

INFRARED STUDY OF BENZONITRILE (C_6H_5-CN)-MONT-
The MORILLONITE COMPLEXES.

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ABSTRACT

Infrared absorption study of the Mg-saturated montmorillonite complex with benzonitrile shows when compared with Ca- and Ba-saturations that the benzonitrile molecules coordinate regularly about the exchangeable ions. The array of the benzonitrile ligands as for the square hybrid complex, holds water to complete the octahedron in proportion to the polarizing strength of the metal-ion.

INTRODUCTION

The mechanism of sorption of organic molecules by layer silicates is not yet fully understood. Sorbed molecules can be associated with the mineral surface and with the exchangeable cations. Both mechanisms must be effective in the process and their relative importance must depend on the nature of the sorbate and the cation present. In earlier studies the association with the silicate surface was considered as the most important mechanism, but in recent years it is becoming increasingly evident that a predominant role is played by the exchangeable cations.

Infrared spectroscopy affords a valuable method for the study of the sorption mechanism (Farmer and Russell, 1967). The type of association can be ascertained by the perturbation of the frequencies of the sorbed molecules, specially when the molecule has functional groups that produce defined absorptions. Also the orientation of the molecules can be determined by the change in intensity of specific bands with the incidence angle (Serratosa 1965). This paper is concerned with the sorption of benzonitrile in montmorillonite. The band corresponding to the stretching vibration of the CN group is well characterized and appears in a region that is free of silicate absorption, and the symmetry of the molecule presents a favorable case for the analysis of the orientation by infrared spectroscopy. Also because substituted benzonitriles are used as herbicides, it becomes important to know the factors that influence their association with silicate minerals surfaces.

EXPERIMENTAL

Thin films of Na montmorillonite (Wyoming) were prepared by passing enough of a dilute suspension of the clay thru a micropore filter to provide thicknesses when dry corresponding to 2 or 3 mg of solid per cm^2 . Films were then converted to other ion saturations by washing with the proper chlorides. These stripped-off dry films are self-supporting and exhibit a high degree of preferred alignment of clay layer normals parallel to the normal to the clay film. An essentially unpolarized infrared source is then suitable for the absorption

observations. Vibrations in the specimen in the plane of the electric vector of the light are actively absorbing, but leave the transmitted beam unpolarized. Vibrations normal to the plane of the flake are not active at normal incidence, but introduce a degree of polarization in the transmitted beam at inclined incidence which is a measure of the resultant of the flake normal on one component of the incident unpolarized beam and is observable as attenuated intensity of the transmitted light. Small departures from exact alignment of normals in the specimen aggregate provides a small unpolarized absorption activity, but moderately inclined incidence permits a semiquantitative measure of the attenuation of intensity due to polarization.

Films to be analyzed were first dried in vacuum and then immersed in benzonitrile liquid. After 24 hours the films were removed from the liquid and the excess of nitrobenzene was evaporated off in a desiccator. The films were transferred to an evacuable cell, and studied immediately after preparation and after several periods of evacuation. A second adsorption was performed after the evacuation in order to assure that the first had been completed. Mg^{2+} , Ca^{2+} and Ba^{2+} were used as exchangeable ions. Concurrently X-ray records were obtained for the 001 sequences.

The amounts of benzonitrile in the complexes were determined by immersing the films in measured volumes of acetone. Acetone replaces the benzonitrile in the solid and dissolves it in the wash liquid. The completeness of the replacement was checked by infrared examination of the films. After the films were removed from the acetone, no benzonitrile absorption features were observed. The concentration of benzonitrile in acetone solution was determined from its infrared absorption at 685 cm^{-1} .

RESULTS AND DISCUSSION

The infrared spectrum of Mg-montmorillonite in equilibrium with the atmosphere presents broad bands corresponding to the stretching and deformation vibrations of the adsorbed water molecules. The maxima are at 3395 , 3250 and 1637 cm^{-1} . The band at 1637 cm^{-1} (Fig. 1), which is in a region free of other silicates absorptions, shows a marked dissymmetry around the maximum. This probably indicates the presence of more than one kind of association between the water molecules and the silicates, and distinguishes water directly coordinated to the cations from that associated only with the mineral surface. As water is lost during evacuation the band corresponding to the deformation frequency becomes completely symmetrical about a maximum at 1623 cm^{-1} (Fig. 1). At the same time the maximum corresponding to the stretching vibrations has moved toward higher frequencies; the exact position of the new band cannot be measured due to the interference of the absorption of the structural OH groups. The positions of the new bands indicate less hydrogen bonded character and represent the water coordinated to the exchangeable ions (Russell and Farmer, (1964).

After immersion in liquid benzonitrile, the water molecules show absorptions at 3348 , 3246 and 1648 cm^{-1} (Fig. 1). The displacement of the water bands after the sorption of benzonitrile indicates that the water molecules are more strongly involved in hydrogen bonding than was true

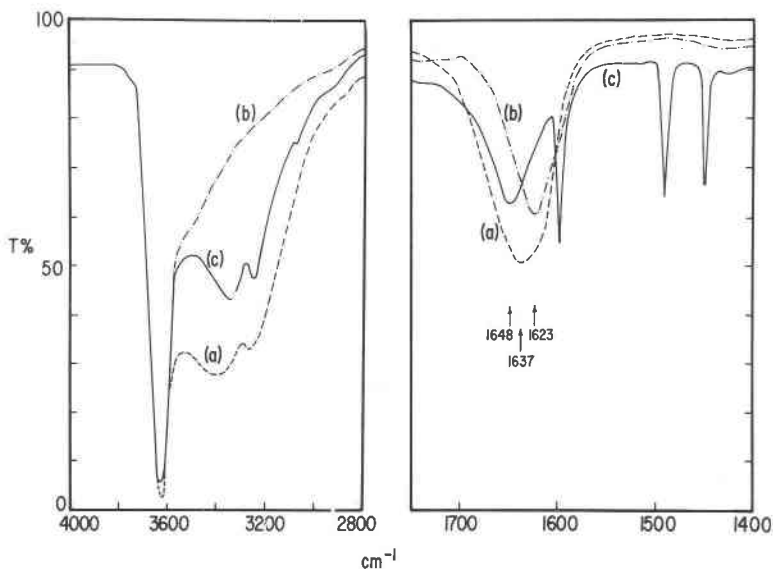


FIG. 1. Water absorption bands in Mg-montmorillonite: (a) in equilibrium with the atmosphere, (b) after evacuation, (c) in the hydrated benzonitrile complex.

of the initial water systems. It is inferred that the water molecules, coordinated around the magnesium ions, are hydrogen bonded to the CN group of the benzonitrile.

The infrared spectrum of the film shows also the characteristic absorption bands of benzonitrile at 685, 758, 1293, 1337, 1449, 1489, 1596, 2240 and 3070 cm^{-1} (Fig. 2). The absorption corresponding to the stretching vibration of the CN group is not single but in the more hydrated complex the most prominent maximum is at 2240 cm^{-1} . This represents a shift toward the higher frequencies of 12 cm^{-1} with respect to the position in liquid benzonitrile (2228 cm^{-1}). The augmented hydrogen bond strength inferred above, with bonds directed to the NC group, conditions this increase. Some of the benzonitrile molecules may have displaced water to become directly coordinated to the cation, providing the complex modification of the $\text{C}\equiv\text{N}$ stretching band on the higher frequency side ($> 2240^{-1}$).

It is a well established fact that, unlike other ligands, the $\text{C}\equiv\text{N}$ stretching bands of -CN and -NC donors shift to higher frequencies upon coordination (Nakamoto, 1963). Several explanations have been proposed for the frequency increase which has been examined recently by Purcell and Drago (1966). In our case it would be considered that the establish-

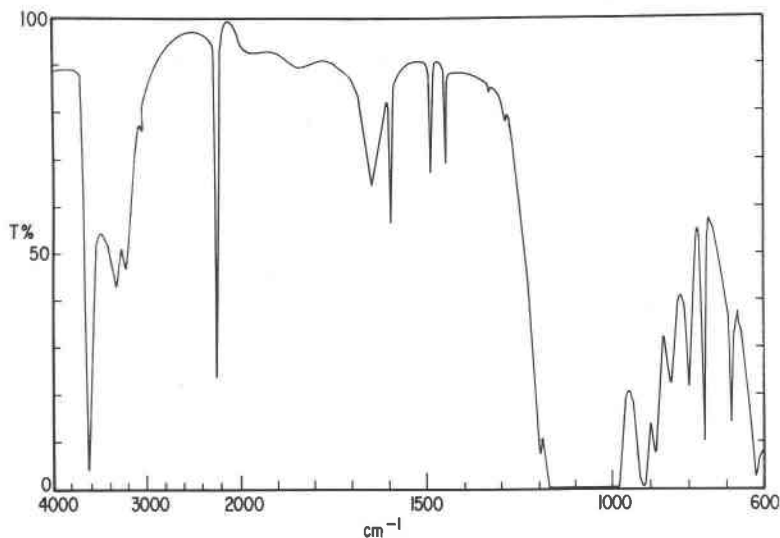


FIG. 2. Infrared spectrum in the 4000–600 cm^{-1} region of the benzonitrile-Mg-montmorillonite complex.

ment of the coordination relation with the metal ion inhibits the conjugation aspect of the aromatic nitrile molecule.

When the films are evacuated, water is lost progressively as indicated by the reduced prominence of the bands at 3348, 3246 and 1648 cm^{-1} . Concurrently in the stretching region of the CN group, a band at 2261 cm^{-1} is clearly observed now, which increases in intensity as the 2240 cm^{-1} band decreases in prominence. After long evacuation at $\sim 80^\circ\text{C}$, only the higher frequency peak is observed. The position of this peak is sensitive to the metal ion present and is at 2261 cm^{-1} for Mg^{2+} , 2249 cm^{-1} for Ca^{2+} and 2240 cm^{-1} for Ba^{2+} . These observations suggest that the benzonitrile has become coordinated directly to the cations. In the hydrated benzonitrile complexes the water bridges between the benzonitrile and the metal ions make the influence of the latter less prominent and the $\text{C}\equiv\text{N}$ stretching band is observed at 2240 cm^{-1} for the three cations. When the films are evacuated and the water is lost, the benzonitrile becomes directly coordinated to the cations.

In the Mg-complex, some water is still present, and prolonged evacuation at 80–100°C fails to remove or even decrease its content. Also the quantity of benzonitrile remains constant after this treatment as indicated by the constancy of the band intensities. A second sorption of benzonitrile confirms the reality of the stoichiometric relationship. The

remaining water presents a relatively sharp band at 1650 cm^{-1} . The position of the bands corresponding to the stretching vibrations can not be determined with certainty because of the overlapping effect of the structural OH groups absorption.

The analysis of the films in this stable state shows a benzonitrile content that corresponds to about four molecules per metal-ion.

Orientation studies. Benzonitrile belongs to the point group C_{2v} . The molecule possesses 33 normal vibrations of symmetry type A_1 , A_2 (infrared inactive), B_1 and B_2 . For the infrared active modes, the dipole moment changes along three mutually perpendicular axes: vibrations of class A_1 have dipole moment changes along the symmetry axis (C_2); those of class B_1 , perpendicular to the axis but in the molecular plane and those of B_2 , normal to the molecular plane (Fig. 3). The frequencies corre-

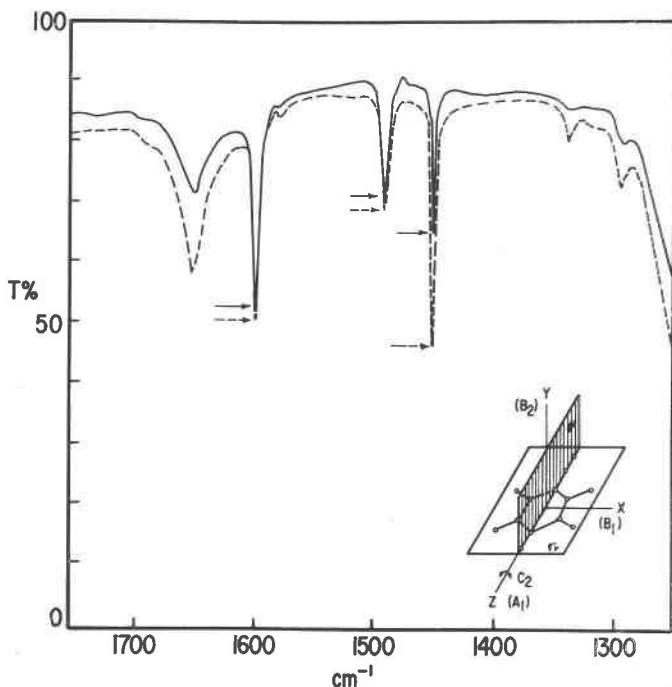


FIG. 3. Infrared spectrum of the evacuated benzonitrile-Mg-montmorillonite complex in the region $1750\text{--}1250\text{ cm}^{-1}$, for two angles of incidence, (— 0° , - - - 40°) showing the directional dependence of the B_1 absorption bands of benzonitrile and of the deformation band of water (symmetry class A_1). The diagram in the lower right corner illustrates the symmetry elements of the benzonitrile molecule (point group C_{2v}) and the directions of the dipole moment change for each vibration class.

sponding to the different vibrational modes are well identified (Green, 1961).

When the spectrum for the evacuated Mg-montmorillonite-benzonitrile complex is recorded with the film inclined to the incident beam (incidence angle $\sim 40^\circ$) only the bands corresponding to the vibrations of class B_1 increase significantly in intensity (1293, 1337 and 1449 cm^{-1}) (Fig. 3). The increase in intensity for this incidence angle is by a factor of 2, and indicates that the molecules are disposed with their molecular planes at a high angle with the silicate layers and with the principal axis ($\text{C}\equiv\text{N}$ bond) parallel to the layers. This is a favorable position to coordinate with the Mg^{2+} ions. X-ray records for the 001 sequences (8 orders observed) correspond to a layer periodicity of 15.1 \AA , which is nearly sufficient to accommodate the molecules in a perpendicular position. A small tilting would be consistent with both the infrared and the diffraction results. The 1650 cm^{-1} band, corresponding to the deformation vibration of the water molecules, also increases by a factor of about 2 with the inclination of the film. The water molecules belong also to the point group C_{2v} . The 1650 cm^{-1} band corresponds to a vibration of class A_1 , with a change in dipole moment along the molecular axis. This indi-

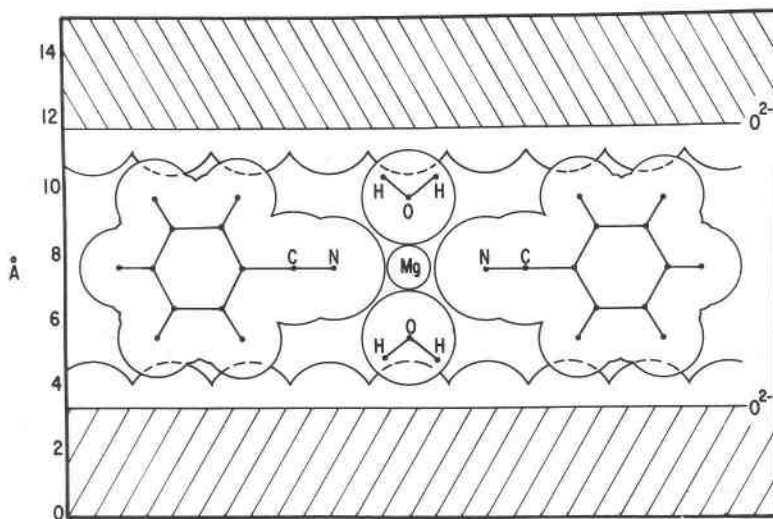


FIG. 4. An arrangement of the interlayer matter in the benzonitrile-montmorillonite complex consistent with the analytical information. The Mg^{2+} ions are midway between the layers coordinated to four benzonitrile molecules (sensibly perpendicular to the layers) and to two water molecules. The water molecules furnish both their protons to $\sim 3.0\text{ \AA}$ hydrogen bonds with the oxygens of the silicate surface.

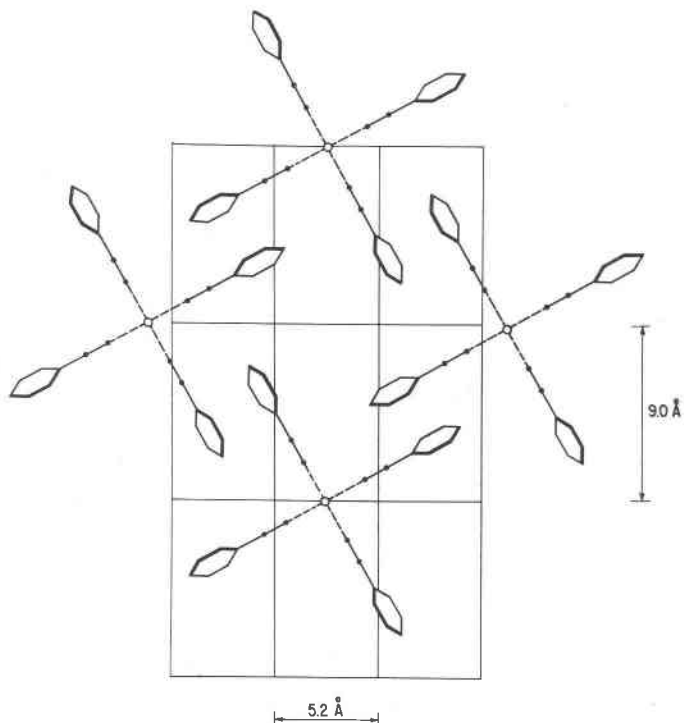


FIG. 5. An idealized model of the interlayer benzonitrile in the a-b plane. A section approximately $15.6 \times 18 \text{ \AA}$ contains two octahedrally coordinated Mg^{2+} ions (four molecules of benzonitrile and two water molecules situated above and below). The Mg^{2+} ion population conforms closely to the layer charge of montmorillonite ($1/3$ per unit cell).

cates that the water molecules are disposed with the axis at a high angle with the silicate layers.

The several lines of evidence can be utilized to construct the model depicted in Figures 4 and 5. The Mg^{2+} ions are coordinated with six molecules, four benzonitriles arranged as a paddle wheel and two water molecules situated above and below at the two remaining corners of an octahedron. The representation in Figure 4 indicates that each water molecule is independent and is 3 \AA or slightly more removed from oxygens of the silicate surface. In Figure 5 an idealized model has been drawn to illustrate the feasibility of the complex in the interlayer space. A six cell unit ($15.6 \times 18 \text{ \AA}$) is nearly enough to contain two $\text{Mg}^{2+} \cdot 4\text{C}_6\text{H}_6\text{CN} \cdot 2\text{H}_2\text{O}$ octahedra. The Mg^{2+} ion population of $\sim 1/3 \text{ Mg}^{2+}$ per cell is consistent with the layer charge of montmorillonite.

Similar complexes are obtained with Ca- and Ba- montmorillonite, but

the substitution of water molecules by benzonitrile and the removal of the additional water by evacuation is more easily accomplished. A completely dehydrated complex can be prepared for Ca-montmorillonite after evacuation at about 80 C. and after evacuation alone in the case of Ba-montmorillonite. The positions of the band corresponding to the stretching vibration of the $C\equiv N$ group in the dehydrated complexes are 2249 cm^{-1} for Ca^{2+} and 2240 cm^{-1} for Ba^{2+} as compared with 2261 cm^{-1} for Mg^{2+} . The perturbation of the $C\equiv N$ stretching frequency is related to the polarizing capability of the cation. This indicates that in this case, the explanation for the frequency increase of the $C\equiv N$ stretching band upon coordination must involve the strength of the coordination association with the metal ion. Also the positions of the bands of the water coordinated to the cation and hydrogen bonded to the benzonitrile depends on the cation present: $3390, 1635\text{ cm}^{-1}$ for Ca^{2+} , and $3405, 1630\text{ cm}^{-1}$ for Ba^{2+} as compared with $3348, 1648\text{ cm}^{-1}$ for Mg^{2+} . This indicates that the more strongly polarizing ions cause the coordinated water to form stronger hydrogen bonds with the CN group of the benzonitrile.

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