerize in the interlayer space forming polymeric cations. The ammonium cation is expelled from the aqueous solution and is adsorbed in excess of the cation exchange capacity of the clay, forming hydrogen bonds with oxygens belonging to the polymeric metallic cations. The following reaction is suggested for exchangeable aluminum polymerization:

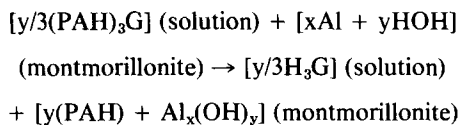
Table 5. Characteristic absorption bands (in cm^{-1}) of *iso*-propylammonium adsorbed on homoionic montmorillonite from 5% ethanol solution of Roundup.

| Exchange cation | NH_3^+ asym. def. | | NH_3^+ sym. def. | |
|-----------------|----------------------------|--------|---------------------------|------|
| | (2) | (1) | (1) | (2) |
| H | 1610 | 1497 | 1497 | 1492 |
| Li | 1612 | 1500 | 1500 | 1495 |
| Na | 1611 | 1500 | 1500 | 1493 |
| K | 1610 | 1498 | 1498 | 1495 |
| Cs | 1612 | 1504 | 1504 | 1493 |
| NH_4 | 1613 | 1502 | 1502 | 1492 |
| Mg | 1613 | 1500 | 1500 | vw |
| Ca | 1611 | 1501 | 1501 | vw |
| Ba | 1615 | 1500 | 1500 | — |
| Al | 1625vb | 1520 | 1520 | 1510 |
| Fe | 1610vb | 1510 | 1510 | 1506 |
| Ag | 1610 | 1497 | 1497 | 1491 |
| Mn | 1610 | 1510sh | 1510sh | vw |
| Co | 1610 | 1510 | 1510 | 1492 |
| Ni | 1610 | 1510 | 1510 | vw |
| Cu | 1620 | 1513 | 1513 | 1515 |
| Zn | 1615 | 1513 | 1513 | 1510 |
| Cd | 1610 | 1510 | 1510 | vw |
| Hg | 1612 | 1501 | 1501 | 1495 |

sh—shoulder; vw—very weak; vb—very broad.

(1) Air-dried.

(2) Dried under vacuum at 200°C .



where Al denotes a monomeric aluminum cation and $\text{Al}_x(\text{OH})_y$ denotes a polymeric aluminum cation in the interlayer space. This type of polymerization of Al ions gives rise to fixation of exchangeable cations. Heller-Kallai et al. (1973) showed that cations other than Al (and even Na) can become fixed in the presence of Al during the polymerization of the latter by the interaction with organic proton acceptors.

CONCLUSIONS

iso-propylammonium from Roundup is adsorbed by montmorillonite. The adsorption occurs by two different ion-exchange mechanisms: (1) the ammonium ion exchanges metal cations in the interlayer space, and (2) the ammonium ion exchanges protons originating from the hydrolysis of interlayer water. In the latter process, which takes place from concentrated solutions of Roundup, protons are transferred from the interlayer space to the aqueous solution, where they are accepted by the anionic component of Roundup, that is G^{-3} . Mechanism (1) gives rise to the adsorption of amounts not greater than those equivalent to the cation exchange capacity of the clay whereas the amount of ammonium sorbed by mechanism (2) is much higher. Exchangeable

aluminum and iron in the interlayer space are polymerized during the interaction between montmorillonite and Roundup. The adsorbed PAH⁺ forms hydrogen bonds with water molecule hydroxyl ions or with polymeric cations in the interlayer space of the montmorillonite. Hydrogen bonds between the NH₃⁺ group and the hydroxyls or polymeric metal cations stabilize associations which are formed by the excess adsorption of the ammonium ion by montmorillonite from concentrated solutions of Roundup.

ACKNOWLEDGMENTS

We are grateful to the Monsanto Company (Belgium) and to their agent in Israel "Paz-Chim" for providing Roundup. We are also grateful to Dr. H. Cross from Jerusalem for the useful discussions and to Dr. Menashe Horowitz from the Volcani Center for Agricultural Research (Neve Ya'ar) who encouraged us to perform this research.

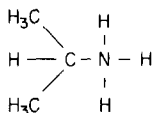
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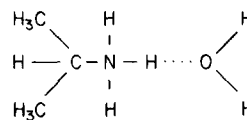
Scheme I. The associations formed by *iso*-propylammonium in the interlayer space of montmorillonite and the characteristic frequencies (in cm⁻¹) of NH₃⁺ symmetric deformation band.

1. Adsorption in the range of the CEC of montmorillonite.

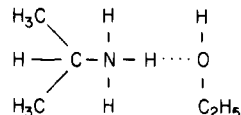
A. 1492 cm⁻¹—anhydrous.



B. 1500 cm⁻¹—hydrated.

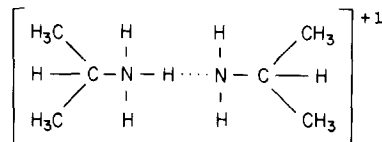


C. 1510 cm⁻¹—solvated by ethanol.

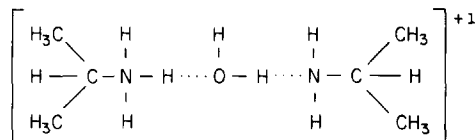


2. Adsorption of amounts in excess of the c.e.c. of montmorillonite.

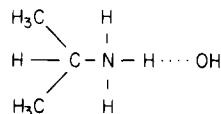
A. 1507 cm⁻¹—ammonium amine formation.



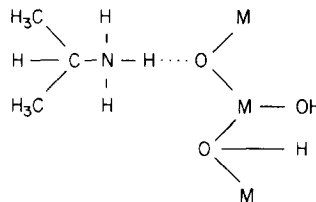
and/or



B. 1512 cm⁻¹—hydrogen bonds with hydroxyl ions.



C. 1518 cm⁻¹—hydrogen bonds with polymeric AlOH and FeOH cations.



Резюме- Изучались механизм адсорбции изо-пропиламмония, PAH^+ , (катионный компонент Раундапа) различными гомоионными монтмориллонитами и структуры ассоциаций, образующиеся в межслойных промежутках с использованием инфракрасных и рентгеновских лучей и углеродных методов анализа. Изучалась адсорбция из водных и этаноловых растворов Раундапа. Инфракрасные спектры сравнивались со спектрами, полученными в результате обработки монтмориллонитов этаноловыми и CCl_4 растворами свободного изо-пропиламина (PA). Адсорбция PA из этанола способствует присоединению протонов к амину. PA, сорбированный из раствора CCl_4 , образует амониево-аминовую ассоциацию. Адсорбция PAH^+ из спиртового раствора Раундапа происходит в результате катионного обмена. С обменными катионами переходных металлов PAH^+ сорбируется в избытке, образуя водородные связи между группами NH_3^+ с образованием гидроксидов в результате диссоциации водных молекул. Процесс адсорбции PAH^+ из водных растворов Раундапа зависит от концентрации растворов. Если монтмориллонит реагирует с 0,5-процентным раствором Раундапа, PAH^+ адсорбируется с помощью обмена металлических катионов и адсорбционная способность глины не превосходит катионной обменной способности. Если монтмориллонит реагирует с 5-процентным раствором Раундапа, PAH^+ обменивает протоны, образующиеся в результате гидролиза межслойной воды. Протоны, которые перемещаются из межслойного промежутка в водный раствор, присоединяются к анионному компоненту Раундапа. Количество PAH^+ , адсорбированного из концентрированных растворов Раундапа, намного выше, чем катионная обменная способность монтмориллонита. В межслойных промежутках возникают водородные связи между аммонием и водой или гидроксильными группами. С трехвалентными обменными ионами Al и Fe, которые склонны полимеризоваться в межслойных промежутках, избыточная сорбция приводит к водородному связыванию NH_3^+ с кислородом полимера.

Kurzreferat- Der Mechanismus der Adsorption von Isopropylammonium (PAH^+), dem Kationenanteil von Roundup, auf verschiedene homoionische Montmorilloniten und die Strukturen der Kombinationen, die im Zwischenschichtraum entstehen, wurden mit Infrarot-, Röntgen- und Kohlenstoffanalyse untersucht. Adsorption von Roundup aus wässrigen- und Äthanolösungen wurde untersucht. Die Infrarotspektren wurden mit den Spektren verglichen, die durch die Behandlung von Montmorilloniten mit Äthanol und CCl_4 Lösungen des freien Isopropylamins (PA) erhalten wurden. Die Adsorption von PA aus Äthanol verursacht Protonation des Amins. Wenn PA von CCl_4 Lösungen adsorbiert wird, formt es eine Ammonium-Amin Assoziation. Die Adsorption des PAH^+ aus Alkohollösungen von Roundup nimmt durch Kationenaustausch Platz. Mit austauschbaren Übergangsmetallkationen wird PAH^+ im Überschuss adsorbiert und formt Wasserstoffbrücken zwischen NH_3^+ Gruppen und Hydroxygruppen, die ein Resultat der Dissoziation von Wassermolekülen sind. Der Ablauf der Adsorption von PAH^+ aus wässrigen Lösungen von Roundup hängt von der Konzentration der Lösung ab. Wenn Montmorillonit mit einer 0,5 % Lösung von Roundup reagiert wird, dann wird PAH^+ von austauschenden Metallkationen adsorbiert und die Adsorptionskapazität des Tones überschreitet die Kationenaustauschkapazität nicht. Falls das Montmorillonit mit einer 5,0% Lösung von Roundup reagiert wird, dann tauscht das PAH^+ Protonen aus, welche von der Hydrolyse des Zwischenschichtwassers her stammen. Protonen, welche von dem Zwischenschichtraum an die Wasserlösung übergeben werden, werden von dem Anion des Roundup akzeptiert. Der Anteil von PAH^+ , der von konzentrierten Rounduplösungen adsorbiert wird, ist viel höher als die Kationenaustauschkapazität des Montmorillonit. Wasserstoffbrücken werden zwischen dem Ammonia und Wasser oder Hydroxylgruppen auf dem Zwischenschichtraum geformt. Mit den trivalenten Austauschionen Al und Fe, welche eine Tendenz zur Polymerisation im Zwischenschichtraum haben, ein Überschuss an Adsorption ergibt Wasserstoffbrücken von NH_3^+ zum Sauerstoff des Polymer.

Résumé- Le mécanisme d'adsorption d'iso-propylammonium (PAH^+), (le constituant cationique de Roundup) par diverses montmorillonites homoioniques, et les structures des associations obtenues dans l'espace interfeuillet ont été étudiés, utilisant des méthodes d'analyse à l'infrarouge, aux rayons-X et au carbone. L'adsorption de solutions aqueuses et de solutions d'éthanol de Roundup a été étudiée. Les spectres infrarouges ont été comparés avec ceux obtenus par le traitement de montmorillonite à des solutions d'éthanol et des solutions CCl_4 d'iso-propylamine (PA) libre. L'adsorption de PA de l'éthanol entraîne la protonation de l'amine. PA sorbée de la solution de CCl_4 forme une association ammonium-amine. Le mécanisme d'échange de cations entraîne l'adsorption de PAH^+ d'une solution d'alcool de Roundup. Avec des cations de métal de transition échangeables, PAH^+ est sorbée de manière excessive, formant des liens d'hydrogène entre les groupes NH_3^+ et les hydroxyles résultants d'une dissociation de molécules d'eau. Le processus d'adsorption de PAH^+ de solutions aqueuses de Roundup dépend de la concentration de la solution. Si la montmorillonite réagit avec une solution de 0,5% de Roundup, PAH^+ est adsorbé par des cations de métal de transition en échange, et la capacité d'adsorption de l'argile ne dépasse pas la capacité d'échange de cations. Si la montmorillonite réagit avec une solution de 5,0% de Roundup, le PAH^+ échange des protons venant de l'hydrolyse de l'eau interfeuillet. Les protons transférés de l'espace interfeuillet à la solution d'eau sont acceptés par le constituant anionique de Roundup. Les quantités de PAH^+ adsorbées de solutions concentrées de Roundup sont beaucoup plus élevées que la capacité d'échange de cations de la montmorillonite. Des liens d'hydrogène sont formés entre l'ammonium et l'eau ou les groupes hydroxyles sur l'espace interfeuillet. Avec les ions d'échange trivalent Al et Fe qui ont tendance à se polymériser dans l'espace interfeuillet, un excès de sorption entraîne la liaison de l'hydrogène de NH_3^+ à l'oxygène du polymère.