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Hydrogen Bonding Between the Carbonyl Group and Wyoming Bentonite

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HYDROGEN BONDING BETWEEN THE CARBONYL

GROUP AND WYOMING BENTONITE

by

Robert A. Kohl

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of the requirements for the degree

of

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Robert Kohl

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INTRODUCTION

The vibrational frequencies of atom to atom bonds within a molecule are a function of the bond energies. Each bond has its characteristic frequency, and most of these frequencies can be detected with the infra-red spectro-photometer. When one compound reacts with another or is adsorbed on the surface of a solid, detectable frequency changes or shifts may occur. These changes or shifts yield valuable information about the bonds which are formed or broken.

Infra-red spectroscopy was used in this study to investigate the nature of the bonds that might form between organic molecules and silicate minerals.

REVIEW OF LITERATURE

Early in the study of factors affecting soil aggregation, good correlations were found to exist between aggregate stability and the organic and clay contents of the soil (1, 22). Inorganic oxides were also found to be important in the aggregation of some soils. In a detailed study Kroth and Page (18) showed that inorganic oxides (iron and aluminum), fats, waxes, and resins formed a continuous matrix which bound the soil particles together by physical forces alone.

Soil microbiologists found that the products of active microbial decomposition were much more effective aggregators than fresh organic matter or completely composted organic matter (5, 19, 20, 21, 25). These products often carry several active groups, the most common of which are the hydroxyl, carboxyl, and amino groups. Few studies have given direct evidence as to the methods by which these groups may enhance aggregation.

Workers who have encountered difficulty in extracting organic matter from the soil noted that polyuronides were not removed during the extracting process and that the C/N ratio in the residue was lower than that of the original soil (32). The lower C/N ratio in the residue suggested that nitrogenous organic compounds form strong bonds with inorganic colloids.

When large organic cations were adsorbed on montmorillonite the c-axis spacing was greatly increased (13, 16). Only other large organic cations were able to replace the adsorbed cations. It was concluded that organic molecules which are cationic in nature, perhaps as a result

of amino groups, are attached to the inorganic colloid by coulombic forces (13, 16).

Several workers (9, 10, 29) have presented further evidence that amino cations form bonds with clay minerals by noting that bacteria encountered difficulty in attacking proteins which were adsorbed on montmorillonite.

Amino acids and free amino groups have been found to exist in soil organic matter (27, 31). It is therefore possible that long chain organic molecules containing amino acids may bind soil particles together into aggregates by being adsorbed at cation exchange sites on the clay minerals and by acting as bridges between the particles.

X-ray defraction analyses have shown that organic anions do not enter between the montmorillonite lattice. However, since synthetic polymers which contain carboxyl groups (soil conditioners) stabilize inorganic soil colloids, it has been postulated that organic anions are adsorbed on the edges of the crystals where anion adsorption sites are known to exist (7, 8, 14, 15, 17, 26, 30). Definite evidence to support this theory has not appeared in the literature as yet.

Using electron micrographs, Kroth and Page (18) noted that polar substances which resulted from the decomposition of fresh organic matter were uniformly distributed throughout natural and synthetic aggregates. The dried aggregates were not easily disrupted on rehydration. The authors concluded that the polar organic substances probably formed physicochemical bonds with the surface active clays.

A similar linkage was proposed by Michaels (23), who used the sediment volume technique. Noting that the best flocculation was obtained with polyelectrolytes which were 33 percent hydrolyzed, he postulated that the polymers effected aggregation by the adsorption (via

ester formation or hydrogen bonding) of hydroxyl or amide groups on the solid surfaces, each polymer chain adsorbing on, and bridging between, more than one solid particle.

Recently Emerson (8) compared the effects of synthetic soil conditioners and soil organic matter on aggregate stabilization. He used three polymers, polyvinyl alcohol, a non-ionic polymer, and two carboxylated polymers, high molecular weight sodium alginate and vinyl acetate maleic acid (VAMA). Because sodium hydroxide and an excess of sodium pyrophosphate displaced the carboxylated polymers to various degrees, it was concluded that these polymers were hydrogen bonded to the edge of the clay materials. Polyvinyl alcohol was not displaced by sodium hydroxide because its hydrogen bonds are probably independent of pH. Since the alcohol entered between the clay lattice, it was protected from the effect of sodium pyrophosphate as the pyrophosphate anion could not enter between the lattice due to its charge. Strong sodium hydroxide and sodium pyrophosphate did not displace the binding organic matter from the natural soil aggregates. Emerson concluded that natural aggregates are bound together by organic molecules between the crystal lattice joined by hydrogen bonding.

Peterson (28) noted an increase in the thixotropy of clay suspensions to which he had added calcium and pectin. Based on the research of Bower and Truog (4) who found that polyvalent cations hydrolyze in the following manner

clay   Mg — OH

clay   Fe⟨ OH / OH

clay   Th⟨ OH / OH

clay   Fe — OH

clay   Th — OH with OH, OH
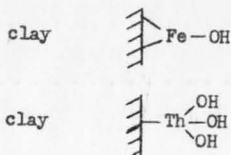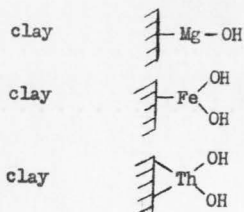
Peterson postulated a calcium linkage of the form

clay-Ca-OOC-R-COO-Ca-OOC-R-COO-Ca-clay.
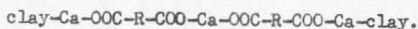
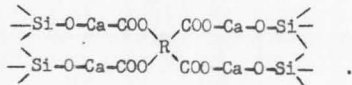Capon, as reported by Tiulin (35), proposed a similar calcium linkage between the oxygen layers of silica sheets and the negative humic acid particles which may be diagramed as

$$—\overset{\diagdown}{\underset{\diagup}{Si}}-O-Ca-COO\diagdown_{\underset{R}{}}\diagup COO-Ca-O-\overset{\diagup}{\underset{\diagdown}{Si}}—$$
$$—\overset{\diagdown}{\underset{\diagup}{Si}}-O-Ca-COO\diagup \diagdown COO-Ca-O-\overset{\diagup}{\underset{\diagdown}{Si}}— .$$

Mortensen (24) suggested a similar coulombic linkage because he found that hydrolyzed polyacrylonitrile (HPAN), a soil conditioner, adsorbed to a greater extent on kaolinite saturated with polyvalent cations than with monovalent cations. However, Emerson (7) found that divalent cations were not essential for the linkage of carboxylated polymers to clay minerals as his results show that stabilization was equally effective when sodium ions only were present.

Many authors suggest hydrogen bonding as a possible mechanism by which soil particles are bound together into aggregates, but little information is given which would indicate the actual groups and atoms that would be involved.

Infra-red spectroscopy has become a useful tool in the identification of organic and inorganic molecules. The frequencies with which atoms vibrate within a molecule fall in the infra-red spectrum. If "white" infra-red radiation is passed through a sample and defracted with a rock salt prism, a characteristic spectrum results due to the absorption of various amounts of the incident radiation by the various chemical bonds within the molecules. Within limits, the amount of the radiation that is absorbed is directly proportional to the number of molecules in the path of the beam.

Theoretically one should be able to determine the structure of a

pure compound by noting the frequencies at which absorption takes place
and recalling the bonds which absorb at those particular frequencies.
In practice this can only be approximated as resonance and coupling take
place between bonds with similar frequencies.

It is of importance in this study to note that group frequencies
are altered as a result of hydrogen bonding. When the carbonyl group
undergoes hydrogen bonding, the oxygen carbon double bond is slightly
weakened which results in a slight lowering in its vibration frequency.
This shows up as a shift in the infra-red band attributed to the
carbonyl group.

Infra-red absorption has been used to study the adsorption of
organic and inorganic substances on the surfaces of metals, oxides, and
silicates (6, 11, 34).

Infra-red absorption was used by Holmes and Toth (17) to determine
a possible linkage between a synthetic soil conditioner and clay miner-
als. It was noted that the absorption band indicating free OH groups
on the clay mineral disappeared when large amounts of the conditioner
were adsorbed. This indicated that hydrogen bonding had taken place
between the soil conditioner and the clay mineral, but it was not deter-
mined which of the available groups, the amide, phenolic, or the carboxyl
groups, were active.

It appears that further use of infra-red spectra may provide infor-
mation about the actual mechanisms by which organic molecules are linked
to silicate minerals.

EXPERIMENTAL METHODS

Montmorillonite no. 26 (bentonite from Clay Spur, Wyoming) was obtained. The bentonite, as received, contained significant amounts of quartz. Therefore, the bentonite was dispersed in deionized water and centrifuged in a Sharples Super Centrifuge. Only that portion below $0.2\,\mu$ was retained for use, as it was relatively free of quartz.

Using an International Centrifuge, size 2, the centrifuged bentonite samples were saturated with calcium and hydrogen using calcium chloride and hydrogen chloride in dilute solutions. Enough calcium chloride or hydrogen chloride was added to the bentonite solution to cause flocculation. The samples were centrifuged and the supernatant liquid was decanted and discarded. Deionized water was added, the samples were shaken for five minutes and recentrifuged. The supernatant liquid was again discarded and the process repeated until the suspensions were dispersed again. The flocculation, centrifuging and dispersion was repeated four times to assure saturation with the desired ion. After washing with deionized water to the point of dispersion the last time, the calcium saturated bentonite had a pH of 6.6 and the hydrogen saturated bentonite a pH of 1.7.

Several organic compounds were used to determine a possible linkage between organic materials and montmorillonite. The organic compounds used were acetic acid, diethyl ketone, vinyl acetate maleic acid (VAMA), a copolymer of isobutylene and the half ammonium-half amide salt of maleic acid (IBMA), the sodium salt of hydrolyzed polyacrylonitrile (HPAN), and polygalacturonic acid. The structural formulas of the less

common organic compounds are:

VAMA

HPAN

IBMA

Polygalacturonic acid

Samples were prepared by placing various quantities of the adsorbate in a 50 ml Erlenmeyer flask containing 5 ml of deionized water. Five ml of a solution containing 0.021 g of bentonite per ml were added to the flask. The mixture was shaken on a wrist action shaker for one hour and allowed to stand for 16 hours.

The samples were poured into a petri dish and dried at 55° C in an oven. The residue was ground with a mortar and pestal and then subjected to infra-red inspection by the KBr pressed-disk technique (33), using a

Beckman die of diameter one-half inch. A Perkin-Elmer Model 21 Double Beam Recording Spectro-photometer was used to obtain the spectra.

EXPERIMENTAL RESULTS

The spectra of several organic compounds adsorbed on centrifuged Wyoming bentonite were obtained. That portion of the spectra of these mixtures which showed a change due to adsorption is given in figures 1 through 10. Most of the compounds showed activity in the 5.5μ to 6.5μ region though some were active over the 5.5μ to 7.5μ region.

The band which appears at 6.16μ in all spectra containing bentonite is due to the adsorbed water on the bentonite itself.

The units on the absorbance scale of the figures are not necessary as quantitative data was not sought. It was found convenient to space the spectra so as to get several in one figure. Therefore it would not be convenient to place units on the absorbance scale as several scales would be required in each figure.

DISCUSSION

The infra-red absorption band arising from the C=O stretching vibration has been extensively studied, and much is known of the factors which influence its frequency. This band lies in the region between 5.8μ and 5.9μ (3) unless it is hydrogen bonded, part of an anhydride linkage, or in the dipole field of a halogen.

Hydrogen bonding or the forces attracting a proton to the carbonyl oxygen causes a slight weakening in the C=O bond. This weakened bond has a lower frequency of vibration than the original carbonyl double bond, and results in a small increase of the resulting wave length. Thus, the absorption band arising from the carbonyl frequency will be shifted toward the right or to a longer wave length. The literature reviewed indicated that only hydrogen bonding could lead to a 0.05μ or greater shift to the right in the carbonyl wave length.

When two carboxyl groups form an anhydride, two carbonyl frequencies show up in the infra-red spectrum, one between 5.60μ and 5.75μ, and one between 5.40μ and 5.55μ. The two bands are usually about 0.2μ apart. If the anhydride linkage is part of a strained cyclic structure, the two carbonyl frequencies are slightly greater than the open-chain frequencies. The reason for the splitting of the carbonyl band has not yet been adequately solved. The most likely explanation is that the two carbonyl frequencies are coupled together, leading to resonance splitting (3).

An α-halogen-substituted carbonyl containing compound shows an increase in the carbonyl frequency. Bellamy (3) suggests that the near

approach of a negatively charged halogen atom to the readily polarisable negatively charged oxygen of the carbonyl group would result in a mutual induction of opposite charges. The negative character of both the halogen and oxygen atoms would be diminished and the C-X and C=O bonds would become less polar. This would result in a rise of their vibrational frequencies.

Figure 1 shows the spectra of hydrogen bentonite, acetic acid, and the acid adsorbed on hydrogen saturated bentonite. The carbonyl wave length of 5.90μ for the acid has shifted to 5.97μ in the adsorbed spectrum. This suggests that hydrogen bonding has taken place between the double bonded oxygen of the carbonyl group and the clay mineral. This shift in the carbonyl band could not represent the formation of an ionic bond with an adsorbed polyvalent cation as the ionized carboxyl group does not absorb radiation at this wave length.

Figures 2 and 3 show the spectra of VAMA adsorbed on calcium and hydrogen saturated bentonite. The C=O band at 5.82μ in the acid shifts to 5.89μ when VAMA is adsorbed on bentonite. This suggests that strong hydrogen bonds are formed between the carbonyl groups of VAMA and the bentonite. As larger amounts of VAMA were added to a constant quantity of bentonite, the 5.82μ band of the free carbonyl group shows up in the adsorbed spectra. This indicates that some C=O groups are present which are not bonded to the clay.

Comparing figures 2 and 3, VAMA showed a similar degree of hydrogen bonding through the carbonyl group to calcium bentonite as to hydrogen bentonite. This indicates that the adsorbed cation does not affect the hydrogen bonding of the carbonyl group in VAMA.

Figure 4 shows the acid form of HPAN and HPAN adsorbed on hydrogen saturated bentonite. The carbonyl band at 5.80μ shifts to 5.85μ when
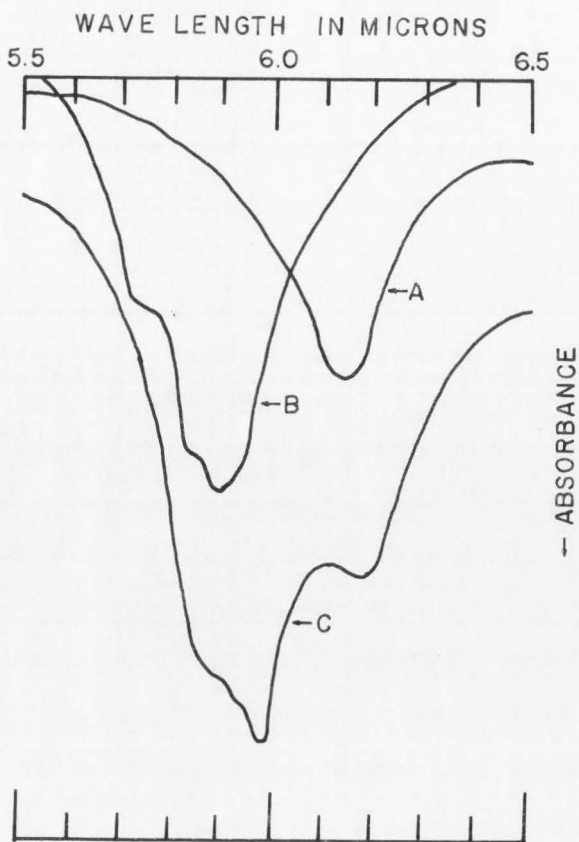
FIGURE 1. THE SPECTRA OF HYDROGEN BENTONITE (A), ACETIC ACID (B),

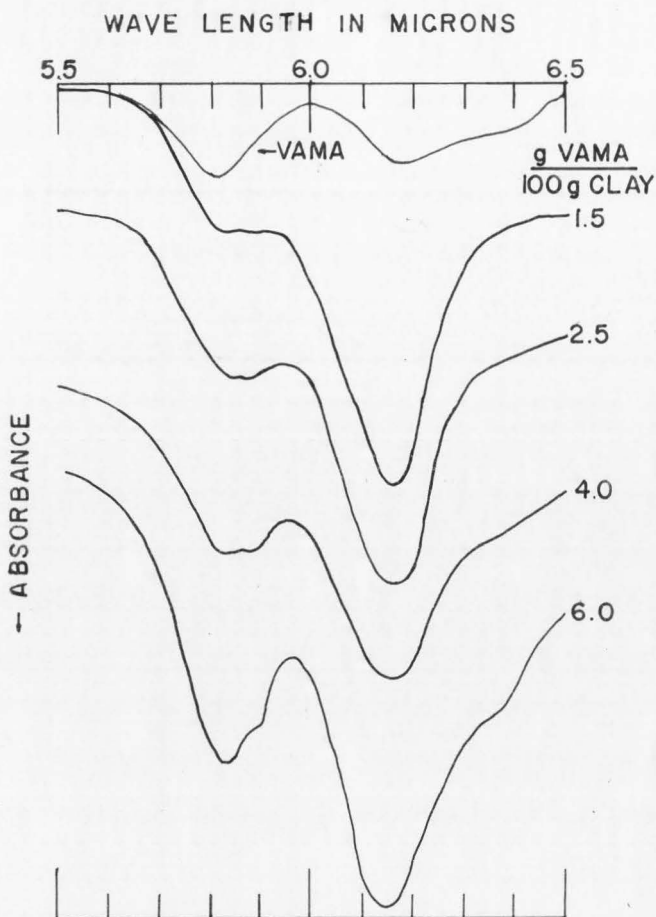AND ACETIC ACID ADSORBED ON HYDROGEN BENTONITE (C)

FIGURE 2. THE SPECTRA OF VAMA AND VAMA ADSORBED ON CALCIUM
BENTONITE IN VARIOUS CONCENTRATIONS
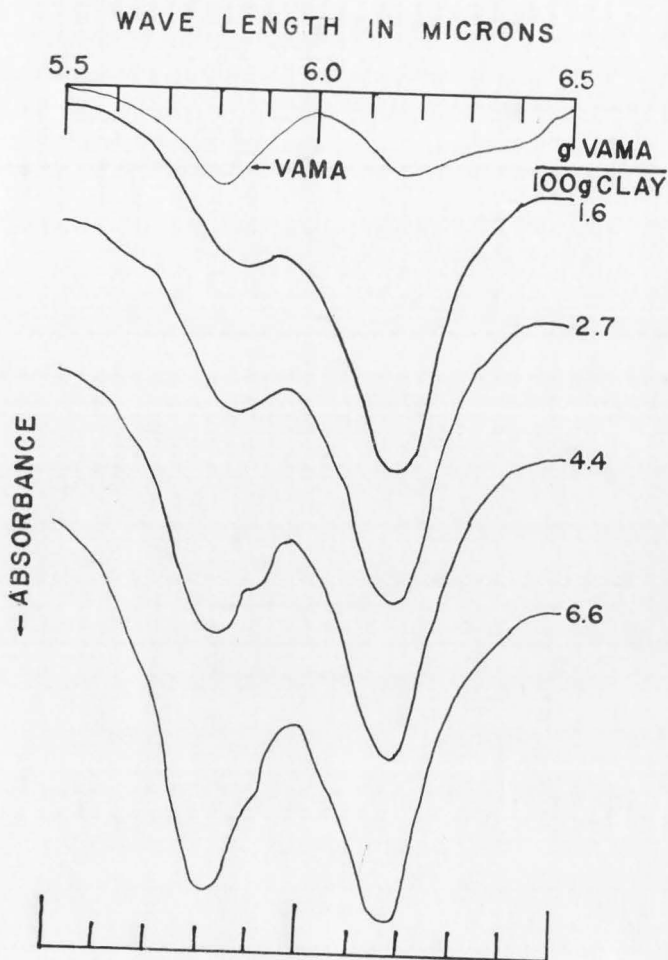
FIGURE 3. THE SPECTRA OF VAMA AND VAMA ADSORBED ON HYDROGEN
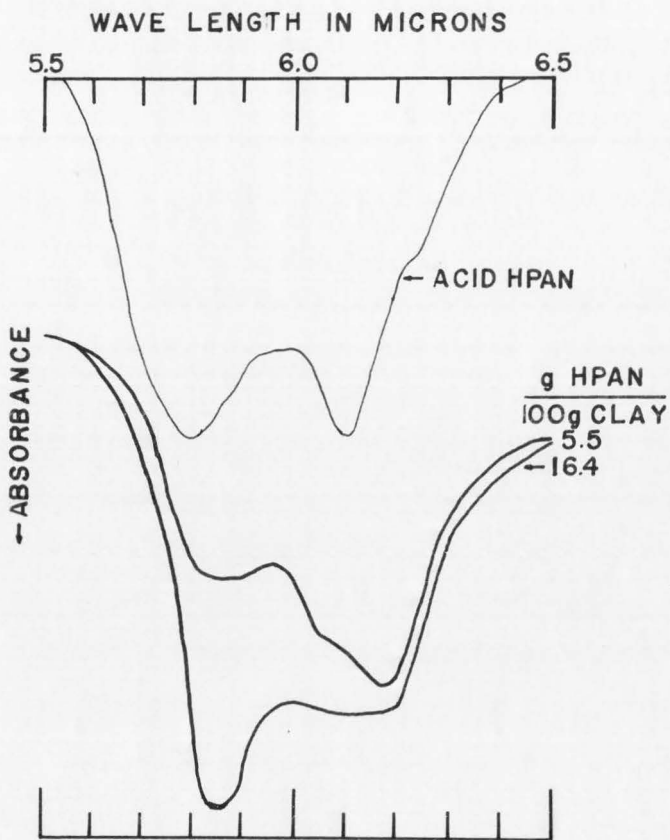BENTONITE IN VARIOUS CONCENTRATIONS

WAVE LENGTH IN MICRONS

FIGURE 4. THE SPECTRA OF THE ACID FORM OF HPAN AND HPAN
ADSORBED ON HYDROGEN BENTONITE IN TWO CONCEN-
TRATIONS

HPAN is adsorbed on the clay mineral. This also suggests hydrogen bonding.

Diethyl ketone was studied in an attempt to isolate the effects of the carbonyl group. Figure 5 shows the spectra of diethyl ketone and the ketone adsorbed on calcium saturated bentonite. It is noted that the strong carbonyl band of the ketone at 5.85μ shifts to 5.94μ when the ketone is adsorbed on bentonite. This indicates that the carbonyl group is active in hydrogen bonding to the clay mineral.

Since the carbonyl group does hydrogen bond to the clay mineral, one might speculate as to the site on the clay mineral which is taking part in the bond formation.

Several workers (7, 15, 17, 30) have shown by X-ray defraction that organic anions such as the ones used in this study do not enter between the crystal lattice of montmorillonite type clays. Since a hydrogen atom is necessary and since one attached to an oxygen atom has been shown to be effective in forming dimers and polymers in alcohols and acids, it is proposed that a hydroxyl group exposed on the broken edge of the clay crystal is the reactive site.

When a hydroxyl group is involved in hydrogen bonding, it has been shown that the OH stretching frequency is reduced and the OH deformation frequencies are increased. These frequency shifts were not observed due to the masking of these regions by two factors: (a) by the many internal hydroxyl groups of the clay mineral which are not in a position to take part in the proposed mechanism and (b) by the adsorbed water on the clay mineral.

Several authors (7, 8, 17, 26, 30) have proposed hydrogen bonding to the edge faces of the clay crystal but have not suggested that the
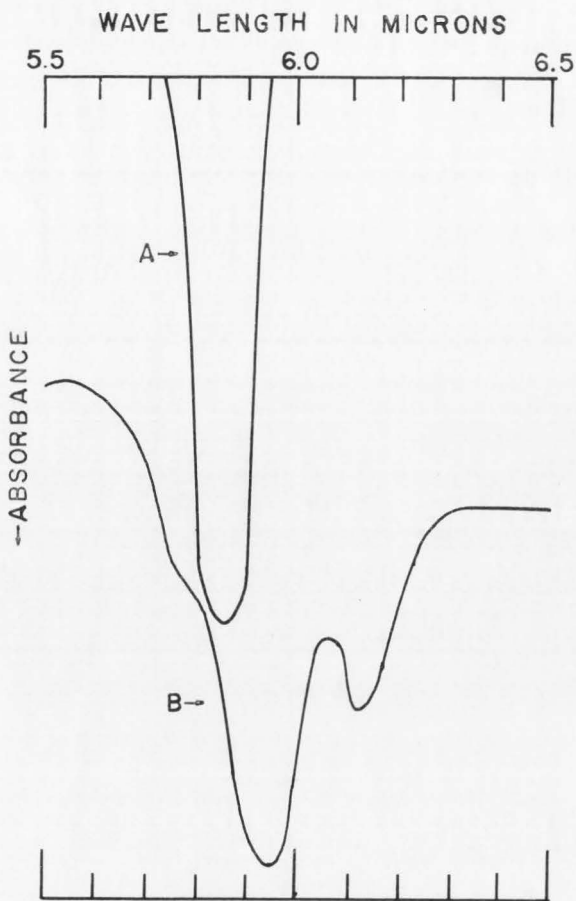
FIGURE 5. THE SPECTRA OF DIETHYL KETONE (A) AND DIETHYL
KETONE ADSORBED ON CALCIUM BENTONITE (B)

carbonyl group is responsible. They have either failed to suggest the reactive groups altogether or have speculated that the hydroxyl group of an organic acid was the reactive group.

The data presented in this paper agree in principle with the above authors except for showing that the carbonyl group is active.

It has been found that polygalacturonic acid is a constituent of soil organic matter (12). Figure 6 shows the spectra of polygalacturonic acid and the acid adsorbed on hydrogen saturated bentonite. The 5.78 μ band of polygalacturonic acid shifts to 5.88 μ when adsorbed on hydrogen bentonite. Again, this indicates that the carbonyl group has hydrogen bonded to the bentonite.

Since polyuronides may represent 30 percent of the soil organic matter (12), this suggests a possible mechanism by which organic matter may bind soil particles together into aggregates. However, it should be emphasized that other mechanisms are also possible and that this study does not indicate their presence nor confirm their absence.

Since postulations on the mechanisms involved in binding the remaining compounds to the clay mineral are highly speculative, they are included in the appendix along with suggestions for further study.
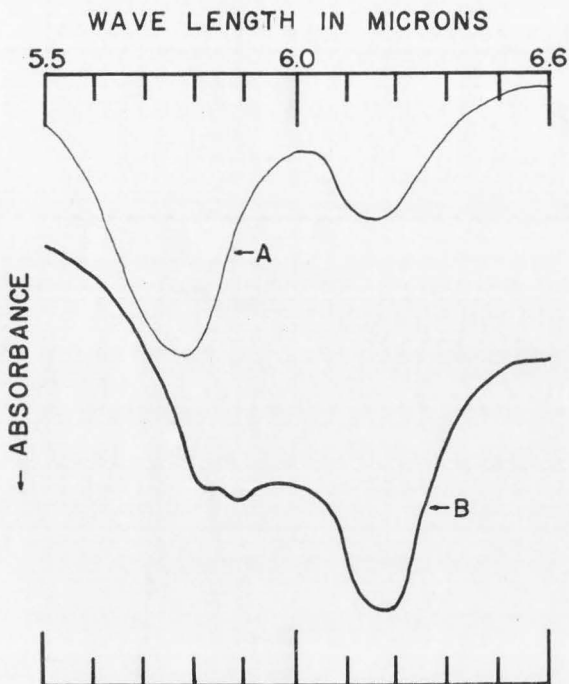
FIGURE 6. THE SPECTRA OF POLYGALACTURONIC ACID (A) AND 4 g
OF POLYGALACTURONIC ACID ON 100 g OF CALCIUM
BENTONITE (B)

SUMMARY

Several organic compounds were adsorbed on centrifuged Wyoming bentonite. Their infra-red spectra were obtained and studied for a possible mechanism by which they were bound to the clay mineral.

A definite shift to the right in the carbonyl stretching frequency has been shown. This shift is the result of hydrogen bonding between the double bonded oxygen of the carbonyl group and a hydrogen atom in the clay crystal. It is postulated that an exposed hydroxyl group on the broken edge of the clay crystal is the reactive group on the bentonite.

Polygalacturonic acid, a polyuronide, also indicated hydrogen bonding through its carbonyl group. Since polyuronides may represent 30 percent of the soil organic matter, it is suggested that hydrogen bonding between the carbonyl group of an organic compound and an exposed hydroxyl group on the edge of the clay crystal is a possible mechanism by which organic matter may bind soil particles together into aggregates.

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APPENDIX

APPENDIX

Two of the compounds that were studied did not show hydrogen bonding through the carbonyl group when the carboxyl group was ionized.

Figure 7 shows the spectra of HPAN as the natural sodium salt, as the calcium salt, and as the acid. The band at 6.42μ is a result of the anti-symmetrical vibration and the one at 7.10μ or 7.16μ is a result of the symmetrical vibration of the COO- structure. The band at 6.90μ is due to the CH_2 deformation mode. The symmetrical, ionized carboxyl band in the calcium salt lies to the left of that of the sodium salt. A small unidentified band at 6.02μ is present in the sodium salt form of HPAN.

Figure 8 shows the spectra of HPAN adsorbed on calcium saturated bentonite in various concentrations. It is noted that when the natural sodium salt of HPAN is adsorbed on calcium saturated bentonite, the symmetrical ionized carboxyl band resembles that of the calcium salt of HPAN. This might suggest a linkage similar to that proposed by J. B. Peterson (28). However, the evidence is meager and further work should be carried out using bentonite saturated with various mono- and polyvalent ions and using various salts of HPAN.

It is interesting to note the increased prominence of the unidentified band at 6.02μ. If this band could be identified, it would help in determining the mechanism by which HPAN is bonded to montmorillonite type clay minerals.

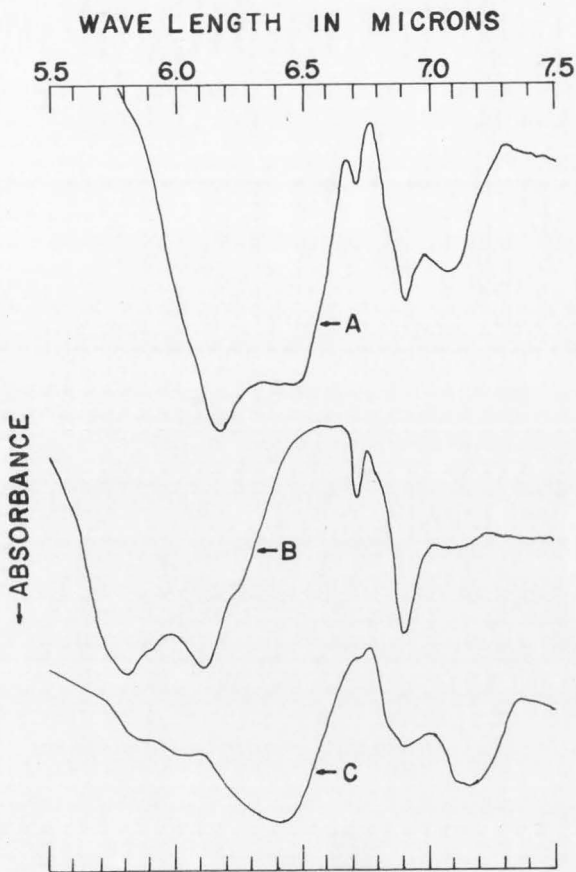Figure 9 shows the spectra of IBMA as the calcium salt, as the

FIGURE 7. THE SPECTRA OF HPAN AS THE CALCIUM SALT (A), AS
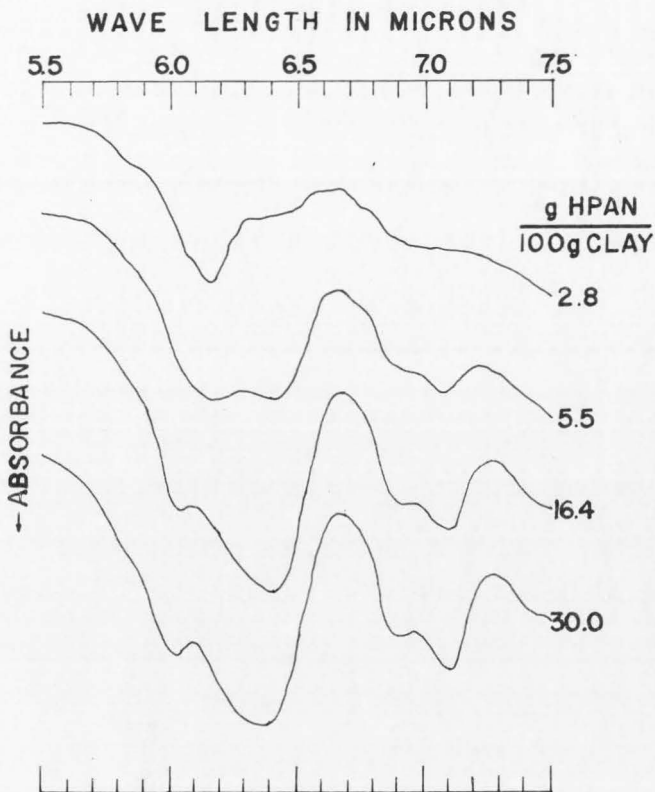THE ACID (B), AND AS THE NATURAL SODIUM SALT (C)

FIGURE 8. THE SPECTRA OF HPAN ADSORBED ON CALCIUM
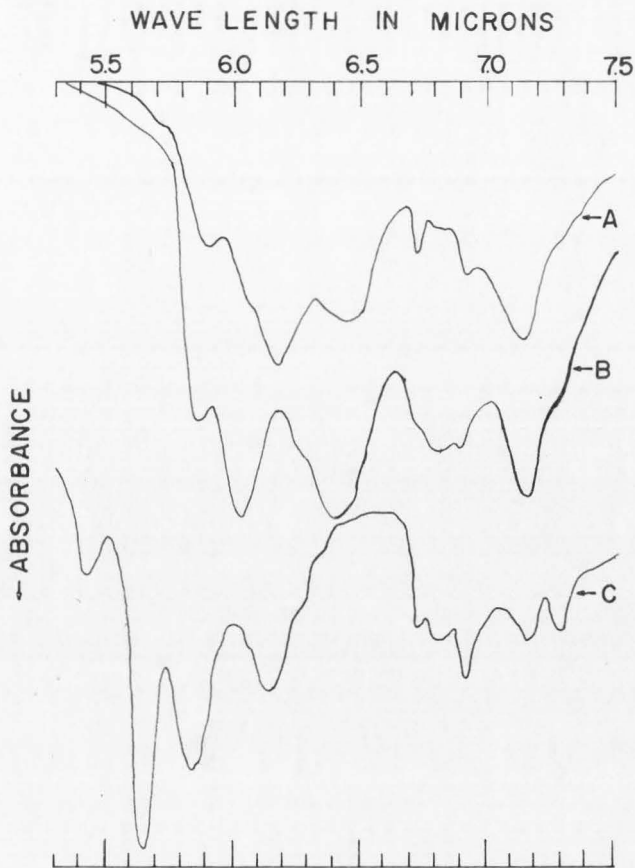BENTONITE IN VARIOUS CONCENTRATIONS

FIGURE 9. THE SPECTRA OF IBMA AS THE CALCIUM SALT (A), AS
THE NATURAL AMMONIUM SALT (B), AND AS THE ACID (C).

natural ammonium salt, and as the acid. The band at 5.85μ is due to the carbonyl group. The two bands at 6.43μ and 7.16μ are due to the anti-symmetrical and symmetrical vibrations of the ionized carboxyl group. The bands at 5.44μ and 5.65μ in the spectrum of the acid form of IBMA seem to be due to the formation of an anhydride.

Figure 10 shows the spectra of IBMA adsorbed on calcium and hydrogen saturated bentonite. The anhydride bands show up only slightly when IBMA is adsorbed on calcium saturated bentonite but are quite pronounced when adsorbed on hydrogen saturated bentonite. The ionized carboxyl bands are present in the case of the calcium bentonite and the carbonyl band is present with hydrogen bentonite. However, in both cases there is a new band at 7.02μ.

There is a possibility that this new band is the result of a shift in the symmetrical ionized carboxyl vibration. Such a shift might be caused by the approach of the ionized carboxyl group to a positive exchange site on the edge of the clay mineral.

Suggestions for future work

Further study should include the adsorption of IBMA and HPAN in various salt forms onto bentonite saturated with different ions. This should provide data to either confirm or contradict the linkage proposed by J. B. Peterson (28).

It should be of interest to study a few samples using clay of a smaller size fraction. This should provide more surface area per gram of bentonite and make it possible to take full advantage of the double beam infra-red spectro-photometer.
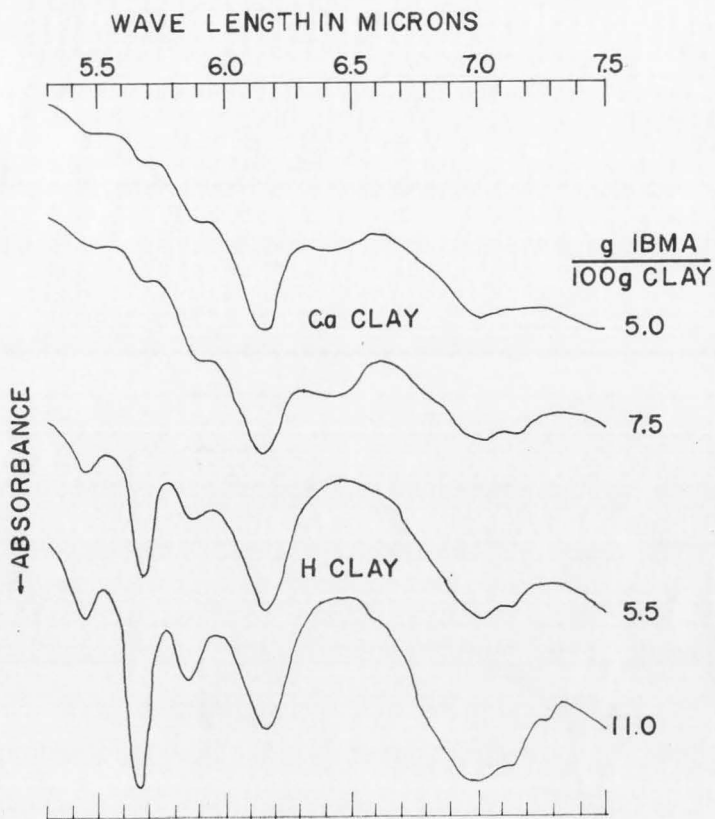
FIGURE 10. THE SPECTRA OF IBMA ADSORBED ON CALCIUM BENTONITE
IN TWO CONCENTRATIONS AND ON HYDROGEN BENTONITE IN
TWO CONCENTRATIONS.