

INFRARED STUDY OF PYRIDINE ADSORBED ON MONTMORILLONITE SURFACES

by

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ABSTRACT

THE NATURE of pyridine adsorption by acid- and base-saturated montmorillonite from Otay, California (A.P.I. no. H-24) was studied by infrared adsorption. The spectrum for chemisorbed pyridine was found to be distinctively different from physically adsorbed pyridine; the latter gave a spectrum very similar to liquid pyridine. Upon exposure of the clay films to pyridine at low vapor pressures, only the pyridinium ion spectrum was obtained; but when the vapor pressure was increased, both chemisorbed and physically adsorbed pyridine was detected. The intensity of the spectrum for physically adsorbed molecules could be reduced by a vacuum, whereas the intensities of the peaks for the chemisorbed pyridinium ions were unaffected.

Interlayer water was replaced by adsorption of pyridine. Water, in turn, replaced physically adsorbed pyridine from the clay surface but was unable to replace chemisorbed pyridine.

SORPTION of gases on surfaces of colloidal solids is frequently used as a means of characterizing the acidic nature of solid surfaces. Eischens and Pliskin (1958) have given an extensive discussion of the sorption of molecules on surfaces and an interpretation of their infrared spectra. Mapes and Eischens (1954) have used the infrared spectrum of ammonia chemisorbed on cracking catalysts to differentiate between Lewis and Bronsted type acid sites.

Clays, even when saturated with basic cations, act as moderately strong acids. Benesi (1956), using adsorbed color indicators, reported that sodium- and ammonium-saturated kaolinite had stronger acid sites than did montmorillonite that was saturated with the same cations. Considerable work has been done on the adsorption of ammonia on large surface area solids. Mortland *et al.* (1963) studied the adsorption of ammonia on montmorillonite and vermiculite extensively and found that the basic ammonia molecule reacted with adsorbed interlayer water to form ammonium ions that are chemisorbed on the clay surfaces. They were unable to obtain an infrared spectrum for physically adsorbed ammonia molecules at room temperature but were able to do so at -150°C .

Ammonia, being a relatively strong base ($\text{p}K_b = 4.7$), will react with extremely weak acid sites. By using a weaker base one may obtain a better

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understanding of the surface acidity of clays. Pyridine, which has a pK_b of 8.8, is a much weaker base than ammonia and thus will not react with some of the weaker sites that will react with ammonia. Parry (1963) found that there were no Bronsted sites on the surface of alumina strong enough to react with pyridine, although Eischens and Pliskin (1958) had previously reported that Bronsted sites on alumina were strong enough to react with ammonia.

Infrared spectroscopy provides a means of determining the manner in which molecules are adsorbed by clay surfaces. The literature on the adsorption of organics by clays is, however, limited. The object of this paper is to show that physically and chemically adsorbed pyridine molecules on Otay montmorillonite can be distinguished by infrared spectroscopy. The manner in which the molecules are adsorbed is also of interest.

EXPERIMENTAL PROCEDURE

Materials

Montmorillonite from Otay, California, was used. The $<2\mu$ fraction was saturated with magnesium by washing five times with 1.0 N magnesium chloride. Excess salts were removed by washing with distilled water until the supernatant gave a negative test for chloride. Acidic clays were prepared by passing a $<2\mu$ Na-saturated clay suspension through an OH-saturated anion exchange resin column and then through an H-saturated cation exchange resin column.

The clay suspension was then stored at 5°C to reduce the rate of H-induced lattice decomposition. A portion of the H-saturated clay was dried at 60°C and ground to pass a 60 mesh sieve.

A new technique was developed for obtaining infrared spectra of liquid vapors adsorbed on clays. This consists of sedimenting a dilute suspension (approximately 1 per cent) of clay on nylon mesh (60 mesh) which is taped to an aluminum frame. On evaporation, a continuous thin film is obtained. No difference was found between the spectra obtained by this technique and that obtained by the conventional KBr-pellet technique. After the clay suspension dried, the sample was introduced into an infrared cell.

Apparatus

The sorption system was designed so that adsorption and desorption could be measured gravimetrically at the same time as infrared spectra were being obtained for another portion of the sample. The system consisted of a Pyrex vacuum manifold connected to an infrared vacuum cell (Fig. 1) and to a calibrated quartz helix contained in a Pyrex sorption tube. A mercury manometer was used to determine the equilibrium vapor pressure. The manometer read with a cathetometer to ± 0.1 mm.

The extension of the quartz helix was also measured with a cathetometer to ± 0.1 mm. Sensitivity of the helix was 2.05 mg per mm and gave a linear response in the weight range used. Reading the extension of the helix gave

an error in determining the weight of pyridine adsorbed per gram of clay of ± 1.5 mg per g for a 150 mg sample.

The infrared cell (Fig. 1) consists of a Pyrex glass body with Irtran-2 windows. The window housings are fabricated of cell mounts from demountable-type liquid cells (No. FT-1-CM, Barnes Engineering Co., Stamford, Connecticut). The housings are fastened by screws to 4-in.² plexiglass plates

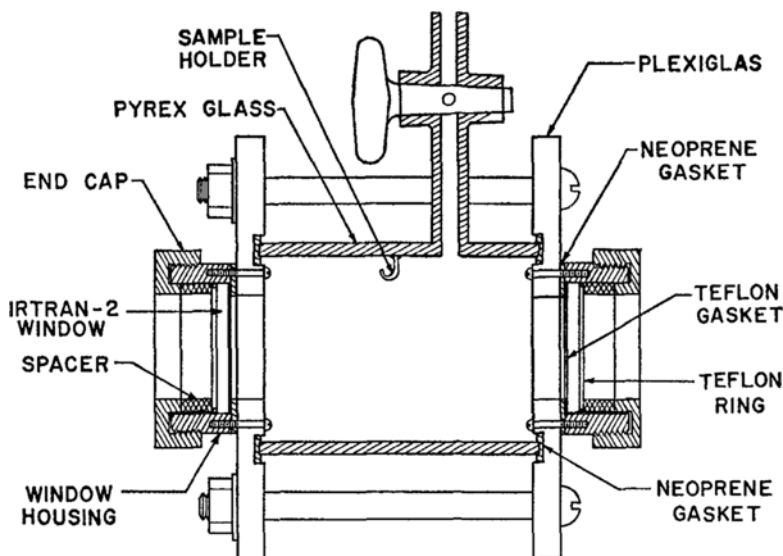


FIG. 1. Cut-away of infrared vacuum cell designed for this study.

that are sealed to the glass body by neoprene gaskets. Dow Corning high vacuum silicone grease was used to seal all joints. The cell is designed for mounting in the Beckman IR-8 (double-beam, filter-grating) infrared spectrophotometer. It was necessary to attenuate the reference beam with nylon mesh or screens and to widen the slits to compensate for loss of energy by scattering.

Procedure

One hundred and fifty milligrams of clay were weighed into an aluminum foil boat and suspended from the calibrated quartz helix. The sample weight determined by the helix generally agreed to within 1 mg of the weight determined by an analytical balance. After a sample was placed in the infrared cell and another portion of the sample suspended from the helix, the system was evacuated to less than 20μ Hg. After evacuation at room temperature, a spectrum of the clay was obtained. A small volume of pyridine vapor was then admitted and allowed to equilibrate before further spectra and

weight measurements were obtained. Preliminary work showed that adsorption was almost instantaneous and essentially complete after equilibrating for about 10 min at a given pressure. To ensure equilibrium conditions, 2 hr were allowed to elapse before weight changes and infrared spectra were obtained.

RESULTS AND DISCUSSION

Only slight perturbation would be expected of physically adsorbed molecules that are not strongly bound to the surface of the adsorbant. Therefore, the infrared spectrum of such molecules would be expected to be very similar to that of molecules in the liquid state, although a slight shift in some of the bands might be expected. On the other hand, considerable perturbation would be expected of chemisorbed molecules.

The infrared bands of pyridine, which are of interest in this study, are the C-H stretching frequencies in the 3020–3070 cm^{-1} range as well as the C-C and the C-N stretching frequencies at 1590–1660 cm^{-1} and near 1500 cm^{-1} (Klingsberg, 1960). Structurally, pyridine is very similar to benzene. The difference is that one of the carbon atoms is replaced by nitrogen, resulting in one less hydrogen.

TABLE 1. INFRARED BANDS OF PYRIDINE ON ACID SOLIDS IN THE 1400–1700 cm^{-1} REGION (PARRY, 1963)

Hydrogen-bonded pyridine	Co-ordinately bonded pyridine	Pyridinium ion
1400–1447 (vs)*	1447–1460 (vs)	
1485–1490 (w)	1488–1503 (v)	1485–1500 (vs)
		1540 (s)
1580–1600 (s)	1580 (v)	
	1600–1633 (s)	1620 (s)
		1640 (s)

* Band intensities: vs, very strong; s, strong; w, weak; v, variable.

Parry (1963) has reported infrared bands in the 1400–1700 cm^{-1} region for pyridine adsorbed on acid solids (Table 1). The bands for hydrogen-bonded pyridine are very similar to those of liquid pyridine except that they occur at slightly higher frequencies. Co-ordinately bonded pyridine can be distinguished by the band that occurs near 1600–1633 cm^{-1} ; however, the O—H bending frequency of adsorbed water occurs in the same region and may interfere. Pyridine chemisorbed as the pyridinium ion can be distinguished by the bands at 1540 and 1640 cm^{-1} . Further characterization is provided by the complete absence of the strong band around 1445 cm^{-1} of hydrogen-bonded pyridine. Barrow (1956), on the basis of some deuteration experiments, assigned the 1540 cm^{-1} pyridinium band to a combination mode that involves the N⁺—H deformation. The N⁺—H stretching vibration of the

pyridinium ion is generally a very broad structureless band at approximately 2450 cm^{-1} . Due to strong bonding with the oxygens of the clay surface, this band could not be observed.

To determine if the $\text{N}^+\text{-H}$ deformation frequency of the pyridinium ion could be detected, pyridine was adsorbed on acid Otay montmorillonite (initially H-saturated). Fig. 2 shows the spectra obtained at two different

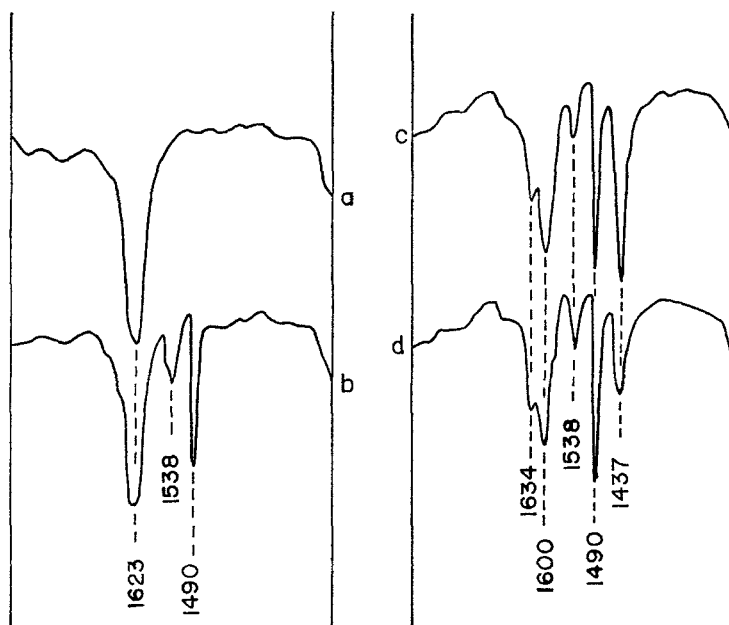


FIG. 2. Infrared spectra of pyridine adsorbed on acid Otay montmorillonite at 25°C .: (a) sample evacuated for 10 hr at $50\mu\text{ Hg}$; (b) after exposure to pyridine at 2.0 mm Hg; (c) after exposure to pyridine at 21.0 mm Hg; (d) evacuated for 15 hr at $70\mu\text{ Hg}$.

vapor pressures of pyridine and then after desorption by vacuum. Spectrum a was obtained after evacuating the system for 10 hr at $50\mu\text{ Hg}$. The band at 1623 cm^{-1} is the O-H deformation frequency of adsorbed water. Spectrum b was obtained under pyridine pressure of 2.0 mm Hg. The band at 1538 cm^{-1} indicates the interaction of pyridine with the protons of the acid clay and the formation of positively charged pyridinium ions that are chemisorbed by the clay. The absence of a band around 1440 cm^{-1} indicates that no physically or co-ordinately bonded pyridine is present. The vapor pressure was increased stepwise, and the first indication of physically adsorbed pyridine appeared at 3 mm Hg. Spectrum c, Fig. 2, was obtained at a pressure of 21 mm Hg. The band at 1437 cm^{-1} results from physically adsorbed

pyridine on the clay surface. Physical adsorption of pyridine molecules did not occur until chemisorption was complete. The bands at 1437 cm^{-1} and 1600 cm^{-1} could possibly result from co-ordinately bonded molecules (Table 1). However, the ease of complete removal of these bands by evacuation at slightly elevated temperatures and data to be presented later indicate that no co-ordinately bonded molecules were present on any of the samples studied. The 1623 cm^{-1} frequency of adsorbed water has been replaced by a doublet at 1600 and 1634 cm^{-1} , indicating that adsorbed water is replaced by the physically adsorbed pyridine molecules. The band at 1437 cm^{-1} is assigned to physically adsorbed molecules; and the 1490 , 1538 and 1634 cm^{-1} frequencies are assigned to chemisorbed pyridinium ions. Both physical and chemisorbed pyridine have band frequencies around 1600 cm^{-1} . Spectrum d was obtained after evacuating for 15 hr at $70\mu\text{ Hg}$. There is a distinct decrease in the intensity of the bands at 1437 and 1600 cm^{-1} but no noticeable decrease in the pyridinium ion bands. Evacuation for as long as 30 hr resulted in only slight further decrease in intensity of the 1437-cm^{-1} band indicating that some physically adsorbed molecules are strongly adsorbed to the clay surfaces.

To determine whether hydrolysis of adsorbed water at the clay surface will cause the formation of pyridinium ions, a Mg-saturated clay was exposed to pyridine vapor. Spectrum a, Fig. 3, was obtained after evacuating the Mg-saturated montmorillonite at $20\mu\text{ Hg}$ for 24 hr. Adsorption of pyridine at 2.4 mm Hg is shown in spectrum b. The bands at 1490 and 1545 cm^{-1} indeed indicate that the first molecules that are adsorbed are pyridinium ions. The acid nature of the clay surface is therefore, strong enough to hydrolyze adsorbed water and promote the formation of pyridinium ions. Recent evidence from nuclear magnetic resonance studies (Ducros and Dupont, 1962; Pickett and Lemcoe, 1959) of water adsorbed by clays indicates that the acidic nature of the clay surface may cause adsorbed water molecules to be much more dissociated than usual. This high degree of dissociation is thought to enhance the formation of pyridinium ions at the clay surface.

A weak band at 1439 cm^{-1} , which is indicative of physically adsorbed pyridine, first appeared when the vapor pressure was increased to 3.4 mm Hg . Physical adsorption of pyridine, therefore, occurred between 2.4 and 3.4 mm Hg . Initial physical adsorption on the acid clay occurred at similar pressures. Spectrum c was obtained after equilibrating the sample at 14.8 mm Hg . (Note the 1600 and 1634 cm^{-1} doublet for physically adsorbed pyridine and the absence of the 1623 cm^{-1} water band.) Evacuation of the sample for 12 hr at $50\mu\text{ Hg}$ (spectrum d) again shows that some of the physically adsorbed molecules are bound strongly enough to the clay surface to resist desorption under vacuum.

The characteristic 1490 cm^{-1} band for chemisorbed pyridine was unaffected for both the Mg-saturated and acid clays as the amount of physically adsorbed pyridine increased. When the samples were evacuated, the band at 1439 cm^{-1} , which is characteristic of physically adsorbed pyridine, decreased;

but the intensity of the band at 1490 cm^{-1} remained constant. It can be shown by a plot of the intensities of these two bands, as a function of the amount of pyridine adsorbed, that the intensity of the band at 1490 cm^{-1} becomes constant when chemisorption ceases, while the intensity of the 1439 cm^{-1} band continues to increase with the amount of pyridine adsorbed. This indicates that the band at 1490 cm^{-1} is solely due to chemisorbed pyri-

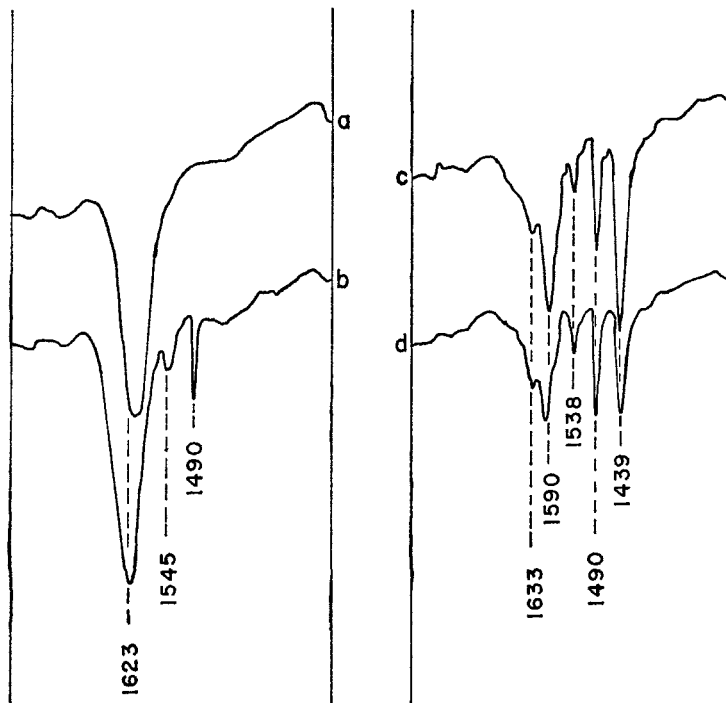


FIG. 3. Infrared spectra of pyridine adsorbed on Mg-saturated Otay montmorillonite at 25°C : (a) sample evacuated for 24 hr at $20\mu\text{ Hg}$; (b) after exposure to pyridine at 2.4 mm Hg ; (c) after exposure to pyridine at 14.8 mm Hg ; (d) evacuated for 12 hr at $50\mu\text{ Hg}$.

dine. Liquid pyridine has a sharp, intense band at 1480 cm^{-1} ; therefore, the complete absence of this band for physically adsorbed pyridine indicates strong perturbation of the molecules. This band has been attributed to the C-N stretching vibration (Klingsberg, 1960). The frequency of the C—C bond in liquid pyridine occurs around 1580 cm^{-1} , but shifts to 1600 cm^{-1} when pyridine is physically adsorbed on the clay surface.

Since physically adsorbed molecules do not contribute to the intensity of the band at 1490 cm^{-1} of chemisorbed molecules, an estimate of the amount

of chemisorbed pyridine was obtained by plotting the intensity of this band against the weight of pyridine adsorbed (as determined with the quartz helix). There is a sharp break in the curve when chemisorption ceases and the intensity of the 1490 cm^{-1} band becomes constant. The amount of chemisorbed pyridine was found to be 1.52 and 1.77 meq per g for the acid and the Mg-saturated clays respectively. These values are very similar to the cation exchange capacity (1.53 meq per g) given for this clay in the A.P.I. Report no. 49 (Lewis, 1951, p. 96).

The effect which adsorbed pyridine has on hydrogen bonding of water adsorbed by a Mg-saturated montmorillonite is shown in Fig. 4. Spectrum a shows the typical O-H stretching vibration of hydrogen-bonded water on montmorillonite after evacuating for 24 hr at $50\text{ }\mu\text{ Hg}$. The band at 3623 cm^{-1} is due to the O-H stretching frequency of lattice hydroxyls. Spectrum b was obtained at a pyridine vapor pressure of 2.4 mm Hg. Only chemisorbed pyridine was present on the clay surface. The broadening of the water band indicates that the chemisorbed pyridine molecules have somewhat disrupted the hydrogen bonding between water molecules. Increasing the pyridine vapor pressure to 3.4 mm Hg. allowed physical adsorption of pyridine to occur, which caused a marked change in the infrared spectrum (spectrum c). The adsorbed pyridine further disrupted the hydrogen bonding between water molecules and between water molecules and the oxygens of the clay surface. Much of the water has been displaced from the surface of the clay.

Spectrum d, which indicates that almost all adsorbed water has been displaced, was obtained after equilibrating at a pyridine vapor pressure of 13.0 mm Hg. Evacuation of the sample for 20 hr before adsorption of pyridine failed to remove much of the adsorbed water; however, after adsorption of pyridine essentially all the water was removed by only slight vacuum. This would appear to indicate that pyridine is bonded much more strongly to the clay surface than is water. However, when all the interlayer water was first removed from a Na-saturated montmorillonite by evacuation and then pyridine vapor admitted, no adsorption of the vapor was detectable by infrared analysis. When the sample was rehydrated by the adsorption of water vapor and pyridine vapor again admitted, pyridine was readily adsorbed by the clay.

From the infrared spectra presented thus far and from adsorption isotherms, it is concluded that chemisorbed pyridine does not replace any of the adsorbed water, but rather water desorption from the clay is caused by physically adsorbed pyridine. There is a straight-line relationship between the intensity of the chemisorbed infrared frequencies and the amount of pyridine adsorbed, but an equally good straight-line relationship was not found for physically adsorbed pyridine. It is believed that the chemisorbed molecules are distributed rather uniformly over the surface of the clay and are surrounded by water molecules. The extreme broadening of the water band in Fig. 4 appears to indicate that the first physically adsorbed molecules are also

dispersed in the water layer, rather than being adsorbed in "patches" over the surface.

Since pyridine was found to be capable of displacing adsorbed water, it was of interest to determine whether water would displace physically adsorbed pyridine. Pyridine was adsorbed on acid-saturated montmorillonite and then evacuated for 15 hr (spectrum a, Fig. 5). Water vapor was then admitted for

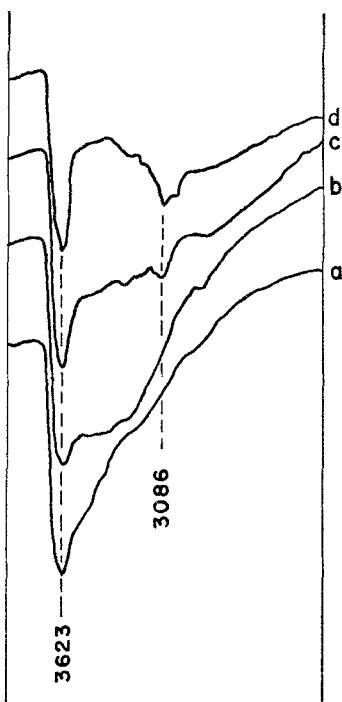


FIG. 4. Infrared spectra in the 2.5–4.0 μ region of pyridine adsorbed on Mg-saturated Otay montmorillonite at 25°C: (a) sample evacuated for 24 hr at 20 μ Hg; (b) after exposure to pyridine at 2.4 mm Hg; (c) after exposure to pyridine at 3.4 mm Hg; (d) after exposure to pyridine at 13.0 mm Hg.

6 hr, followed by evacuation for 3 hr. Spectrum b shows a slight decrease in the band at 1437 cm^{-1} characteristic of physically adsorbed pyridine. Spectrum c was obtained after the adsorption and desorption by vacuum of D_2O . "Vapor washing" with D_2O caused an additional reduction in the 1437 cm^{-1} band, but the intensity of the frequency at 1488 cm^{-1} has increased considerably owing to the presence of deuterium. Deuteration of lattice hydroxyls was not detected during this brief exposure to deuterium oxide vapors. Washing the sample two more times with water vapor and evacuating

for 2 hr between each admission of water vapor caused the band at 1437 cm^{-1} to all but disappear. Therefore, physically adsorbed pyridine can be replaced by the adsorption of water. The bands at 1488 and 1540 cm^{-1} , which are characteristic of chemisorbed pyridine, were not affected by the adsorption of water.

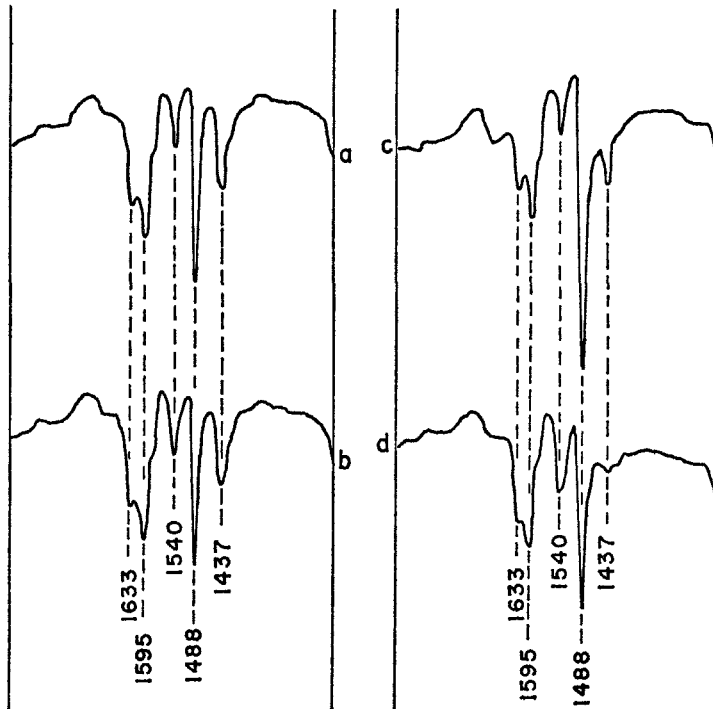


FIG. 5. Spectra of water adsorbed on pyridine-acid montmorillonite complex at 25°C : (a) pyridine adsorbed on acid Otay montmorillonite and then evacuated for 15 hr; (b) after admittance of H_2O vapors and then evacuated for 3 hr; (c) after admittance of D_2O vapors and then evacuated; (d) after two additional desorptions of admitted H_2O vapors.

Since the band at 1540 cm^{-1} has been assigned to a $\text{N}^+\text{-H}$ deformation frequency of the pyridinium ion (Barrow, 1956), an attempt was made to replace the hydrogen atom with deuterium. The isotope exchange is detectable with infrared since deuterium is heavier than hydrogen its presence causes a change in the magnitude of the dipole associated with the bond. Such a replacement would give assurance to the assignment of this frequency. Pyridine vapor was adsorbed by a Mg-saturated montmorillonite and then evacuated for 4 hr (spectrum a, Fig. 6). Deuterium oxide vapor was then admitted to the system and allowed to equilibrate for 4 hr before evacuating.

Spectrum b shows a decrease in the 1538 cm^{-1} band and the formation of a new band at 1299 cm^{-1} . Spectrum c was obtained after D_2O was adsorbed and desorbed four times from the clay surface. The disappearance of the 1538 cm^{-1} frequency and the occurrence of a new band at 1299 cm^{-1} allows the definite assignment of the 1540 cm^{-1} band to a $\text{N}^+\text{-H}$ deformation frequency.

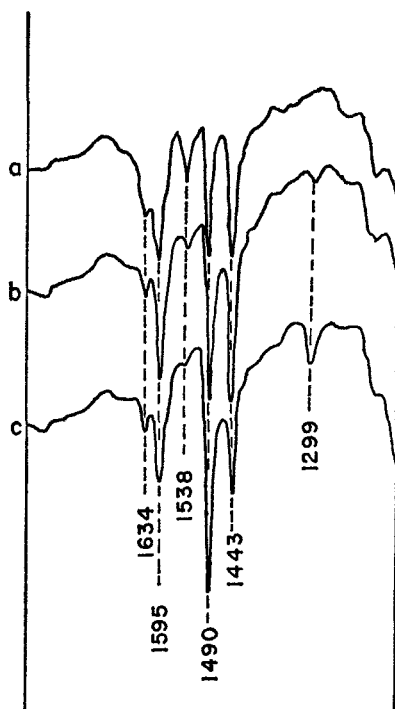


FIG. 6. Spectra of deuterium exchange for hydrogen in the $\text{N}^+\text{-H}\cdots\text{O}$ bond of chemisorbed pyridine: (a) pyridine adsorbed on Mg-saturated montmorillonite and then evacuated for 4 hr; (b) after admittance of D_2O vapors and then evacuated; (c) after three additional D_2O vapor washings.

SUMMARY AND CONCLUSIONS

Infrared spectroscopy was used to distinguish between chemisorbed and physically adsorbed pyridine on acid- and base-saturated Otay montmorillonite. The infrared frequencies of 1490 and 1540 cm^{-1} are attributed to chemisorbed pyridinium ions, while the frequency at 1440 cm^{-1} is characteristic of physically adsorbed pyridine. In the case of the base-saturated montmorillonite, a reaction of the basic pyridine molecules with the adsorbed water is the suggested mechanism by which the pyridinium ion is formed.

As evidenced by infrared spectra, only chemisorbed pyridine is present initially on the clay surfaces at low vapor pressures, which is followed by physically adsorbed pyridine at increased vapor pressures.

The quantity of chemisorbed pyridine may be estimated by plotting the intensity of the band at 1490 cm^{-1} against the amount of pyridine adsorbed.

Infrared spectra and adsorption isotherms indicate that replacement of adsorbed water results from physically adsorbed rather than chemisorbed pyridine. Pyridine was not adsorbed by a water-free Na-saturated montmorillonite; however, after rehydration with water vapor, pyridine was readily adsorbed.

Physically adsorbed pyridine is replaced readily by "washing" with water vapor, but chemisorbed pyridine is not affected.

Deuterium from D_2O was found to replace the hydrogen in the $\text{N}^+\text{-H-O}$ bond of chemisorbed pyridinium ions as evidenced by a shift in the band from 1538 to 1299 cm^{-1} . Deuteration of lattice hydroxyls was not detected as a result of the brief exposure to deuterium oxide vapors.

REFERENCES

- BARROW, G. M. (1956) The nature of hydrogen bonded ion-pairs, The reaction of pyridine and carboxylic acids in chloroform, *J. Am. Chem. Soc.* **78**, 5802-06.
- BENESI, H. A. (1956) Acidity of catalyst surfaces, I, Acid strength from color adsorbed indicators, *J. Am. Chem. Soc.* **78**, 5490-4.
- DUCROS, P., and DUPONT, M. (1962) Etude par resonance magnetique nucleaire des protons dans les argiles, *Compt. Rend.* **254**, 1409-51.
- EISCHENS, R. P., and PLISKIN, W. A. (1958) The infrared spectra of adsorbed molecules. *Advan. Catalysis* **10**, 1-56.
- KLINGSBERG, E. (1960) *Pyridine and Its Derivatives, Part One*, pp 11-12, Interscience, New York.
- LEWIS, D. R. (1951) Base-exchange data, *Reference Clay Minerals, American Petroleum Institute Research Project 49, Preliminary Report 7*, p. 96, Columbia University, New York.
- MAPES, J. E., and EISCHENS, R. P. (1954) The infrared spectra of ammonia chemisorbed on cracking catalysts, *J. Phys. Chem.* **78**, 1059-62.
- MORTLAND, M. M., FRIPIAT, J. J., CHAUSSIDON, J., and UYTTERHOEVEN, J. (1963) Interaction between ammonia and the expanding lattices of montmorillonite and vermiculite, *J. Phys. Chem.* **67**, 248-58.
- PARRY, E. P. (1963) An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity, *J. Catalysis* **2**, 371-9.
- PICKETT, A. G., and LEMCOE, M. M. (1959) An investigation of shear strength of the clay-water system by radio-frequency spectroscopy, *J. Geophys. Res.* **64**, 1579-86.