COMPLEXES OF MONTMORILLONITE WITH PRIMARY, SECONDARY, AND TERTIARY AMIDES

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Salah A. Tahoun 1965



This is to certify that the

thesis entitled

Complexes of Montmorillonite with Primary, Secondary, and Tertiary Amides

presented by

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has been accepted towards fulfillment of the requirements for

Ph.D degree in Soil Science

Major professor

Date July 19, 1965

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ABSTRACT

COMPLEXES OF MONTMORILLONITE WITH PRIMARY, SECONDARY, AND TERTIARY AMIDES

by Salah A. Tahoun

The nature of interaction between clay minerals and organic molecules was studied through the nature of adsorption of amides on montmorillonite. Amides were chosen as a working material for two reasons: (1) they contain two functional groups and therefore, the reaction of either could be checked by the other and (2) to gain some insight into the reactions of proteins and some of the bioactive materials, i.e., pesticide, with clay minerals by using their simpler analogues - the amides. Infrared spectroscopy and X-ray diffraction as well as conventional chemical analyses were utilized in this work.

It was found that amides form complexes with montmorillonite. The stability of these complexes seems to depend on three factors. First is the presence of water which competes with amides for adsorption sites. Second is the order of the amide where tertiary amide complexes are more stable than the secondary which in turn are more stable than the primary. Third is the exchangeable ion on the clay. In acidic systems (H-, Al-, or Pt-montmorillonite) it was

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found that the amide was protonated through the oxygen atom. When the protonated amide-clay complex was dehydrated, the amide reverted to molecular form. On rehydration the protonated amide was again formed showing the importance of water in the cation formation.

In the case of Cu-montmorillonite, amides were held through the formation of a coordination complex. Evidences were obtained which indicate that coordination takes place through the oxygen atom of the carbonyl group. In both Naor Ca-montmorillonite, coordination does not seem to be as important as in the copper system and other forces such as hydrogen bonding and van der Waals forces increase in their relative importance.

COMPLEXES OF MONTMORILLONITE WITH PRIMARY, SECONDARY, AND TERTIARY AMIDES

Ву

Salah A. Tahoun

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science

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INTRODUCTION

Many studies have been concerned with the inorganic nitrogen compounds in soils. A conclusion drawn from these studies has pointed out the dynamic equilibrium between the inorganic nitrogen forms and the organic forms. Much of the work on the more complex organic nitrogen compounds, proteins for example, preceded the study of the reaction of simpler nitrogen organic compounds in soils. For this reason many observations made in protein studies did not yield a clear physical picture of the nature of the intimate interaction between protein and clay minerals. In fact, since proteins are indeed polyamides, it was considered useful to investigate the nature of the interaction between simple amides and clay minerals. Such a study of the interaction might be approached from the following aspects:

- (1) the identification of the complex
- (2) the effect of the saturating cation on the complex
- (3) the effect of the order of the amide on the complex
- (4) the stability of the complex

(5) the nature of the bonds in the complex and these were pursued in this work.

LITERATURE REVIEW

Significance of the surface

Soils, as a collection of different phases, are not an exception to the rule regarding the importance of specific surface. Mortland (1954) found a very high correlation between the specific surface of soils and their cation exchange capacity, percentage of the < 2 μ clay, and moisture retention.

Actually, the properties of many systems are materially affected by the presence of surface (Lewis and Randall, 1961). The greater the extent of the surface in relation to the amount of material, the larger is the part which the nature and structure of the surface play in determining the energy and in influencing the properties of the system.

The tendency to minimize the free energy in general is manifested for surfaces as a tendency either to reduce the area of the surface or to decrease the surface tension or both. It should be remembered that the free energy of a surface is equal to the work required to produce the surface. The amount of this work is the product of the surface tension and the surface area of the system. Since the surface of a clay mineral is fixed in shape and concentration,

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the free surface energy of this clay cannot be reduced by changing the shape of the surface or by molecular orientation as it is the case in a gas or a liquid. However, the clay surface can be covered with a layer of adsorbate held to or adsorbed on the surface. The effect of this adsorption is to replace the surface of the solid with other interfaces and this reduces the total surface energy.

Toth (1955) reviewed the theories advanced as to the causes of adsorption. First is the potential theory which postulates existence of some attractive force that results in the production of an adsorption potential. This would account for ion adsorption through the existence of residual valency forces on the surface of the crystal lattice. Second, is the chemical theory which views adsorption as a mechanism for forming a compound between the adsorbant and adsorbate having the least solubility product. Third, is the electric theory which considers the adsorbant as being continuous and conducting, and the approaching dipoles will be attracted to it just as if the surface were a mathematical plane midway between the dipole and its mirror image with the poles reversed. This would indicate that the energy of adsorption decreases rapidly with distance from the surface of the adsorbant.

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Adsorption by clay minerals

Adsorption of water

Winterkorn (1943) has shown that water held directly on the surface of clay particles is in a different physical state from that of liquid water in being more dense and more viscous. The question of as to how the adsorbed water is oriented is of theoretical interest. Grim (1953) reviewed this subject in detail. On the basis of the dipole character of water, it is assumed that water is oriented into layers the first of which is laid such that the center of positive charge is attracted to the negative oxygen of the lattice surface. This orientation extends outward up to a point where the translational energy of the molecule is greater than the orientation energy. This concept was criticized for assuming the clay mineral surface to be a uniformly charged plane and picturing water molecules strictly as little magnets. The next concept is based on the uneven charge distribution on water molecule to allow hydrogen bonding which forms a hexagonal network tied to the surface oxygen of the clay mineral. This configuration was criticized because it ignores the presence of adsorbed cations in the interlayer space. The third concept states that at very low states of hydration, water molecules are oriented to give tetrahedrons with the top oxygen of the silicate sheets. At higher states of hydration water forms hexagonal rings.

Se∵e advi Surr "It açı ini zer. cor. Ais Ir. is 17. 1. of se ∵e • St C 0 . . 4 . . 0 Ş Several modifications as well as new concepts have been advanced to meet the defects in the old ones. Nevertheless, summing the picture up, Grim is still justified in saying: "It is obvious that students of clay minerology are not in agreement regarding the nature of the configuration of the initially adsorbed water. There is, however, general agreement that this adsorbed water has some sort of definite configuration."

Adsorption of organic molecules

To start with, the organic could be ionic or nonionic. In case of ionic molecules, the reaction with montmorillonite is comparatively straight forward since coulombic forces are involved. Gieseking (1949) stated that clay minerals enter into exchange reaction with organic cations. The most common of these cations contain basic amino groups. He reviewed several works which showed that proteins and amino acids are very strongly sorbed by montmorillonite and consequently, were more resistant to enzymatic attack than in the free state. Hendricks (1941) showed that the cation exchange capacity of montmorillonite determined with relatively small organic cations, is nearly the same as that determined by using the barium ion. Hendricks also showed that organic ions are held by van der Waals forces in addition to the coulombic forces and in general, the larger ions are more strongly adsorbed because of the greater van der Waals forces.

Adsorption of nonionic organics is not as well defined because the binding forces are more involved and because adsorbed water, which cannot be eliminated completely from the system, is expected to play some role in the interaction. MacEwan (1947) is of the opinion that nonionic organics have to have polar groups to be adsorbed by montmorillonite. This is bound up with the fact that the montmorillonite sheets are charged, and are held together by mobile positive ions in the space between the sheets. The energy of formation of a purely van der Waals adsorption complex is presumably insufficient to lead to the breakup of the complex "charged sheet - ion - charged sheet." This conclusion is supported by the data which show that montmorillonite forms complexes with alcohols, ketones, and nitriles but does not form any with aliphatic hydrocarbons. Using different sets of functional groups he came to believe that polar molecules are held to the surface through a C-H...O bond. MacEwan did not observe any effect for the saturating cation on the degree of adsorption nor on the adsorbate orientation. This is an unjustifiable conclusion from several considerations: the first is that he used just two cations, calcium and ammonium, which are insufficient to make such a general statement. Second, is the fact that adsorption studies where X-ray diffraction is used to measure the 001 spacing are not sufficient to draw a conclusion about the nature of the bond between the organic and clay surface.
pla; ais S7.3 the ate sat ca: to W11 in ać Cā -<u>I:</u> **.**.a 17 £t e; 16 às i, 0 SC i.a Barshad (1952) found that the exchangeable cation plays a prominant role in the degree of expansion upon adsorbing a given organic. He states that the expansion is smaller, the larger the radius of the cation and the greater the charge. It is a common experience that hydrogen saturated montmorillonite gives a much lower pH than sodium saturated montmorillonite. This says that the saturating cation is not inactive and therefore it should be expected to modify, if not control, the nature of reactions of clay with organic materials. In order to fully understand these interactions, the status of the functional groups of the adsorbed organic material must be closely examined. This can be achieved by utilizing infrared spectroscopy.

Infrared in surface reactions

Infrared spectroscopy provides direct evidence on the nature of surface chemisorption (Eischens, 1964). When infrared radiation is passed through a sample material, atomic vibrations within the sample cause absorption of energy from the beam at certain wave lengths. The wave length of the absorbed radiation depends on the energy changes associated with atomic vibration, and these energy changes depend on the mass of the vibrating atoms and the strength of the bonds between atoms. Thus, the pattern of the absorption of radiation in an infrared spectrum gives information on the nature and quantity of the atomic groupings

in t abso 1118 (195 and inte base Sind mig: ven: nore the <u>The</u> Str •:.e à<u>-</u> àn Ter. gi:: str Fie res in the absorbing material. For theoretical background and absolute identification of compounds using infrared, the literature is rich with many good works. Among them Bellamy (1958), Cotton (1960), Nakanishi (1962), Nakamoto (1963), and Rao (1963). It should be stated, however, that the interpretation of the spectra of chemisorbed molecules is based on analogy with spectra of conventional compounds. Since there is a strong force field at solid surfaces, some might question the validity of direct comparison with conventional compounds. Eischens (1964) regards this as no more than a philosophical weakness that does not undermine the interpretation.

The chemistry of amides

Structure

Amides are functional derivatives of carboxylic acids where the -OH group is replaced by an amino group or an amine (Morrison and Boyd, 1959). If the molecule contains an amino group it is a primary amide, and successive replacement of the hydrogens of the amino group by alkyl groups gives secondary and tertiary amides, respectively.

The general consensus is that amides are a hybrid structure (Bellamy, 1958, Pauling, 1960, and Fieser and Fieser, 1961). In the case of a primary amide the principal resonance structures are:

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As (A) is a bit more stable, it is expected to contribute somewhat more than (B) to the structure of the parent molecule. The percent contributions are set at 60 and 40, respectively. This picture gives a resonance energy of 21 kcal/mole which agrees fairly well with experiment. Spinner (1959) takes a rather radical position in discarding resonance structures for amides. He thinks that it is because of the small electronic repulsion in the C-N bond and the intramolecular van der Waals attraction between NH_2 and C = O group that produce a shorter C-N bond and additional stability. A critical evaluation of the general concept and Spinner's conclusion will be dealt with in the discussion section.

Protonation of amides

Amides are very weak bases. The hydrochlorides are thrown down when dry hydrogen chloride is passed into dry ether solution of the amides. The question as to where the protonation occurs has been disputed, since the amide molecule contains two possible protonation sites; oxygen and nitrogen atoms. Pauling (1960) states that resonance with

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structure (B) is nearly completely inhibited by addition of a proton to the nitrogen atom and, therefore, amides should not form salts with acids by adding a proton to the amino group. Fieser and Fieser (1961), using structural models, argue in favor of O-protonation.

Recently, two powerful tools, nuclear magnetic resonance (n.m.r.) and infrared spectroscopy (IR) have been used to study amide protonation. The data presented by Berger et al. (1959) and Loewenstein (1961), using n.m.r. technique, provide the evidence for O-protonation. But the data presented by Cannon (1955), and Spinner (1959), using IR technique, provide the evidence for N-protonation. Kumler (1961) interpreted his infrared spectrum of protonated amides as to indicate O-protonation. Kutzelnigg and Mecke (1961), Janssen (1961) and Cook (1964), using the same technique, arrive at the same conclusion of Kumler.

Spinner (1960), using configurational models as basis for his argument, interprets the n.m.r. spectra as to mean N-protonation. While Janssen (1961) agrees with the substance of Spinner's argument, he does not carry the models as far as to agree on the conclusion.

It is true that the majority seem to favor the O-protonation. But this does not eliminate certain features which indicate the other case. A more vigorous review, and evaluation of the problem will be taken up later.

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Coordination chemistry is the chemistry of the bond between a metal ion and a ligand. The ligand is defined to be any atom, ion, or molecule capable of functioning as the donor partner in one or more coordinate bonds (Cotton and Wilkinson, 1962). One approach to this field is the valence bond theory. The theory postulates that each of the ligands is considered as the donor of an electron pair to the metal ion. The resultant configuration being one in which electrons tend to be as far apart as possible; square, tetrahedral, and octahedral being the most common depending upon the number of equivalent 6 orbitals that the metal ion can provide. It has been found by experimental study of a large number of complexes containing various metal ions and various ligands, that ligands may be arranged in a series according to their capacity of providing electrons, which consequently would affect the bond strength. This series, for more common ligands, is: $F < OH < C_2O_4^{-2} \sim H_2O < py$ ridine ~ NH_3 < ethylendiamine < NO_2 < CN . It should be remembered, however, that this is a general rule, and exceptions are not uncommon.

In non-aqueous solution, it was found that amides could act as coordinating agents. Kutzelnigg and Mecke (1962) prepared the copper and cadmium complex of acetamide. Rollinson and White (1962) have reported the preparation of

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a number of Cr⁺³ complexes of various amides. Bull et al. (1963) prepared various complexes with dimethylacetamide. Drago et al. (1963) prepared the complexes of nickel and chromium ions with primary, secondary, and tertiary amides. In all these cases it is reported that coordination takes place through the oxygen of the carbonyl group of the amide. Martinette et al. (1959), however, believe that coordination of amides is through nitrogen and present infrared data which support their conclusion.

A concluding statement

It is true that the basic information about amides is meager and sometimes conflicting. Yet, it should be emphasized that most of what was accomplished was done in nonaqueous solution. How they would react to the surface forces of the clay, in the field of exchangeable ions and the inescapable presence of adsorbed water, is unknown. The search for the facts in this heterogeneous media is the task of this work.

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METHODS AND PROCEDURE

Material and sample preparation

Wyoming bentonite, the $< 2 \mu$ fraction of which is pure montmorillonite as indicated by X-ray diffraction and infrared, was used in this study. The homoionic Na, Ca, Al, and Cu-clay were prepared by saturating the colloidal fraction with normal chloride solutions of the respective cations and the supernatant solution removed after settling of the flocculated clay. This treatment was repeated four times. The clay suspension was then purified by dialysis against distilled water until it was chloride free.

H-saturated montmorillonite was prepared by passing a dilute suspension of Na-saturated montmorillonite through the resin IR-20 which was saturated by hydrogen by leaching with 0.1 \underline{N} HCl and the excess chloride washed out.

A small amount of Pt-saturated montmorillonite was prepared by leaching Na-montmorillonite on a buchner funnel with a solution of platinum chloride for three times. Then washed with distilled water to get rid of the excess chloride.

In all cases, the clays were stored in a dark room at a constant temperature of 20⁰C. to avoid any algae growth. H-saturated montmorillonite was either used freshly prepared or after storage in a refrigerator to retard conversion to Al-montmorillonite.

evaç and I was : neld . be re <u>Deter</u> Adapt hydro ation of an hydro hydro hydro metr: tenpe spec idea ટેક^૦c duce: 3 =1 Zl. † Thin films (2-3 mg/cm²) of the clay were prepared by evaporating suspension in dishes of aluminum. Since copper and platinum ions reacted with the aluminum surface, it was necessary to line the dishes with polyethelene film, held in place by a smear of vacuum grease. The films could be readily stripped from these surfaces.

Determination of amide nitrogen

Adaptation of the method.

The method used, adapted from Siggia (1963), utilizes hydroxamic acid-ferric complex for colorimetric determination of amides. The method is suitable for trace quantities of amides. The reagents used are fresh solution of 2.0 <u>N</u> hydroxylamine sulphate, 3.5 N sodium hydroxide, 3.5 Nhydrochloric acid, and 0.74 M ferric chloride in 0.1 Nhydrochloric acid. Due to the fact that the maximum colormetric value in this method is a complicated function of temperature, amount of reagents, time of reaction, and the species of amide, an experiment was set up to ascertain the ideal conditions at room temperature which varied around 28° C. For this purpose aliquots of the amide were introduced to 50 ml. volumetric flasks and digested with either 3 ml. or 5 ml. of the reagents. It was found that the 5 ml. treatment is superior. are : 2710 acet: Aisco was 1 forma aided bring few : susp dete by c were the je: thr Seat Bec die til

Another set of experiments showed that optimum results are obtained when the digestion time was 2 hours for formamide, 8 hours for acetamide, and 24 hours for N-ethylacetamide.

Adsorption isotherms.

A volume containing 0.2 gm. Al-saturated montmorillonite was introduced into 100 ml. volumetric flasks and aliquots of formamide solution in the range of 0.25 to 16 symmetries were added. Different amounts of distilled water were used to bring the volumes to 100 ml. The mixture was stirred for a few minutes and allowed to equilibrate. After ten days the suspension was filtered and the amide in the filtrate determined by the colorimetric method. The amount adsorbed by clay could be obtained by difference.

Infrared absorption and X-ray diffraction studies

Acetamide, N-ethylacetamide, and N,N-diethylacetamide were added to homoionic clay suspensions in amount covering the range of 0.25 to 8 symmetries. The suspension was left to evaporate and become air-dry in a period of two to three days. The infrared spectra were recorded with the beam at right angle to the films or at a 45° angle on a Beckman IR7 spectrophotometer (600 to 4000 cm⁻¹). A Philips diffractometer was used to observe the 001 spacing in the films. In order to investigate the reaction of amides with

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clay under a more dehydrated condition, the amide-treated film was mounted in an evacuable brass cell fitted with sodium chloride windows. After evacuating by rotary pump for 5 minutes, the film was heated at 80° C. for one hour under continuous evacuation. The infrared spectrum was then recorded. The film was then left in the atmosphere (air-conditioned room at $20 \pm 2^{\circ}$ C and 40 per cent relative humidity) for three weeks and the infrared spectra again recorded in order to see the possible effects of rehydration.

Stability experiments

Pure clay films were placed in aluminum dishes which were then rolled to prevent loss of the film but loose enough to allow amide diffusion into the film in its vapor phase. One gram of acetamide (solid at room temperature), two drops of N-ethylacetamide or N,N-diethylacetamide (both are liquid at room temperature), and the rolled aluminum dishes were introduced into a 500 ml. suction flask. The flask would then be evacuated for five minutes and put in the oven at 110[°]C. for 15, 30, or 60 minutes. One set of such treated films stood in the atmosphere and another set was subjected to a continuous evacuation. An extensive analysis of infrared, X-ray, and nitrogen content (total nitrogen by micro Kjeldahl method, adapted from Black, 1956) was run on both sets several times over a period of one week. The objective was to obtain evidence for comparing the stability of the complexes in the atmosphere against that in vacuum.

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RESULTS AND DISCUSSION

Adsorption of amides from water solutions

That formamide is not a stable system as an aqueous solution was established by two pieces of evidence. When a solution two weeks old was compared with a fresh solution, the decomposition was found to be around 25 percent. The other evidence came from observing dilute suspensions of montmorillonite and formamide, acetamide, and N-ethylacetamide standing in the laboratory for four weeks. Algae growth was apparent as green colonies in the case of acetamide and N-ethylacetamide while there was none in the formamide culture. The reason for this is when formamide hydrolyzes, according to the equation:

 $HCONH_2 \xrightarrow{H_2O} HCOOH + NH_3$

the formic acid would not be expected to favor microorganism's growth. A slight modification in the experimental procedure was implemented to extend the usefulness of the method. This, along with its results are outlined in Table 1.

Acetamide and N-ethylacetamide are stable in aqueous solution for a period of at least two weeks. A small experiment was carried out to detect their adsorption on Al, H, and Ca-saturated montmorillonite. The data in Table 2 were

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Meq. of amide added to the	Equilibrium time, days				
suspension ^b	1	2	3	Blank ^C	
0.345	75	74	73	78	
0.690	62	57	58	58	
1.035	44	47	42	43	
1.380	32	33	37	32	

Table 1.	Transmission	readings	of	filtrate	of	suspension	of
	Al-montmoril]	lonite and	d fo	ormamide. ²	1		

Average of two replications

^bThe final volume of the suspension was 100 ml. and contained 0.5 gm.clay + formamide The final volume of the suspension was 100 ml. and contained 0.5 gm.clay

Transmission readings of filtrates of montmoril-Table 2. lonite containing acetamide or N-ethylacetamide.^a

b	Saturating cation				
Amide ^D	Al	Н	Ca	Blank ^C	
Acetamide		22	22	22	
N-Ethylacetamide	62	58	60	61	

a bAverage of two replications The final valume of the suspension was 100 ml. and contained 0.5 gm. clay + 1.0 meq. amide The final volume of the suspension was 100 ml. and contained

0.5 gm. clay

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obtained by using 0.5 gm. of clay as the absorbing material and equilibrated with amide for two days.

The data in Tables 1 and 2 establish two facts. That amides are not adsorbed by montmorillonite from aqueous solution is apparent. The literature does not provide evidence to confirm or contradict this conclusion. Nevertheless, there is some work with urea, which could be considered as an analoque of amides. Conrad (1940) claims that urea can be adsorbed by soils. Hourigan and Seay (1957) reported that urea was fixed by soil colloids and did not leach under field conditions. Broadbent et al. (1958) observed that urea moved slower than nitrate in soil columns in a leaching experiment and they attributed this to the rapid hydrolysis and weak adsorption of urea molecule. Chin and Kroontje (1962) found that urea was adsorbed by soil and the adsorption decreased under wet conditions. They also used some pure clay minerals and found no relation between the ion exchange capacity of the adsorbents and their adsorbing power. Neither montmorillonite nor pyrophyllite adsorbed any amount. A critical evaluation of these results could be undertaken theoretically, in line with the paper of Frissel and Bolt (1962). It is in accordance with the Boltzmann distribution law that the concentration of adsorbed molecules in the neighborhood of an adsorbing surface is:

$$C = q C_{e} e^{-E_{ads}/RT}$$

where:

Ξ Sew. <u>:.</u>ff tile iist Шđ for X11 sur dis by 110 1. T.e en àg 20 S 19 C_{e} = equilibrium concentration of the adsorbate

E_{ads} = the amount of energy liberated when transferring one mole of adsorbate from the equilibrium solution to a location in the adsorption zone q = a statistical weight factor.

Now, E_{ads} may be regarded as the sum of the effects of the different types of force fields acting upon adsorbate molecules. Considering these force fields, it is convenient to distinguish between forces acting over very short distances and those extending over considerable distances; long range The latter forces, are mainly those associated forces. with the electrostatic field extending from the charged surface (Coulomb and polarization forces) and the London dispersion forces. The short range forces are characterized by a very steep dependency upon distance and comprise the higher-order van der Waals forces, chemical bonds, and hydrogen bonds. Furthermore, it should be remembered that, in calculating the energy of adsorption in aqueous environment, one has to take into consideration the hydration energy of adsorbate and adsorbent.

Applying these principles to urea adsorption from aqueous solution, it is clear that since urea is a neutral molecule, the electrostatic field between urea and the clay surface would be very small. Also, a direct chemical bond is highly improbable. All that is left to consider is hydrogen bonding and van der Waals forces. But it seems unlikely that these two forces are able to create some sort of

stable association between urea and the clay surface for two reasons. The first is that adsorption study is carried out in aqueous medium where water is more tightly held to the clay surface than urea. The second is due to the high solubility of urea in water. A high solubility means a high energy of association between the solute and the solvent which is in all probability higher than the association between the clay and urea. This point is substantiated by Brey (1958). He states that the greater solubility of the solute in the solvent, the less the extent of its adsorption. This explains why organic substances are adsorbed on charcoal in decreasing amounts from water, ethyl alcohol, pyridine, benzene, ether.

The second significant feature of the data in Tables 1 and 2 is that montmorillonite did not catalyze amide hydrolysis. This is supported by infrared data to be presented later.

Infrared absorption and X-ray diffraction studies on amide-montmorillonite complexes

Acetamide - montmorillonite

The hydrated complex--A proton could be provided to acetamide by montmorillonite through two mechanisms; either the active fraction of the exchangeable hydrogen ions or the highly dissociated residual water of aluminum saturated clay. The fact that acetamide accepts a proton to form the

cation $[(CH_3CONH_2)H]^+$ is clearly indicated by Fig. 1. Curve (a) could be identified with the infrared spectra of the acetamide cation reported by Albert and Badger (1958), Spinner (1959) and Kutzelnigg and Mecke (1962). The common features are the two bands around 1700 and 1500 cm^{-1} . The 1700 cm⁻¹ band is assigned to C=O stretching by Spinner (1959) while Kumler (1961) and Cook (1964) assign the band near 1700 cm^{-1} in amide cations to the C=N stretching. The second band at 1500 cm⁻¹ is assigned to the C-H assymmetric bending by Spinner (1958) while Kutzelnigg and Mecke (1962) assign it to vibration involving the C=O group of the oxygen protonated amide. Figure 1 also reveals the fact that as the level of acetamide in proportion to the available proton increases, the intensity of these two bands decreases with a concomitant increase in background absorption in the 1700-1100 cm⁻¹ region, noting that all those curves had the same base line at 2000 cm⁻¹. This increase in background is interpreted as to be due to the hemisalt formation (White, 1955; Albert and Badger, 1958; and Farmer and Mortland, 1965) in which two molecules share a proton through a symmetrical hydrogen bond. At the highest level of acetamide, the spectra is similar to that of the neutral molecule. This was expected because it is known that acetamide is a very weak base and therefore, it requires a rather high acidity level to be protonated. Berger et al. (1959) in working with N-substituted amides found that the pH of the



media has to be below 0.8 to form any appreciable amount of the cation. Since the N-substituted amides are stronger bases than primary amides, it is certainly logical to conclude that the pH of the media has to be far below 0.8 if the acetamide cation is to be formed.

Copper-acetamide complex formation on montmorillonite surface is indicated by Fig. 2. In the low level of acetamide, the presence of some residual water is evident by the broad absorption at about 1635 cm⁻¹ and the portion of the spectra around 3400 cm⁻¹ in figure 5. This residual water, which is known to be highly dissociated could account for the weak bands at around 1500 and 1550 cm⁻¹. The first being either a vibration involving the C=O group of the protonated amide or a C-H asymmetric bending and the second being Amide II band of the protonated acetamide. As the amide concentration increases, the sign of protonation decreases while the sign of coordination becomes more apparent.

If curve (b) of the figure 2 were to be contrasted with that of solid acetamide, it is noted that the C-N and C=O stretchings of the solid at 1400 and 1681 cm⁻¹ have suffered considerable shifts; the first to a higher frequency and the second to a lower frequency. It is concluded by arguments that will be discussed in detail later that a coordination complex between copper and acetamide was formed in which coordination is taking place through the oxygen of the carbonyl group. Similar results were obtained by Kutzelnigg



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and Mecke (1962) and Bull et al. (1963) which enabled them to draw the same conclusion. At the very high level of acetamide, there will be an excess of the amide which is not coordinated. Curve (c) of the figure bears this, as indicated by the weak band near 1400 cm⁻¹. Also by broadening of C=O stretching due to hydrogen bonding between the amide molecules.

The calcium-acetamide system is presented in Figure 3. Generally the spectra of this system can be identified with the spectra of the α modification of solid acetamide. The bands appearing at 1670 and 1610 cm^{-1} are the Amide I (C=0 stretching) and Amide II (NH₂ deformation), respectively. Curve (a) of the figure indicates the possible formation of small quantities of the acetamide cation, in a similar fashion to the copper system. If this is valid, the bands around 1550 and 1515 cm⁻¹ could be accounted for while the band at 1635 cm^{-1} can be assigned to the O-H deformation of the residual water. Aside from the displacement of water by the amide at higher concentration, the only change that takes place is the general increase in band intensities. That is to say, the amide tends to preserve its identity by forming a sort of pseudo-crystalline structure. Calcium ions could be part of this structure either indirectly through hydration water acting as a bridge, or directly through coordination. The indirect association between pyridine and Mg^{+2} or Cu^{+2} on the surface of montmorillonite
WAVE NUMBERS (cm-1)



is postulated by Farmer and Mortland (1965). At any rate, the data seem to suggest that the association is through the oxygen atom even though the bond is rather weak.

The data for acetamide in the sodium system (Fig. 4) are similar to that of the acetamide-calcium system. This is taken to indicate that the status of acetamide in both cases is similar and, therefore, the conclusions drawn previously for the calcium system still hold.

The portion of the spectra of acetamide-montmorillonite complex in the NH stretching region is shown in Fig. 5. According to Bellamy (1958), the NH stretch for free (unbonded) amides gives rise to two bands near 3500 and 3400 cm^{-1} , but for bonded primary amides, the two bands are at 3350 and 3180 cm⁻¹. In all cases studied in this work, no band as low as 3180 cm⁻¹ was found. This is taken to mean that interaction between the amide and montmorillonite resulted in a decrease in the strength of association between acetamide molecules; reduction in the hydrogen bond strength of N-H...O. The same observation was found by Ledoux and White (1965) for formamide adsorbed on kaolinite surface. They interpret their result on the basis of breaking down of the intermolecular hydrogen bonds within the formamide chains and the formation of weaker hydrogen bonds between the extremities of the broken chains (NH₂ and CO) and the OH and the O ions of the internal kaolinite surfaces.

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Undoubtedly, different cations on the clay surface represent different reaction media, and therefore the nature of reactions will differ. The NH stretch of the free amide in the copper system gives two bands at 3440 and 3365 cm^{-1} , bearing a strong evidence for association. A possible explanation for this is the coordination of the amide through nitrogen. But this is not true based on the mode of the C=O and C-N bands. The same mode indicates that indirect association of the amide and Cu⁺² though water bridge is not taking place. Therefore the possibility of a hydrogen bond between the amide groups and water, or the silicate sheet oxygen, or both, lends a reasonable interpretation.

The 3500 cm⁻¹ band is absent in hydrogen saturated system in the 0.25 symmetry level, and shows up as a weak shoulder at 1.0 symmetry. It is of interest to contrast this with the sodium saturated system, where the intensity of the band is much higher. This may suggest that acetamide is being protonated on the nitrogen atom, and therefore the NH frequency is depressed to a lower wave number. Another auxiliary factor in depressing the NH frequency of the protonated amide to a lower frequency is the fact that it is able to form the hemiacetamide cation through a symmetical hydrogen bond which will certainly decrease the amount of free amide.

The 4.0 symmetry level in the calcium saturated system is unique, as it shows the displacement of the whole

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spectrum to the right compared with the 1.0 symmetry level. Such displacement could not be due to hydrogen bonding to water, because at such high level of amide, water would be replaced by the amide to a considerable extent. It also could not be due to association between the amide and the surface oxygen or the cation, because the general features of the deformation region do not substantiate this. It only can mean that at higher levels of acetamide, interaction between neighboring molecules occurs by hydrogen bonding, thus lowering the NH stretch frequency.

Penland et al. (1957), Cotton (1960), and Nakamoto (1962) state that platinum is coordinated by urea through the nitrogen atom. That this is not the case for acetamide is indicated by data of Fig. 6. In curve (a) for the fresh complex (amide is adsorbed from the vapor phase for 30 minutes), the Amide I band at 1662 cm^{-1} and the free NH stretching bands at 3475 and 3380 cm⁻¹ are indication for oxygen coordination. Moreover, the broad band around 1425 cm⁻¹ adds up the evidence favoring O-coordination. Upon standing in atmosphere for one week, the excess amide is lost, and the residual water provides a proton which is accepted by acetamide to form the cation as indicated by curve (b) of Fig. 6. Here, the bands at 3475 and 1400 cm⁻¹ have almost disappeared while the band at 1500 cm^{-1} is very distinct. The band around 1700 cm⁻¹, which is characteristic of amide cations, appears as a broad but distinct shoulder at 1713 cm⁻¹.



The dehydrated and rehydrated complex--As was previously shown in Tables 1 and 2, amides are not adsorbed from aqueous solution. This might suggest that water is too strongly held on the clay to be displaced by amides. The previous figures indicate however, that this is not true at low hydration states, and that at low moisture levels, acetamide competes very successfully with water for adsorption sites. In fact, upon subjecting clay films containing the water-acetamidemontmorillonite complex to heat and vacuum, acetamide is retained and water is removed.

The acetamide cation, formed on the hydrogen saturated montmorillonite is not stable when heated in vacuum. Curve (a) of Fig. 7 is identical with the spectra of acetamide on calcium or sodium saturated montmorillonite with the possible exception of the weak band at 1509 cm⁻¹ which indicates the presence of minute quantity of the cation. Of interest in this spectrum is the distinct bands at 3515 and 3396 cm^{-1} ; the characteristic bands of free NH stretching. An explanation for the thermal instability of the acetamide cation could be due to the thermal instability of H-montmorillonite which is expected to be converted to Al-mortmorillonite according to the equation:

 H_3O -montmorillonite \xrightarrow{heat} Al-montmorillonite + H_2O

Two facts stand against this interpretation. The first is that acetamide was protonated on the surface of Al-montmorillonite, and that when the heated film was left for three

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weeks at room temperature and humidity, the cation was formed again as in curve (b) of Fig. 7. Therefore, it should be concluded that the acetamide cation on montmorillonite surface undergoes the following reaction:

Acetamide cation - montmorillonite $\xrightarrow{\text{heat}}$ CH₃CONH₂ + H-montmorillonite + H₂O

Now, if H-montmorillonite is converted to Al-montmorillonite by heating, which is expected even though it is hard to assign the degree of conversion, aluminum ions are going to rehydrate upon standing in the atmosphere and, consequently, the highly polarized residual water, i.e., a proton source, is in the media. Such mechanism seems to explain neatly the reappearance of the cation features upon rehydration of previously heated H, or Al-acetamide-montmorillonite films.

The characteristic bands of acetamide cation of the rehydrated films are more intense than those of the freshly prepared complex. It is true that the factors controlling band intensities are very involved, but since the spectra in this case belong to the same film, the comparison is more straight forward. The data seem to indicate that some amide is lost upon heating, and therefore, after rehydration, the proton supply in proportion to the amide is greater than in the freshly prepared complex.

When the cation on Pt-montmorillonite is heated, it disintegrates, as was the case on H- or Al-montmorillonite.

Nevertheless, curve (c) of Fig. 6 of the dehydrated platinum system make it unique; the prominance of the C-N band at 1425 cm⁻¹, the rather low frequency of the carbonyl group, and the presence of free NH stretch indicate a coordination complex with an oxygen coordinate bond. More significant is the fact that when the complex is rehydrated, a spectrum identical to that of curve (b) is obtained. Presumably then, the status of the complex in the hydrated and rehydrated complex is the same. Once again, the reversibility of the amide cation formation in the dehydration-rehydration cycle is demonstrated. At any rate, a more detailed discussion of this cycle is due later.

Acetamide coordinated to copper on montmorillonite did not change much upon heating as shown by curve (a) of Fig. 8. That the complex is stable to heat treatment, in contrast to the cation, is clear from the mode of Amide I band at 1661 cm^{-1} Amide II band at 1576 cm^{-1} , and the C-N band at 1416 cm^{-1} . A considerable amount of water was lost (contrast with the fresh complex) and could not be regained upon rehydration (contrast with curve (b) of Fig. 2). The loss of water has contributed to the general sharpness of the bands, and to the appearance of a new band at 3490 cm^{-1} , corresponding to free NH stretching. Since the presence of free NH stretch and coordination through nitrogen is incompatible, the band at 3490 cm^{-1} , along with those at 1661, 1576, and 1416 cm^{-1} constitute conclusive evidence of coordination through oxygen.



On calcium and sodium montmorillonite, the spectrum reflects significant changes. For the calcium system, curve (a) of Fig. 9, dehydration was complete as signified by the loss of band at 1638 cm^{-1} (deformation of OH of water) and the shape of the spectrum in the OH stretching region. The shift of Amide I band from 1670 cm^{-1} in the fresh complex, to 1659 cm⁻¹ in the dehydrated complex, indicates coordination through the carbonyl group. The free NH stretching bands at 3500 and 3382 cm^{-1} eliminate possible coordination through nitrogen. On rehydration, the amide seems to dissociate itself from the metal cation as evidenced by the shift of Amide I band from 1659 cm^{-1} to 1664 cm^{-1} . In all likelihood, the amide will be attached to the cation through water bridges in the rehydrated complex. The rehydration water is indicated by the band at 1637 cm^{-1} and a broad band in the $3600-2800 \text{ cm}^{-1}$ region. Amide-water-ion association is conveyed by the rather low frequency of Amide I band; at 1664 cm^{-1} , and the band at 3250 cm^{-1} for bonded NH stretching.

Fig. 10 shows the 001 spacing of montmorillonite as affected by the saturating cation and acetamide concentration. In almost all cases, just one layer of acetamide is taken up by montmorillonite. The cation exerts its effect on the observed 001 spacing through the amount of water which is retained as well as through orientation of the adsorbed amide. The question of orientation will be dealt with in more detail later.







N-Ethylacetamide-montmorillonite

The hydrated complex--N-Ethylacetamide was protonated on the surface of H- and Al-montmorillonite. The evidence for this is the band at 1692 cm⁻¹ (Fig. 11). Cannon (1955) was able to protonate N-ethylacetamide in a solution of CCl₄ by bubbling anhydrous HCl through the dry solvent. The spectra of the cation gave a characteristic band at 1718 cm⁻¹ which Cannon allocates to C=O stretching of the cation. However, Kumler (1961) prepares the same compound but he believes that it is just as logical if not more so to assume the band around 1700 cm⁻¹ in the amide cation arises mainly from the C=N vibration as to assume it arises mainly from a C=O. The two views are very different from each other because the first implies N-protonation while the second implies O-protonation.

The intensity of this band increases in going from the 0.25 symmetry level (Curve a) to the 0.5 symmetry level (Curve b), then decreases again on passing to the 1.0 symmetry level (Curve c). Along with this trend, there is a marked increase in background absorption in the 1700-1100 cm^{-1} region in going from low to higher level of amide. These observations are explained on the basis that, at the lowest level, the amide available in the media was not enough to react with all the available protons while at the 0.5 symmetry level most of the available protons have reacted to give the amide cation. At the 1.0 symmetry level, an



excess of amide molecules are present in comparison with the number of available protons. Therefore the hemisalt is formed where two amide molecules share a proton through a symmetrical hydrogen bond. This is indicated by the broad increase in absorption in the 1700-1100 cm⁻¹ region which is characteristic of such bonding.

The band at 1638 cm⁻¹ which is shifted to the right by about 12 cm⁻¹ if compared with the spectra of pure liquid N-ethylacetamide, could be assigned to two different possible modes: First, either the amide is coordinating through the carbonyl group the Al ions which are present in both Al and H-saturated montmorillonite. Such coordination would shift the C=O stretching to the right. Second, it could be assigned to the C=O stretching of the hemisalt which forms when two amide molecules share a proton. It is hard to dismiss either possibility in favor of the other because it seems that both might simultaneously take place.

Figure 12 shows N-ethylacetamide-copper complex. Clearly, the complex is a coordination one with an oxygencopper linkage. The C=O stretching band is at 1621 cm⁻¹; a shift to the right of 29 cm⁻¹ compared with liquid N-ethylacetamide. It is true that nitrogen atom of this molecule is more basic than that of acetamide, but steric factors undermine this added bascity, and therefore a nitrogen coordinate bond formation is improbable. However, Martinette et al. (1959) studying the complex of cadmium



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with N-methylacetamide believes that it is a nitrogen coordination complex. His argument goes as follows: "N-Methylacetamide is an associated liquid with strong hydrogen bonding. Coordination through the nitrogen atom generally results in the lowering of the N-H stretching frequency. However, since the liquid is highly associated by hydrogen bonding, this band may become weaker in the coordinated complex and consequently the N-H stretching frequency may be raised rather than lowered." This is a fallacious argument because it would imply that the amide-amide bond is stronger than the amide-metal ion bond, and therefore there could be no coordination complex in the first place.

Contrary to the conclusion of Martinette et al., Diorio et al. (1962) presents evidence for an oxygen coordinate bond in lithium-N-methylpropionamide complex. They concede the disruption of the hydrogen bonded network of the pure liquid amide upon the introduction of lithium ion, as indicated by the displacement of the NH stretching bands to a higher frequency, but they use the shift of the C=O stretching band to lower frequency as a more reliable and reasonable way to indicate a metal-oxygen linkage. Drago et al. (1963) using a spectrophotometric method to study the complexes of N-methylacetamide with chromium and nickel ions came to the same conclusion of Diorio et al. regarding the nature of the coordinate bond.

The origin of the bands at 1561, 1490, 1336, and 1289 cm⁻¹ is of interest. According to Bellamy (1958), it is an over-simplification to consider any single motion of a pair of atoms of the CO-NH system in isolation. The double-bond character and charge distribution of both the C=O and C-N links change during the vibration itself. thereby affecting the frequencies of other vibration of the group. Coupling between these two bands leads to an asymmetric OCN mode (Amide I) and symmetric frequency. The latter then couples with the NH deformation mode. Accordingly, the Amide II is a mixed vibration, which can best be described as an out-of-phase combination of OCN and NH vibration in which the angular displacement of the hydrogen atom plays the greater part. The corresponding in-phase-mode, which has primarily a C-N stretching character, is assigned to Amide III band and occurs near 1290 cm⁻¹. On this basis, the bands at 1561, 1490, 1336, and 1289 cm^{-1} could be accounted for. It seems that coordination through oxygen has induced the split of Amide II band, which is usually at 1550 cm⁻¹ into two bands; 1561 and 1490 cm⁻¹ corresponding to NH deformation and CN stretching, respectively. Similarly, Amide III band is split into two bands, a sharp band at 1336 cm⁻¹ corresponding a C-N stretching mode, and a broad band at 1289 cm⁻¹ corresponding to NH deformation with some contribution from unbonded amide. This band separation is in line with an observation reported by Penland et al. (1957) on work with urea.

The data of Figs. 13 and 14, for the calcium and sodium complexes show a coordination complex too. The Amide I band in the calcium complex is not shifted by a great deal which suggests the weakness of the bond. Nevertheless, the split of Amide III band into two bands at 1336 and 1289 cm⁻¹ is identical with the copper complex. However, the split of Amide II band is complicated. The small band at 1578 cm⁻¹ is at a too low frequency to be assigned to a coordinated C=O group. A vibration involving a weakly bonded NH seems to be the only possibility. In the sodium complex the C=O stretching is at 1626 cm⁻¹ but the split of Amide II band is not distinct; Amide II band is at 1542 cm⁻¹ with weak shoulders on the high frequency side. However, Amide III shows up clearly at 1335 and 1288 cm⁻¹.

The spectra of the complex in the NH stretching region is given in Fig. 15. The band around 3455 cm^{-1} is assigned to a free NH stretching of the amide which has the trans configuration (Bellamy, 1958). It is of interest to note that this band was absent in the hydrogen system at the 0.25 symmetry level, while present in all other systems. The same observation was noted in the acetamide complex and probably the reasons in both cases are the same. According to Cannon (1955) this is an indication for N-protonation.

The band near **3**320 cm⁻¹ is assigned to a bonded NH stretching of trans configuration while that near 3125 cm⁻¹ is for a cis. Bellamy states that in normal secondary amides











such as N-methylacetamide the trans-form predominates to the extent of 95 percent but in sterically hindered compounds, such as N-tert-butylphenylacetamide, the cis-form is present to the extent of approximately 70 percent. N-Ethylacetamide is not normally a sterically hindered compound but it might become so in accommodating its configuration to fit structural considerations in the interlamellar space of the clay mineral. Such considerations will be dealt with in detail later.

Pt-montmorillonite adsorbed N-ethylacetamide when treated with the vapor for 30 minutes as shown by curve (a) of Fig. 16. The shift of the C=O stretching to a frequency lower than that in the liquid and the presence of the free NH stretching frequency at 3450 cm⁻¹ suggest a coordination complex through the carbonyl group. When the complex was left in atmosphere for 50 days, some of the amide was lost as indicated by the absence or the weakness of the bands for bonded NH stretching; at 3290 and 3100 cm⁻¹. Also some amide cation was formed as indicated by the shoulder at 1688 cm⁻¹. Significantly, then, when the excess amide was lost, the proportion of protons provided by residual water to the amide was favorable for amide protonation.

As it was mentioned earlier, adsorption is a reversible reaction, therefore, the principle of mass action is important. Under conditions of a purely reversible system where water is abundant, as was the case with data reported



left at room temperature for one week, and (c) the complex of (b) is heated at 80°C. in vacuum (0-1 mm. Hg) for one hour.

in Table 2, N-ethylacetamide was not adsorbed by montmorillonite. Yet, when conditions were changed to differentially decrease the amount of water in the system, N-ethylacetamide was preferentially adsorbed in such an amount as to change the c-spacings of the clay crystals. This is shown by the data of Fig. 17.

Calcium and Cu-montmorillonite show the most marked expansion. There is a difference between the two systems though; the two layer expansion in Ca-montmorillonite is randomly interstratified with that of one layer and the boundary between these is more or less distinct while in Cu-montmorillonite the two layer expansion, besides being less than that of calcium, is gradually and smoothly giving way to a one layer expansion. Nevertheless, both calcium and Cu-montmorillonite yield an incomplete one layer expansion as the level of amide drops from 4.0 symmetry to the 0.25 symmetry level.

Hydrogen and aluminum saturated montmorillonite show the unusual feature of the decrease in the c-spacing as the level of amide was decreased from 4.0 to 1.0 symmetry and then showed a slight increase as the level of amide is decreased further from 1.0 to 0.25 symmetry. It is improbable that this is a coincidental experimental error. It seems that the status of the amide at the different levels has some effect on clay-water interaction which, consequently, controls the function of water as a complementary ingredient




in layer formation. The same principle applies in the sodium system but in a simpler fashion. At the 4.0 symmetry level, a one layer structure is well-developed as shown by the high intensity of the peak. As the amide level decreases, the structure of the one layer suffers fragmentation which is reflected by a decrease in intensity of the peak; the decrease being more pronounced in the 0.25 symmetry level than that of the 1.0 symmetry.

The dehydrated and rehydrated complex--The spectrum of the dehydrated Al-montmorillonite-N-ethylacetamide complex is given by curve (a) in Fig. 18. Dehydration was not complete as indicated by the presence of the band at 1686 cm⁻¹; the characteristic band of amide cation for which water is necessary to be formed. The band at 3515 cm⁻¹ is at too high a frequency to be assigned to NH stretching. Actually, if dehydration is incomplete and therefore the cation is present, the nitrogen atom of the amide will carry a positive charge. This is true regardless of the controversy of where the proton in an amide cation is located. For if amide is protonated on the nitrogen, most of the positive charge will be on the nitrogen atom, but if the amide is protonated on the oxygen a considerable amount of positive charge will be located on the nitrogen through resonance:

$$CH_{3} - C - N - CH_{2}CH_{3} \longleftrightarrow CH_{3} - C = N - CH_{2}CH_{2}$$





Thus, if nitrogen carries a positive charge, the force constant of the N-H bond is expected to decrease and consequently, the NH stretch will be shifted to a lower frequency. Therefore, the band at 3515 cm^{-1} is assigned to O-H stretching of the remaining residual water which has protonated some of the amide molecules. Considerable amount of the cation has disappeared upon heating, as evidenced by the presence of the band at 3450 cm^{-1} for free NH stretch and that at 1545 cm^{-1} for the Amide II band of the unprotonated amide.

Upon rehydration, curve (b), enough water is taken up to lead to an almost complete protonation of all the amide. The band at 1686 cm⁻¹ of the dehydrated complex is shifted to 1694 cm⁻¹ and is far more intense. The bands at 1575 and 1545 cm⁻¹ of the Amide II bands (which signify the presence of two species of the amide) are coupled to give a fairly strong band at 1560 cm⁻¹ with small satellites on its low frequency side. Also the bands at 3515 and 3450 cm⁻¹ have disappeared. In summary then, it should be said that the spectrum of the rehydrated complex is very similar, actually almost identical to that of the hydrated complex, indicating reversibility and the contribution of water to cation formation in amides.

As was found for H and Al-montmorillonite, the cation of N-ethylacetamide formed on the surface of Pt-montmorillonite is converted to the amide upon dehydration as revealed

by curve (c) of Fig. 16. Since the rehydrated complex was almost identical to that given by the hydrated complex (curve b), it is reasonable to conclude that the factors which govern protonation of N-ethylacetamide on the surface of acidic montmorillonite are the same for H, Al, and Pt-clay systems.

Curve (c) of Fig. 18 shows the dehydrated copper complex. Comparison with the hydrated (Fig. 12) and the rehydrated complex of (curve d, Fig. 18) shows that the Amide I band is at 1605 cm^{-1} in the dehydrated complex as contrasted with 1621 and 1618 cm⁻¹ in the hydrated systems. This lowering of frequency could be explained in two ways. If the amide was held to the metal ion through a water bridge, the removal of water would force the formation of a direct amide-metal coordinate bond which is stronger and therefore the C=O stretch would be shifted to a lower frequency. It is doubtful, however, that coordination through a water bridge could be responsible for lowering the C=O stretching to 1620 cm^{-1} , as well as the split of the Amide II and III bands mentioned previously. Actually at the 0.5 symmetry level, if no amide is lost during the complex preparation, which is problematical, there would be just one amide molecule for every metal ion. Therefore, the strength of the bond between the amide and the metal ion will be stronger, on the average, than that of the complex where the complete coordination requirement is satisfied, either by amide, or water, or a mixture of both.

Such a possibility seems to offer a reasonable interpretation to the added shift of the C=O group upon dehydration. A proof to the validity of this interpretation comes from comparing the spectra of the complex under different conditions. Aside from the added shift of the C=O group and a slight decrease of the NH stretching bands, the spectra of the Cu-complex in various environments are very similar.

Dehydrated sodium and calcium complexes are represented by curves (a) and (c) of Fig. 19, while those of the rehydrated complexes are represented by (b) and (d). The spectra are relatively unchanged in the dehydrated systems. It is interesting to note that even though dehydration was effective in driving out most of the water, there was no additional decrease in the frequency of the Amide I band as was the case with the copper complex. In fact, this was not expected, because a coordinate bond between a ligand and a transitional metal ion such as Cu^{+2} is known to be far stronger than that of an alkali ion such as Na⁺ or an alkaline earth ion such as Ca^{+2} .

N, N-Diethylacetamide-montmorillonite

The hydrated complex--N,N-Diethylacetamide was protonated on the surface of acidified montmorillonite. However, the acidifying agent shows a differential effect in the process. Figs. 20, 21 and 22 for H-, Al-, and Pt-montmorilloniteamide complex shows such effect. Fig. 20 for











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H-montmorillonite indicates that a considerable amount of hydration water was displaced by the amide even at the lowest level; 0.5 symmetry, as shown by the absence of the 1635 cm⁻¹ band for water. The prominant feature of curve (a) is the presence of the 1672 and 1625 cm⁻¹ bands. The first is undoubtedly an indication of cation formation and is assigned to either a C=O or C=N stretch depending on where the proton on the cation is located. The second band at 1625 cm^{-1} could be assigned to several possible modes. At such low level of amide, water displacement could not be complete, and therefore, the band at 1625 cm^{-1} could be the O-H deformation of the residual water. Nevertheless, three facts stand against this assignment. First, the O-H deformation of H-montmorillonite is at 1637 cm^{-1} , and no explanation as to why this shift took place would seem to be reasonable. Second, the intensity of the 1672 cm^{-1} indicates that an appreciable amount of the amide was protonated but hence an almost complete protonation could not take place in the presence of too much water, as indicated by the rather prominant band at 1625 cm^{-1} , therefore this band is not a water band. Third, it is seen that the 1625 cm^{-1} increases in intensity and sharpness, with a concomitant slight shift to a lower frequency, as the amide level progresses upward. Considering all possibilities, then, the assignment of this band to amide coordinated through the carbonyl to aluminum seems the most reasonable.

At the 1.0 symmetry level, there are also two bands. The 1674 cm^{-1} band corresponds to the 1672 cm^{-1} band of the 0.5 symmetry level, while the 1617 cm⁻¹ corresponds to that at 1625 cm⁻¹. The slight shift to the right indicates a stronger coordinate bond of the amide molecules which are coordinating with whatever aluminum ions are in the sys-It is of interest to note that at this level of amide, tem. the intensity of bands of protonated and coordinated amide is approximately the same. This is to say, half of the adsorbed amide is protonated while the other half is being coordinated. This rule does not hold, however, at the high level of amide. Curve (c) of the 4.0 symmetry level shows two bands: the one at 1612 cm^{-1} for coordinated amide, and the small band at 1637 cm⁻¹ which falls very close to the Amide I band of liquid N,N-diethylacetamide and, therefore, it is assigned to free amide. So, the behavior of N, N-diethylacetamide indicates that when protons are in excess to the amide, protonation preferentially take place. When the two reactants are present in approximately equal amount, protonation as well as coordination take place.

It might be argued that since amides are monoprotonated in their cations, why did not protonation predominate at the 1.0 symmetry level where there is a 1:1 ratio on H-montmorillonite? On one hand, during the preparation of films, some of the amide is lost by evaporation and several chemical analyses supported this. Such loss would mean that there is an excess of protons in the media than a supposedly 1:1 ratio would indicate. On the other hand, the ratio is shifted

toward the other direction due to the fact that protons on exchangeable sites are not free to react as they please; only the active fraction can do so. At any rate, at the 4.0 symmetry level, it is undoubtedly true that amide is present in excess of monoprotonation potential and hence, coordination predominates. It should be emphasized, however, that protonation is not absent altogether since the marked increase in background absorption indicates the presence of the hemisalt. White (1955), on the basis of a postulated structural formula in which two bonds extend between two molecules, claims that N, N-diethylacetamide is not capable of forming the hemisalt. This is a fallacious assumption. It is true that two bonds between two molecules would enhance the stability of the structure but two bonds are not required. Moreover, Albert and Badger (1958), Pauling (1960) and Kutzelnigg and Mecke (1962) report that in acetamide hemisalt, there is just one bond extending between the two molecules.

Aside from the increase in background absorption, a direct evidence for the presence of the hemisalt, i.e., a C=O stretching band, is absent. Actually, regardless of whether protonation occurs on the oxygen or nitrogen, the C=O groups in the hemisalt would be strongly bound as to give a C=O stretching at a lower wave length than that of a free C=O group. If it would be reasonable to expect such band in such system at about 1650 cm⁻¹, it would be certainly

masked due to the breadth of the bands in this region. The Al-system differs from the H-system in two respects. It is less acidic, and therefore protonation is not as decisive. Also the chance of coordination is greater. Fig. 21 bears this out. Curve (a) in this figure for the 0.5 symmetry resembles that of H-montmorillonite. The main features are the band of the cation at 1670 cm^{-1} and the band of 1625 cm^{-1} for weakly coordinated amide. The only difference between this curve and that of (b) is the general increase in band intensities and the appearance of a distinct shoulder at 1585 cm^{-1} in the latter. This indicates that there are two types of coordinated amides; a weakly held species which gives its C=O stretch at 1625 cm^{-1} , and a strongly held species with its C=O stretch at 1585 cm^{-1} . At the 4.0 symmetry level; curve (c), the band at 1585 cm⁻¹ is greatly enhanced in intensity while that of 1625 cm⁻¹ is greatly deminished. If at such high level it is assumed that the amide was able to displace a considerable amount of hydration water then it is reasonable to attribute the band at 1625 cm^{-1} to an indirect association between the aluminum cations and the amide through water bridges (Farmer and Mortland, 1965), while that of 1585 cm⁻¹ to amide with a carbonyl coordinate bond to Al^{+3} .

At the 4.0 symmetry level, the cation was still present in a considerable proportion in the aluminum case while the evidence for its presence was rather weak in H-montmorillonite.

Also the band at 1637 cm⁻¹ for free amide on H-montmorillonite does not have a counterpart in Al-montmorillonite. This is not taken to mean that Al-montmorillonite is more acidic than H-montmorillonite, but rather, it is more reactive toward the amide for it provides two ways for reaction; protonation and coordination. It is true that the extent of protonation will not be as extensive as with H-montmorillonite, but when combined with coordination, its reaction capacity is greater and, therefore, the absence of free amide was to be expected.

On Pt-montmorillonite (Fig. 22), the reaction of the amide was similar to that on H-montmorillonite with the exception that the band at 1625 cm⁻¹ was absent and replaced by a band at 1615 cm⁻¹ for the coordinated amide. At the highest level of the amide, the 1615 cm⁻¹ is the main feature of the spectrum, beside a small band at 1637 cm⁻¹ for free amide. It seems then, that water bridges are not operative in this case, and the amide is either directly coordinated to the platinum ions or protonated until the metal ions are exhausted, hence the appearance of free amide.

Comparing the background absorption of Figs. 20, 21 and 22, it is clear that it was the highest in the case of H-montmorillonite. Actually, this should have been expected for two reasons: first, is the greater ability of this system to provide protons, and second, its lower ability to coordinate the amide in excess of protonation potential. Both these factors would combine to create a more favorable

condition for the hemisalt formation, a process which involves sharing of a proton between two amide molecules.

N,N-diethylacetamide formed a coordinate link with Cu, Ca, and Na ions on the surface of montmorillonite as indicated by Figs. 23, 24, and 25. The fact that acetamide and N-ethylacetamide formed the same type of complex with the same ions lead to the expectation that N,N-diethylacetamide would do the same. However, due to the inductive effect of the two ethyl groups on the tertiary amide, the nitrogen atom of the amide is more basic than that of the primary or secondary amides, and therefore, a coordinate bond through the nitrogen is a possibility. Nevertheless, the data confirm the formation of a coordination complex through the oxygen.

Curve (a) of Fig. 23 for the copper complex shows two distinct bands in the 1600 cm⁻¹ region. The first band at 1612 cm⁻¹ is at a too low frequency to be assigned for the O-H deformation of water. Also, the possibility of assigning this band to Amide I band of free amide does not seem to be reasonable since at such low level of amide; 0.25 symmetry, copper ions which have a coordination number of 4 are in proportional excess to the amide. A self association of amide molecules through hydrogen bonds is excluded since N,N-disubstituted amides are incapable of forming intermolecular hydrogen bonds. Therefore, the bands at 1612 and 1591 cm⁻¹ have to be the Amide I band of an oxygen coordinated







amide. The reason for this split in the Amide I band could be interpreted through several possibilities. Rollison and White (1962), working on the complexes of chromium (III)amides complex, found that the Amide I band of the coordinated amide showed two bands; the N,N-dimethylformamide complex at 1665 and 1630 cm^{-1} while that of N,N-dimethylacetamide had its bands at 1620 and 1585 cm⁻¹. When chromium was complexed by 2-pyrolidinone, the complex gave just one C=O band. Rollison and White attribute the appearance of two bands in the amides and only one in the ketone to a difference in configurations of the two types of complexes; the ketone being a highly symmetrical structure while that of amides is not. Farmer and Mortland (1965) found that water molecules could act as a bridge linking pyridine with Mg or Cu ions. Such an association would not be expected to affect the vibration of the C=O group of the amide as dramatically as a direct association between the amide and the metal ion, and therefore, the Amide I band shift should be smaller. Thus, the 1612 cm^{-1} represents the amide which is indirectly coordinated to the metal ion while the band at 1591 cm⁻¹ represents the amide which is directly coordinated to the metal ion. Oxidation-reduction reaction offers the third possibility. If Cu^{+2} was reduced on the surface of montmorillonite to Cu⁺¹, the coordinate bond would certainly be different in both cases and, hence, the presence of two Amide I bands. Cloos and Mortland (1965), in working with

complexes of ammonia with Co-montmorillonite, observed the significant effect of the oxidation number of the cobalt ion in determining the band positions of the complex.

Curves (b) and (c) of Fig. 23 are essentially similar to curve (a) in which the 1590 cm⁻¹ band is greatly enhanced in intensity. It should be stated, however, that even in curve (c) of the 1.0 symmetry level, water displacement could not be complete since a coordination number of 4 is not provided by this level. Therefore, water is a part of the structure even though it does not play a prominent role as in the case of the 0.25 symmetry level and may still be acting as a bridge whose characteristic band at 1612 cm⁻¹ might have been masked by the breadth of the 1591 cm⁻¹ band.

Curve (a) of Fig. 24 for the calcium system shows two bands in the 1600 cm⁻¹ region; 1635 and 1606 cm⁻¹. For reasons similar to those presented in the copper system, the band at 1635 cm⁻¹ could not be assigned to a free amide. However, in contrast with the copper system, this band seems to be at a too high frequency to be assigned to the Amide I band of N,N-diethylacetamide which is indirectly coordinated to calcium through a water bridge. In stability studies to be presented later, it was found that Ca-montmorillonite was a unique system. Adsorption of amides from the vapor phase for a short period of time gave rise to two distinct spacing patterns: those of the 17 Å for a two layers of amide and

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those of the 13 Å for a one layer of water. This is explained on the basis that once water displacement by the amide is initiated in a given interlamellar plane, the amide tends to accumulate in this plane till water displacement is complete. In other words, the amide-water clay complex is actually composed of two separate systems; the amide-clay system and the water-clay system. Hence, the band at 1635 cm⁻¹ is, in all likelihood, an O-H deformation of water.

Curves (b) and (c) of Fig. 24 shows the gradual weakening and then the disappearance of the 1635 cm^{-1} band with a concomitant enhancement of the intensity of the 1605 cm⁻¹ band. A similar observation was found in the copper complex. However, the same reasoning does not hold in both cases. Where the copper complex showed two distinct bands in the $3400-2800 \text{ cm}^{-1}$ region, the calcium complex did not show any prominant absorption in this region. Therefore, it must be concluded that the OH deformation of water was absent in the copper complex simply because it was shadowed by the broad absorption of Amide I band, while it was absent in the calcium complex merely because the complex was dehydrated. A possible explanation for this difference is the different abilities of the two systems to retain the initially applied amide. However, chemical analysis showed that films of the calcium and copper complexes of the 1.0 and 2.0 symmetry levels contained a comparable amount of nitrogen. Gieseking (1949) reported that adsorption of organic cations by clay

minerals greatly reduces their water-adsorbing capacity. Yet, in light of the data reported here, it seems that the exchangeable cation plays an important role in determining the extent of such reduction.

The data of Fig. 25 for the Na-N, N-diethylacetamide complex seem to be explained in terms of conclusion offered by Rollison and White (1962). Curve (a) for the 0.5 symmetry level shows two Amide I bands; a shoulder at 1625 cm⁻¹ and a sharp band at 1600 cm⁻¹. Along the line of argument presented previously, the band at 1625 cm^{-1} could not be attributed to either a free amide nor water. Since the 3400 cm⁻¹ region of the spectra (not shown) does not indicate the presence of much water, it seems logical to conclude that water bridges are rather inoperative at this level. Therefore, the only possible interpretation as to origin of the 1625 cm^{-1} shoulder is to assume a rather unsymmetrical complex. That is to say, there is a variation in the strength of the bond between the amide molecule and the cation, and therefore, the vibration of the C=O groups of the complex are not the same all over.

In the 1.0 symmetry level shown in curve (b), the complex was rather homogeneous, and this gave rise to a symmetrical structure with a very sharp Amide I band at 1592 cm⁻¹ while the 1625 cm⁻¹ shoulder has almost disappeared. In curve (c) of the 4.0 symmetry level, however, there are two distinct bands at 1628 and 1600 cm⁻¹, indicating once more, a rather unsymmetrical structure.

The X-ray diffraction data for Pt, H, Cu, Ca, Na, and Al-montmorillonite is shown in Fig. 26. The different response of H and Al-montmorillonite to the high level of amide indicates that H-clay was not completely converted to an Al-clay. The same observation was referred to previously based on infrared data. Also, the X-ray data conform to the conclusion drawn previously as to the status of the amide in the complex. For the calcium systems at the 4.0 symmetry level the sharp peak at 14.8 Å indicates a complete one layer of the amide, while at the 0.25 symmetry level there is an interstratified system which has its most intense peak at 12.7 Å of the one layer of water. In the copper system, a spacing of 15.5 Å is too high for one layer of the amide. It could be considered as a two layer structure of water, yet the infrared data indicate that the amide represent the greater share of the complex cation-amidewater. Therefore, it would seem reasonable to assume that the 15.5 Å spacing is one layer of the amide in which water is a part of the established complex. This portion increases with the decrease in the amide level and at 0.25 symmetry, water is the dominant adsorbate.

The data for Na- N,N-diethylacetamide complex are similar to the complexes of acetamide and N-ethylacetamide where interstratification was a common feature. At the lowest level of amide, the high-angle side of the peak is the most intense giving a spacing of 12.0 Å while at the highest level of





amide, the low angle-side of the peak is the most intense giving a spacing of 16.4 Å.

The dehydrated and rehydrated complex--The data for the dehydrated complex of N,N-ethylacetamide on the surface of Cu, Ca, Na-montmorillonite support the conclusions drawn previously regarding the status of acetamide and N-ethylacetamide in such systems. However, the status of the dehydrated complex on the surfaces of H, and Al-montmorillonite even though it does not lead to conclusions contradicting those outlined previously for acetamide and N-ethylacetamide, it brings up some more interesting facts.

Curve (a) of Fig. 27 indicates that a considerable amount of water was lost upon heating the 0.5 symmetry complex. With such loss the characteristic band near 1670 cm⁻¹ amide cation has greatly diminished in intensity. It might be argued that residual water is not as important for protonation in the case of H-montmorillonite as it is for Al-montmorillonite. Furthermore, it might be said that the thermal instability of amide cation on the surface of H-montmorillonite has nothing to do with the loss of residual water. Nevertheless, these arguments fall apart if the band at 3400 cm^{-1} is to be accounted for. The only reasonable assignment to this band is that of an O-H stretch of water. Thus, the incompleteness of dehydration should account for the minute guantity of the protonated amide





in the dehydrated complex which are responsible for the 1675 $\rm cm^{-1}$ band.

Curve (a) also shows two bands for the carbonyl group at 1618 and 1608 cm⁻¹. Whether such a split is due to the presence of water as bridges between the amide and the aluminum ions or to the assymmetry of the complex is hard to decide. Actually, the difference between the two causes is very subtle because the presence of a small quantity of water in the complex might, besides acting as a bridge, lead to the assymmetry of the complex.

Curve (b) of Fig. 27 indicates rehydration of the film as evidenced by the broad absorption in the 3500-3000 $\rm cm^{-1}$ region. This rehydration was responsible for the extensive protonation of the amide as indicated by the sharp band at 1674 $\rm cm^{-1}$. There is no apparent counterpart of the 1608 $\rm cm^{-1}$ band of the dehydrated complex in the rehydrated complex, but the band at 1618 $\rm cm^{-1}$ has a counterpart at 1621 $\rm cm^{-1}$.

The data for the 2.0 symmetry level, shown by curves (c) and (d) in Fig. 27 support what was said about the status of water in the complex. Undoubtedly, at such high level of the amide, water displacement upon heating is more likely to be complete as indicated by the absence of the band at 1675 cm^{-1} , while the band at 3400 cm^{-1} is very weak to be of any significance. Furthermore, the high level of amide was effective in reducing the extent of rehydration.

This reduction is indicated by the rather weak band at 3475 cm^{-1} and the weakness of the amide cation shoulder at 1675 cm^{-1} . Based on the position of the Amide I band in both curves (c) and (d); at 1610 and 1613 cm⁻¹ respectively, it seems justifiable to conclude that both bands along with that at 1608 cm^{-1} in the dehydrated complex of the 0.5 symmetry level, correspond to a direct coordinate bond between the aluminum ions and the amide through the C=0 group. In the meantime, bands at a little higher frequency; the 1618 and 1621 cm⁻¹ of the 0.5 symmetry level, correspond to an indirect coordinate bond between the ion and the amide in which water plays a certain role.

The cation of N,N-diethylacetamide on the surface of Al-montmorillonite is not stable when heated. Curve (a) of Fig. 28 shows clearly this fact. As was the case with the low level of amide in H-montmorillonite, dehydration is not complete in Al-montmorillonite as indicated by the band at 3385 cm⁻¹. Curve (b) for the rehydrated 0.5 symmetry complex is of particular interest. It shows the simultaneous presence of three species of N,N-diethylacetamide: protonated, which has its band at 1675 cm⁻¹, coordinated through a water bridge which has its band at 1623 cm⁻¹, and that which is directly coordinated to Al⁺³ giving a band at 1577 cm⁻¹.

It is not peculiar that the relative intensity of the coordinated species is greater than that of the protonated





in the case of Al-montmorillonite while the opposite is true for H-montmorillonite. This observation suggest three facts. First, is that the rehydrated H-montmorillonite is more acidic than the Al-montmorillonite, and this subsequently suggests that heating treatment did not convert the hydrogen system to a completely aluminum system. Second, is that once the amide is in the bonding field of the metal ion, the resultant bond is strong enough to prevent amide displacement by water. Third, is that, the status of the amide on the surface of an acidic clay is a function of the relative affinity between three agents; the metal ion, the water molecule, and the amide molecule. If the affinity between the amide and the protons of water is greater than that between the amide and the metal ion, protonation will be preferred, otherwise, coordination will take place. The relative abundance of a product over another is controlled by the relative abundance of the reactants.

Curves (c) and (d) for the dehydrated and rehydrated 2.0 symmetry level complex on Al-montmorillonite substantiate what was said about the same complex on H-montmorillonite regarding the role of water in the complex. It is rather unusual, however, to note that the Amide I band in the dehydrated complex is at 1623 cm⁻¹ while that of the rehydrated complex is at 1587 cm⁻¹. To interpret this additional shift, it should be remembered that the fresh

(hydrated) complex showed two bands; 1670 cm^{-1} for the protonated amide and 1585 cm^{-1} for the coordinated. When this fresh complex is heated, water is preferentially lost from the system. In the meantime heating might have disturbed the complex in such a way as to weaken the bond between the metal ion and the amide. Hence, the band at 1585 cm^{-1} of the fresh complex is shifted to a higher frequency, i.e., to 1623 cm^{-1} in the dehydrated complex. During the period of rehydration, the components of the complex come closer to each other again, and therefore, forming a stronger bond. Such cycle is indicated by the prominance of the 1587 cm^{-1} band, in the hydrated and rehydrated complex.

The stability of amide-montmorillonite complexes

Acetamide-montmorillonite

When montmorillonite was treated with acetamide vapor for 15 minutes, both Al and Cu-montmorillonite did not expand beyond one layer of adsorbed acetamide (Fig. 29). However, Na and Ca-montmorillonite expanded beyond that limit. The calcium system showed two distinct peaks at 17.0 and 14.5 Å while the sodium system showed a random interstratification with the 16.5 Å region diffusing into that of the 12.8 Å.



Figure 29. X-Ray diffraction patterns showing the 001 spacing in A° when different montmorillonite systems were treated with acetamide vapor for 15 minutes and then left in atmosphere for; A = 0, B = 1, C = 2, D = 3, and E = 7 days.

It seems that lattice expansion to a higher c-spacing value does not necessarily mean greater adsorption. Nitrogen analyses for amide content of the films presented in Fig. 30 bear out this point. Nevertheless, several reasons could be cited as to how this could be so. If a fraction of the adsorbed amide is held on the external surface of montmorillonite, this part is ineffective in increasing the 001 spacing, yet, it is of course effective in increasing the nitrogen content of the sample. It is known that the amide externally bound to the clay is very weakly bonded and, therefore, should be easily lost. This seems to be the case in Al-montmorillonite. Nitrogen analysis data of this system indicate that the rate of amide loss in the first 24 hours of the experiment is unusually high.

Another explanation that might resolve the discrepancy between the X-ray and the nitrogen analysis is the effect of the cation on the orientation of the adsorbed amide. Cu^{+2} forms coordination complex by bonding to 4 ligands and the resultant structure is a planar square, but Ca^{+2} forms the same type of complex by bonding to 6 ligands and the resultant configuration is usually octahedral. If the plane of the square of the Cu-acetamide complex is in the plane of the silicate sheet it would not be expected to expand the c-spacing as great as an octahedral complex. A third reason for the discrepancy might be the fact that some layers in Na-montmorillonite have



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B = adsorption time was 30 minutes and the complex was left in atmosphere, C = adsorption time was 60 minutes and the complex was left in atmosphere, and D = adsorption time was 60 minutes and the complex was left in vacuum (0.1 mm. Hg). A solid mark indicates an average of two samples while an open mark indicates one sample. The stability of acetamide-montmorillonite complexes as affected by the exchangeable ion when; A = adsorption time was 15 minutes and the complex was left in atmosphere, Figure 30.

collapsed to a 10.0 Å spacing and therefore, they are not available for amide uptake. This would explain the rather low content of amide in the sodium system.

The data of Fig. 29 also reveal the fact that the acetamide-montmorillonite complex is not stable if the adsorbed amide exceeds one layer. Gradually, the 001 spacings and nitrogen content decrease, and after a period of one week in atmosphere, they approach a constant value which is characteristic of the saturating cation.

When the treatment time was raised to 30 minutes, acetamide was adsorbed in such amount to give a two-layer expansion as indicated by Fig. 31. The two layer expansion was discrete in Na, Ca, and Cu-montmorillonite but randomly interstratified with one layer in case of Al-montmorillonite. As was found in the 15 minutes treatment, the complex is not stable against room humidity, and after one week the OO1 spacings in the 15 and 30 minute treatments are comparable.

The infrared data for the 15 and 30 minute treatments in the 3600-3000 cm⁻¹ region are shown in Fig. 32. Because adsorption in these systems is a diffusion-controlled process which in turn is time dependent, more amide is taken up in the 30 minute treatment as indicated by the increase in intensity of the band near 3200 cm⁻¹. This band is ascribed to associated amide molecules through intermolecular hydrogen bonding. In Ca-montmorillonite, not



Figure 31. X-Ray diffraction patterns showing the OOl spacing in A° when different montmorillonite systems were treated with acetamide vapor for 30 minutes and then left in atmosphere for; A = 0, B = 1, C = 2, D = 3, and E = 7 days.




only the band near 3200 cm^{-1} increases in intensity, but also, there is a slight shift of the whole spectrum in this region to the right indicating a stronger degree of association.

After one week of standing at room temperature some amide is lost from the complex. In Na-system this is shown by a general decrease in band intensities which is especially clear upon comparing curves (a) and (c) with (b) and (d). Such indicates the breaking down of the hydrogen bonds which leads to a weaker degree of association. In the Cu-system, it seems that the amide loss is accompanied by rehydration because the band at 3500 cm^{-1} in the fresh complex disappears after one week and is replaced by a small band at 3440 cm^{-1} which could be interpreted in terms of acetamide hydrogen bonded to water. Rehydration took place in calcium and aluminum complexes too. However, no marked shifts in band position have been observed, rather, the general increase in band breadth is the evidence for rehydration in this particular case.

In the one-hour treatment, acetamide is adsorbed in such amount as to give two layers in Al, Ca, and Cusystems and 3 layers in the Na-system (Fig. 33). This third layer was very weakly held that after 24 hours, the 001 spacing obtained indicates just two layers. Upon standing in the atmosphere, a considerable amount of the



Figure 33. X-Ray diffraction patterns showing the 001 spacing in A° when different montmorillonite systems were treated with acetamide vapor for 60 minutes and then left in atmosphere for; A = 0, B = 1, C = 2, D = 3, and E = 7 days.

amide was lost. Probably, most of the early loss is the amide bound to the external surface of the clay. Then as the internally-bound amide is being lost, presumably due to displacement by water, the 001 spacing decreases. And after one week, the spacings are very close to those of the 15 and 30 minute treatments.

In contrast, after one week in vacuum, the 001 spacings indicate a two layer complex in Na, Ca, Cu-system and one layer in the Al-system (Fig. 34). This is supported by the fact that, the amide content in the vacuum treatment experiment is much higher than that of the atmospheric treatment, both after a period of one week (Fig. 30). A point of interest is brought up when the slope of the curves, which expresses the rate of loss of amide per 100 gm. clay per day of the atmosphere experiment is compared with that of the vacuum experiment. Ca and Na-clay have about the same slope in both cases. Actually, infrared data showed that acetamide in these systems to be almost identical to that of solid acetamide. That is to say, acetamide may not, in a strict sense, be chemically bound to the clay. If this is true, it seems that the amide is easily removed in both vacuum and atmosphere. On the other hand, the rate of loss from the aluminum complex in the atmosphere was twice that of vacuum, because competition by water was eliminated and, therefore, the complex was more stable. For the copper complex, the rate of loss was greater



Figure 34. X-Ray diffraction patterns showing the OOl spacing in A° when different montmorillonite systems were treated with acetamide vapor for 60 minutes and then left in continuous vacuum (0.1 mm. Hg) for, A = 1, B = 2, C = 4, and D = 5 days.

in vacuum. The data for nitrogen analysis offer an explanation for this observation. After a week in vacuum the amount of amide found gives copper a coordination number of 6 which indicates that two acetamide molecules were physically adsorbed, and expectedly, easily removed. This may be contrasted with the amount of acetamide after one week in atmosphere, which almost gives copper its normal coordination number of 4, its most stable configuration.

N-Ethylacetamide-montmorillonite

When montmorillonite was treated with N-ethylacetamide for 15 minutes the 001 spacing of Ca-montmorillonite indicated a two-layer adsorption while those of Na, Al, and Cu-montmorillonite indicated an incomplete one layer (Fig. If hydration water was held tightly by Cu and Al-35). montmorillonite which could only be displaced completely with difficulty by the amide is a possible explanation, another one is needed for Na-montmorillonite. A reasonable explanation might be invoked if the mode of hydration and dehydration of both Na and Ca-montmorillonite are considered. At 40 percent relative humidity, where this work was done, only one layer of water was held by Na-montmorillonite, and therefore, upon heating in vacuum during the process of amide introduction, water diffusion out of the interlayer space might have been faster than the amide



diffusion into the interlayer space. Certainly, this would decrease the chance of N-ethylacetamide, which is a fairly large molecule, of penetrating the collapsed layers. That there was a collapse in some layers is indicated by the small peaks around the 10.0 Å spacing. In contrast, Ca-montmorillonite contained two layers of water. While it is being treated by amide vapor, the component of one layer is lost, and during this process, the amide is diffusing in and replacing the second layer. That this is true is shown by the X-ray pattern of the fresh complex. There are two discrete peaks; the 16.9 Å is that of two layers of amide while the 13.4 Å is that of one layer of water.

However, the corresponding nitrogen analysis data in Fig. 36 does not seem to confirm this explanation since Na-montmorillonite contained more adsorbed amide than Camontmorillonite. Nevertheless, the two pieces of data would simultaneously confirm each other if it is assumed that the adsorption of amide by Na-montmorillonite was distributed over several "islands" with vacant areas in between. On the other hand, amide adsorption by Ca-montmorillonite was marked by the accumulation of a relatively large amount of the amide in a limited number of interlayer spaces. The overall adsorption, however, was greater when the amide was held by greater number of layers; Na-montmorillonite.



B = adsorption time was 30 minutes and the complex was left in atmosphere, C = adsorption The stability of N-ethylacetamide-montmorillonite complex as affected by the exchangeable time was 30 minutes and the complex was left in vacuum (0.1 mm, Hg), and D = adsorption time was 60 minutes and the complex was left in atmosphere. A solid mark indicates an ion when; A = adsorption time was 15 minutes and the complex was left in atmosphere, average of two samples while an open mark indicates one sample. Figure 36.

It is interesting to note that two layers of Nethylacetamide and one layer of water, both in the neighborhood of each other do not form a stable system. A concentration gradient would force some of the amide of the two layers to diffuse into the lower concentration zone and interstratification develops in a random manner. After one week, while the amide is gradually being lost, a fairly sharp peak at 14.8 Å for homogeneous mixture of water and amide is well-developed.

Aluminum cation, with a high charge on a small size, seems to favor the least expansion. So there would be a barrier to amide diffusion into the interlayer space, and a relatively larger amount of the amide is externally adsorbed. The resistance to expansion is revealed by X-ray data which shows the consistency of the c-spacing over a period of one week. The copper complex, even though it did not show a major change in c-spacing, the low angle side of the peak is gradually declining. Such decrease would count for the very small loss of amide as indicated by the nitrogen content data.

In the 30 minute treatment two layer expansion took place in Na, Al, and Cu-montmorillonite with a spacing around 16.5 Å (Fig. 37). In Ca-montmorillonite the spacing was 19.2 Å which could be an incomplete three layers. A planar type of configuration for the internally adsorbed amide in Na, Al, and Cu-montmorillonite and a three





dimensional configuration, i.e., octahedral, for Ca-montmorillonite is another alternative.

According to X-ray data, the sodium complex was the least stable while that of copper was the most. But according to amide content data when expressed in terms of the rate of loss per day, all the systems have about the same stability excluding the first 24 hours. It was mentioned previously that Al⁺³ favors the least expansion and therefore a considerable amount of the adsorbed amide is held on the external surface. The resistance to expansion is revealed by the low intensity of the two layer adsorption peak, and the consistency of the 13.2 $\stackrel{\text{O}}{\text{A}}$. The external adsorption is shown by the nitrogen content data which show that within the first 24 hours of the experiment a considerable amount of the amide was lost. (It should be remembered that the externally adsorbed amide is held by weak forces and therefore it is easily lost.) It is obvious though, that the 001 spacing is closely related to the internally adsorbed amide and, therefore, it is not a coincidence that Ca and Cu-complexes have higher spacings and nitrogen contents.

The infrared data for 15 and 30 minute treatments are shown in Fig. 38. The general increase in band intensities, especially those of bonded NH stretching, indicates that as the amount of adsorbed amide increases by increasing the treatment time, bonded amide predominate.



Figure 38. Infrared spectra of N-ethylacetamide adsorbed from the week, (c) fthe 30 minutes complex immediately after preparation, vapor phase by; (A) = Na, (B) = Cu, (C) = Ca, and (D) = Al-montmorillonite. (a) = the 15 minutes complex immediately after preparation, (b) = the complex of (a) left in atmosphere for one and (d) = the complex of (c) left in atmosphere for one week. Upon standing in atmosphere for one week, band intensities decrease suggesting a decrease in the amount of the adsorbed amide in agreement with X-ray and nitrogen analysis data. It is of interest to note that this loss was most pronounced in the hydrogen bonded amide while those of the free NH stretching, which correspond to amide held by coordination, were nearly the same as those of the fresh complex.

In the fresh Ca-complex the free NH stretch in the 30 minutes treatment was located at frequency lower than usual, 3420 vs. 3450 cm^{-1} . Whether or not this indicates the presence of the cis-form is a question. Due to energy consideration, however, the trans-form is more stable than the cis, and for this reason when the excess amide is lost, the trans-form dominates, as indicated by the presence of the 3450 cm⁻¹ band of curve (d).

As was the case with acetamide, the complexes of N-ethylacetamide are more stable in vacuum than in atmosphere (Fig. 39). The small decrease in the intensity of the 16.1 Å in the copper complex is accounted for by the very small rate of amide loss as shown in Fig. 36. The rather high loss rates in the case of Na and Ca-montmorillonite points out the rather weak bond by which the amide is held on the clay. Actually, this loss is not shown by a shift in peak's positions but by a decrease in intensity of the low-angle side of the peak. Of course, whatever amount of amide was held on the external surface would be





easily removed. The rate of amide loss for Ca and Namontmorillonite complex in vacuum and atmosphere are comparable, but they are much smaller for Cu and Al-montmorillonite in vacuum than in atmosphere. The reasons cited to explain this trend for acetamide should hold here for N-ethylacetamide.

It is of interest, however, to note that the rates for N-ethylacetamide are lower than those of acetamide. Actually, this should have been expected because of two reasons: first, is that N-ethylacetamide is more basic than acetamide and, therefore, it can compete more favorably with water as far as adsorption is concerned. Second, is the fact that N-ethylacetamide is a larger molecule than acetamide which increases the energy required for desorption.

The infrared data of the vacuum treatment are contrasted with those of the atmosphere in Fig. 40. It is obvious that the persistence of bonded NH stretching bands and the small changes in their intensities over a period of one week in vacuum indicate a high degree of stability. The reason for such added stability will be discussed later.

In the 60 minute treatment, more than two layers of the amide were taken up by both Na, and Ca-montmorillonite (Fig. 41). This third layer was very weakly held as it is lost in the first 24 hours of standing in the atmosphere.









Of particular interest in Fig. 41 is the Na-complex. It could be seen that while some layers of the clay have taken up more than two layers of the amide, some others did not take any, still some collapsed to a 10.0 Å spacing. If this were coupled with the nitrogen analysis data shown in Fig. 36 which indicate that Na-montmorillonite adsorbed the least amide, it should be concluded that the adsorption was a diffusion controlled process which is affected by the presence of "adsorption front." Mortland (1958), in studying potassium release from biotite, found that the weathering of biotite to vermiculite proceeds from the outside edge in toward the center of the particle. This is another case of frontal phenomena in a diffusion controlled process, which lays some background to the postulated adsorption front.

The complexes undergo some decomposition, but even after one week, the OO1 spacings as well as the nitrogen content are higher than those of the 15 and 30 minute treatments. It should be pointed out too, that even though the nitrogen content of this treatment was comparable with the 30 minute treatments of acetamide, the rate of losses were lower in the N-ethylacetamide case. The reason for such difference was outlined previously.

N, N-Diethylacetamide-montmorillonite

The OO1 spacings presented in Fig. 42 indicate that the calcium and sodium systems showed the most expansion

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in the 15 minute treatments as compared with copper and aluminum systems. Yet it is rather interesting to note that the stability of the calcium and sodium systems are the least of all, since within the first 24 hours of the experiment the spacings of these systems slid abruptly to a lower value. This is to be contrasted with copper and aluminum systems where the decrease is gradual in character. The rapid initial loss of the amide is reflected too by the nitrogen analysis data of Fig. 43, where the steep slope of the calcium curve in the first two days is taken to be the evidence. While such initial rapid decrease is not evident in the sodium curve, it should be remembered that the total amount adsorbed by this system was comparatively small. The same observation was encountered in the data for acetamide and N-ethyl acetamide, and it is presumed that the reasons discussed previously are the same in all cases.

The OO1 spacings for the Cu, and Al-complexes were fairly constant over a period of one week. The nitrogen analysis data confirm the stability of the Al-complex over this period, but it does not confirm the stability of the copper-complex as it shows a considerable loss of the amide from the complex in the first 2 days. Such contradiction in the data could be attributed to either an experimental error in the part of nitrogen analysis, or that the amide for one reason or the other, was slow in diffusing into



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left in atmosphere, B = adsorption time was 30 minutes and the complex was left in atmosphere, C = adsorption time was 30 minutes and the complex was left in vacuum The stability of N,N-diethvlacetamide-montmorillonite complex as affected by the (0.1 mm. Hg), and D = adsorption time was 60 minutes and the complex was left in atmosphere. A solid mark indicates an average of two samples while an open mark exchangeable ion when; A = adsorption time was 15 minutes and the complex was indicates one sample. Figure 43.

the interlayer space of Cu-montmorillonite. Therefore, a comparatively large proportion of the amide was externally adsorbed and consequently, easily lost.

When the treatment time was increased from 15 to 30 minutes, neither the 001 spacing (Fig. 44) nor the nitrogen content of the samples (Fig. 43) showed a significant increase. This was not the case with acetamide or N-ethylacetamide where it was observed that adsorption increased as the time of treatment increased. Actually, a direct comparison with the acetamide system is not strictly valid, since the amount of the amide used as adsorption well and its physical state are not the same in both cases. But the comparison could be carried out, at least in a qualitative sense, between N-ethylacetamide and N,N-diethylacetamide since the quantities used and the apparent physical properties of the two amides are about the same. Under the same circumstances, montmorillonite would adsorb greater quantities of N-ethylacetamide than N, N-diethylacetamide for two reasons: first, according to Barshad (1952), in forming complexes of clay-organics, the force of attraction between dipoles, which is a good measure for the quantity adsorbed in forming a complex, is proportional to the dipole moment of the organic. The dipoles movements of N-ethylacetamide and N,N-diethylacetamide are given by Cannon (1955) to be 3.87 and 3.72 debyes units, respectively. Second, is the difference in size between the two molcules;





the nitrogen atom is bonded to a hydrogen atom and an ethyl group in one case, and two ethyl groups in the other.

In the 30 minutes-vacuum experiment, the 001 spacing shown by Fig. 45 as well as the nitrogen content data shown by Fig. 43 indicate that the calcium system contained more amide than the corresponding experiment in the atmosphere. This points out the qualitative nature of the experiment regarding adsorption of the amide from the vapor phase. Two factors would count for a considerable part of the variability: the degree of evacuation and the adsorption temperature.

The X-ray and nitrogen analysis data point out the fact that the stability of the Al-complex in atmosphere is comparable to that in vacuum. They also indicate that the stability of the copper and calcium systems were greater in vacuum than in atmosphere. If the competition between amide and water for adsorption sites is the main factor which contributes to the instability of the amide complexes in atmosphere, then it is certainly obvious that the Alcomplex was protected against water adsorption. It was mentioned previously that clay-organic complexes have a reduced ability for water adsorption. In light of these results, it seems that the bond between the organic and the clay is of primary importance as far as the water relation of the complex is concerned.





The data for the sodium complex are rather straight forward, since the nitrogen analyses reveals that the complex was stable in vacuum. The OO1 spacings support this observation. However, the complex was not stable in atmosphere, which is indicated by the X-ray as well as nitrogen analysis.

In the 60 minutes treatment, the 001 spacings (Fig. 46) are essentially equal to those of the 30 minutes treatment. However, the amide content of the films increased by increasing the treatment time. So it is seen that the difference between the two treatments is a question of crowding the adsorbed amide. In consequence, the range of the stability of the complex as indicated by X-ray was much longer for the 60 minute treatment.

The stability of the complex as reflected by the nitrogen analysis data tends to indicate that a complex of more than one layer of N.N-diethylacetamide is not very stable regardless of the nature of the bond between the amide and the clay. It could be conceived that, were the period of the experiment extended for more than one week, there will come a point where the films contain just one layer of the amide, and, therefore, the slopes of the curves would tend to level off, indicating a stable complex.

The infrared data concerned with the stability of N,N-diethylacetamide-montmorillonite complex do not add much to what has been previously concluded. However, the



X-Rav diffraction patterns showing the 001 spacing in A° when different montmorillonite systems were treated with N,N-diethylacetamide vapor for 60 minutes and then left in atmosphere for; A = 0, B = 1, C = 2, D = 5 and E = 7 days. Figure 46.

data for the complex on sodium montmorillonite is shown in Fig. 47 as a representative sample. In the fresh 15 minutes complex, there are two bands in the 1600 cm^{-1} region; 1630 and 1598 cm⁻¹. The band at 1630 cm⁻¹ could not be attributed to the O-H deformation of hydration water for several reasons. First, is that it has a counterpart in the 30 minutes treatment at 1628 cm^{-1} which contained more amide and in consequence, should contain less water. Second, is that the region of the spectra around 3400 cm^{-1} (which is not shown) does not indicate the presence of such an appreciable quantity of water as would be indicated by the rather strong band at 1630 cm⁻¹. Third, is that the band disappears when the film is left in atmosphere for one week, whereas it should have been intensified due to the possible hydration. In all likelihood then, it is reasonable to assign the two bands at 1630 and 1598 cm⁻¹ to Amide I band of coordinated amide, which arises from the assymmetry of the complex (Rollison and White, 1962). After one week in atmosphere, the excess amide is lost and this leads to a more symmetrical orientation of the complex as indicated by submergence of the two bands into one at 1595 cm^{-1} . The data for the 30 minutes-atmosphere treatments are similar to that of the 15 minute treatment with some minor differences. The band at 1628 cm⁻¹ does not disappear completely but develops into a shoulder at 1628 cm⁻¹ while the main band of the complex seems to have two components at $1607 \text{ and } 1592 \text{ cm}^{-1}$.



In line with the X-ray and nitrogen analysis data, very small amounts of the amide were lost from the complex during the vacuum treatment. The persistence of the 1626 cm^{-1} band in the infrared spectra of this treatment over a period of one week is consistent with these observations. The band at 1606 cm^{-1} was slightly shifted to a lower frequency (1596 cm^{-1}). It is doubtful, however, if such a slight shift could reflect major changes in the complex.

GENERAL DISCUSSION AND CONCLUSIONS

Amide protonation

Theoretical considerations

Α

Amides have two basic sites since either the oxygen or the nitrogen atom could be a proton acceptor. The question as to where the proton goes when the cation is formed has been a subject of controversy.

According to Pauling (1960) amides are a resonance structure. For a primary amide, these structures are:

$$R - \ddot{C} - NH_2 \iff R - \ddot{C} = \dot{N}H_2$$

В

Pauling states that the resonance with structure (B) is nearly completely inhibited by addition of a proton to the nitrogen atom. The corresponding calculated value for the base constant, 1 x 10^{-20} , is so small as to be without significance, except to show that the amides do not form salts with acids by adding a proton to the amino group. Fieser and Fieser (1961) believe that oxygen protonation is more favorable. Their argument goes as follows:



Protonation of nitrogen (C) would eliminate resonance stabilization whereas protonation of oxygen (D,E) would not, hence, the oxygen-protonated system should be the more stable.

Were the resonance theory for amides to be untrue, amide protonation should proceed through the nitrogen atom. Spinner (1959) reported that the ionization potential of uncharged oxygen exceeds that of uncharged nitrogen (in compounds like dimethyl ether and dimethylamine) by about 25 kcal/mole, and the OH bond is stronger than the NH bond (in water and ammonia, respectively) by about 16 kcal/mole, leaving a balance of about 10 kcal/mole in favor of proton addition to a nitrogen atom.

Recently two powerful analytical tools; IR and nuclear magnetic resonance (n.m.r.) have been used in the chemical reaction studies of amides. Table 3 presents the infrared bands and their assignments of acetamide and the acetamide cation. It is of interest to note that the Amide I band of the solid which is mainly C=O stretching, is at a rather lower frequency if compared with esters or ketones. Ferbes et al. (1963) attribute this to the fact that delocalization of the lone-pair electrons from the nitrogen atom into the M-electron system outweighs the inductive effect of N, and also to intermolecular hydrogen bonding.

Spinner (1959) supported by his postulate for amide structure, anticipated N-protonation, and on this basis, he interprets the infrared spectrum of acetamide chloride: there is no absorption band above 3400 cm⁻¹, and therefore there is no indication for a hydroxyl group (of the supposedly O-protonated acetamide). The cation CH_3CONH_3 , could afford

Ban Solid amide ^a	ld position Amide c Cl ⁻	ation of H-mont.D	Band assignment
3330 3160	3310 3125	3412 3238	NH stretching
	1718	1713	C=N assymmetric stretching
1681			C=O stretching
1610	1664	1668	NH deformation
	1497	1508	$-c^{+} c^{H} \leftarrow c^{H} c^{H}$
1458			CH asymmetric deformation
1399	1428	1425	C=N symmetric stretching

The main features in the spectra of acetamide and its cation. Table 3.

^aThe data for acetamide and its chloride are taken from Kutzelnigg and Mecke (1960) with the exception of the two bands at 1718 and 1497 cm⁻¹ which are assigned as given by Kumler (1961).

^bThe data for the rehydrated 0.5 symmetry level.

no resonance, and this is consistent with the assignment of the band near 1700 cm^{-1} to a C=O stretching mode.

Along with this line, Cannon (1955) interprets the spectrum of N-ethylacetamide chloride. He found that the free amide NH band at 3461 cm⁻¹ almost disappears when equimolar quantities of amide and HCl are present. Moreover, he assigns the band at 1718 cm⁻¹ to the C=O stretch of the cation based on the premise that N-protonation impedes resonance. The proximity of this band to the covalent carbonyl frequency of ketones near 1720 cm⁻¹ is a supporting evidence. It should be emphasized here, however, that while Spinner uses the 1700 cm⁻¹ band to discredit the resonance theory of amides, Cannon uses the same band to support the theory.

Protonation studies of amides using n.m.r. technique give still another picture contradicting both Cannon and Spinner. Berger et al. (1959) Fraenkel and Franconi (1960), and Loewenstein (1961), working with a variety of primary, secondary, and tertiary amides are of the opinion that n.m.r. spectra of protonated amides indicate a predominant O-protonation. For example, in working with N-methylacetamide, Berger et al. (1959) found that the doublet of N-methyl of the amide collapses to a singlet at low pH values. The reason for this is that there is a fast exchange of the proton between the neutral molecules, the protonated species, and the acid. At extremely low pH values, however, and in
the presence of dioxane, the amide is almost completely ionized and the exchange is slowed down. Therefore, the $CH_3CONH_2CH_3$ ion should show a triplet for the N-methyl resonance. Indeed, a doublet for the N-methyl resonance is observed. This shows that the alternative ionic species $CH_3C(OH) = NHCH_3$ is the dominant one. Fraenkel and Franconi (1960) support this conclusion and moreover, in working with acetamide solution in 100 percent sulfuric acid, they show that the ratio of the peak areas CH_3/NH_2 is closely 3/2.

Spinner (1959) complicates the problem by interpreting the n.m.r. spectra as to indicate N-protonation. He argues that n.m.r. spectra do not show the signal of the proton that has been added to the basic site; thus there is no direct evidence of hydroxylic or nitrogen-bound proton. Since O-protonation was postulated solely to explain the splitting of the signal of the N-methyl hydrogen atoms in protonated N-methyl-amides; the argument being that in an O-protonated amide, the rotation about the C-N bond is restricted by virtue of its partial or complete double bond character, while in the N-protonated amides there is a free rotation about the C-N bond. Spinner believes that this is not necessarily true because, even for acetaldehyde, acetylfluoride, and cyanide there are barriers restricting rotation, because the C-H bond tends to eclipse the C=O bond due to attraction by intramolecular van der Waals-London and induction forces. Now, the restricted rotation will lead

to the existence of rotational isomerism. Thus, the possibilities of rotational isomerism explains all the splitting of n.m.r. spectra in protonated amides.

It is doubtful, however, that the intramolecular attraction in a protonated amide molecule could be great enough to restrict the C-N bond rotation to a considerable extent according to Janssen (1961). Thus, it seems that Spinner's interpretation of the n.m.r. spectra is erratic. Moreover, in his infrared work, he assigns the band near 1500 cm⁻¹ to the assymmetric C-H bending. Such an assignment does not seem to be reasonable. Table 3 shows that the C-H assymmetric deformation band in solid acetamide is at 1458 cm⁻¹. Supposing that the acetamide cation is N-protonated, it is difficult to conceive any reason that would shift the C-H bending of the cation to such a high frequency. Kutzelnigg and Mecke (1962) assign this band to a vibration involving the protonated C=O group. That is a reasonable statement since O-protonation of acetamide would decrease the double bond character of the C=O group. On the other hand, they assign the band near 1700 $\rm cm^{-1}$ in the acetamide cation to a C=O stretch. This is not compatible with O-protonation which they conclude to be the case. In all likelihood, then, the assignment of this band to a C=N stretch seems to be the most reasonable. The work of Janssen (1961), Kumler (1961), and Cook (1964) with protonated secondary and tertiary amides support this conclusion.

Protonation on the surface of montmorillonite:

The results of the work reported here suggest that acetamide was protonated on the surface of H and Al-montmorillonite. The outstanding significance of such results is fully appreciated when it is recalled that almost all protonation studies reported in the literature were carried out in non-aqueous media.

The extent of acetamide protonation on the surface of montmorillonite was, however, differentially and significantly affected by the exchangeable ion in the environment. The spectra of acetamide cation formed on the surface of H, Al, or Pt-montmorillonite could be identified with that reported by Spinner (1958), and Kutzelnigg and Mecke (1962). Such is evident from the data presented in Table 3. It should be said, however, that the proton availability is associated with the exchangeable hydronium ions in the hydrogen system while it is a function of an extremely highly dissociated water in the Al or Pt-systems. Based on the work of Berger et al. (1959), it is concluded that the pH of these systems is definitely lower than 0.8. The polarizability of water by Cu^{+2} , is not nearly as extensive as with the case of Al^{+3} or Pt⁺⁴, nevertheless, water was dissociated to a limited extent, and therefore, it was capable of a rather limited amide protonation. Such, is indicated by the weak bands near 1550 and 1500 cm^{-1} at the low level of acetamide. The band at 1550 cm⁻¹ was assigned to Amide II band and the 1500 cm⁻¹ is assigned to the carbonyl of protonated amide.

N-Ethylacetamide and N,N-diethylacetamide are more basic than acetamide due to the inductive effect of the one and two ethyl groups, respectively. The lone-pair electrons on the nitrogen are more available for sharing than those of acetamide. Nevertheless, those on the oxygen of the carbonyl group are more so. Drago et al. (1963) reported that the basicity of amides can be estimated from their interaction with phenol. The difference in the frequency of the O-H stretching vibration of phenol in an adduct compared to free phenol is linearly related to the enthalpy of adduct formation when phenol complexes with a large number of oxygen and nitrogen donors. They found that the series of increasing donor strength toward phenol derived from their data to be: acetamide < N-methylacetamide < N,N-dimethylacetamide, which is the same series predicted on the inductive effect. That is to say that successive replacement of hydrogens by alkyl groups on the amide skeleton increases the basicity of the carbonyl oxygen atom.

It is indeed clear that secondary and tertiary amides were protonated on the surface of acidic montmorillonite (H, Al, or Pt) more extensively than was acetamide. Due to the theoretical consideration outlined previously, it is believed that this protonation occurs predominately on the oxygen atom even though a counterpart to the 1500 cm⁻¹ band of protonated acetamide could not be detected. Cook (1964), working with protonated N,N-dimethylacetamide

attributes the band in the 1360-1300 cm⁻¹ region to the O-H deformation of the protonated amide. Kumler (1961) working with protonated N,N-dimethylacetamide reported that there are humps on the long wavelength side of the 1667 cm⁻¹ band, and he assigned these humps to the vibration of the $\dot{c} = OH \iff C-OH$ group. However, it seems that this is a rather high frequency for such vibration. The spectra of N,N-diethylacetamide on H-montmorillonite showed a band at 1290 cm⁻¹ which disappeared upon dehydration but reappeared upon rehydration. In all likelihood, this band is the O-H deformation of oxygen protonated N,N-diethylacetamide.

O-Protonation of amide has been criticized for the absence of O-H stretching bands. Actually, as Janssen (1961) points out, in the discussion of the absence of the O-H stretching, it was assumed that these bands had to be found near their normal frequencies; 3500 cm^{-1} . However, large displacements may be expected because of extensive hydrogen bonding and the polar character of the bonds in protonated carbonyl group. He found strong broad bands to appear at about 2500 cm⁻¹ in the spectra of protonated amides which he assigned to OH stretching. In Fig. 48, it is rather interesting to note that such bands were evident for protonated N,N-diethylacetamide on the surface of H or Al-montmorillonite. In contrast there are no bands in this region for the complex of Ca or Na-montmorillonite. Due to the weakness of this band, upon dehydration it disappears from the Al-system





but merely decreases in intensity in the H-system.

O-protonation of amides and the assignment of the 1700 cm⁻¹ band to the carbonyl stretching of the cation are incompatible. It seems then, that the data reported for acetamide by Kutzelnigg and Mecke (1962) will need reinterpretation. As a matter of fact, the O-protonated amides have one common feature: the resulting structure of all compounds will have a C-N bond with at least partial double bond character. The band belonging to the stretching vibration of the C=N bond occurs at only slightly lower frequency than the C=O vibration and, as reported by Janssen (1961), both may have comparable intensities. Therefore, the assignment of the band near 1700 cm⁻¹ in the amide cations to the C=N stretching mode is certainly reasonable.

The importance of water for amide protonation:

The amide cation on the surface montmorillonite was invariably unstable when the complex was subjected to heat in an evacuated system. There is no evidence that the amide has decomposed under these conditions since the spectra of the complex was reversible with temperature; the cation feature came back upon rehydration. Fraenkel and Franconi (1960) obtained a similar result with N,N-dimethylformamide, using n.m.r. techniques. As the temperature of N,N-dimethylformamide in 100 percent sulfuric acid increased the two-methyl doublets collapse into a singlet

line at 130° C., and the doublet reappears when the solution is cooled to room temperature. In both cases, the results point out the thermal instability of amide cations. Nevertheless, the case of amide protonated on the surface of montmorillonite is more involved since the source of protons here is different than that of a 100 percent sulfuric acid.

It is a misconception to regard a hydrogen saturated clay in an aqueous environment as a bare-proton saturated clay. The fact is that it is impossible for a porton to exist as such in an aqueous solution. Invariably it will exist as a hydronium ion, and therefore, the clay is a hydronium saturated clay. The reaction of such a system with an amide, acetamide for example, is expected to be as follows:

$$[H_3O]^+$$
 [montmorillonite] + $CH_3-C_{NH_2}^{0}$ ->

$$\begin{bmatrix} OH - - OH_2 \\ CH_3 - C \end{bmatrix}^+$$
 [montmorillonite] (1)

A somewhat similar equation could be written to Al or Pt-montmorillonite:

$$[Al(H_{2}O)_{n}]^{+3} [3 \text{ montmorillonite}]^{-3} + CH_{3} - C \xrightarrow{O}_{NH_{2}} \rightarrow [Al(OH)(H_{2}O)_{n-2}]^{+2} \left[CH_{3} - C \xrightarrow{OH---OH_{2}}_{NH_{2}} \right]^{+1} [3 \text{ montmorillonite}]^{-3}$$

$$(2)$$

When the product of equation (1) is heated, the infrared data indicate that water is lost while the amide is retained. This could be accomplished if it is postulated that when the complex is heated the water is lost, disrupting the structure of the complex, and the proton penetrates the hexagonal cavities of the silicate sheet, and hence, it is positionally unavailable for the amide. When the system is rehydrated, hydronium ion is again formed which is capable, due to size consideration, of establishing contacts with the amide molecule, and consequently, the amide cation is reformed.

On the other hand, when the product of equation (2) is heated, water is lost and then the proton of the amide cation combines with the hydroxyl group of the dissociated water forming another molecule of water which is subsequently lost. Upon rehydration, the inorganic cation takes up water, which, for being high polarized, would act as a source of protons. Thus the amide cation features reappear. The reversibility of the cation formation and decomposition could be expressed by the general equaton:

$$\left[\begin{array}{c} R-C & OH---OH_2 \\ N & R' \\ R'' \end{array}\right]^{+} \left[\begin{array}{c} Clay \\ Clay \end{array}\right]^{-} & \underbrace{\begin{array}{c} heat and vacuum \\ H_2O \end{array}}_{H_2O} & R-C & N \\ R' \\ + H - Clay + H_2O \end{array}\right]^{+}$$

The hemisalt formation:

On a stoichiometric basis, since amides are monoprotonated, a 1:1 ratio of amides and protons produces the amide cation. However, when the ratio is 2:1, another kind of protonation takes place in which two amide molecules share a proton through a symmetrical hydrogen bond, forming the so-called hemisalt. Acetamidehemihydrochloride is reported by White (1955), Albert and Badger (1958), Pauling (1960), Fraenkel and Franconi (1960) and Kutzelnigg and Mecke (1962). The existence of the hemisalt was postulated either to explain the intense background absorption in the infrared spectra of a 2:1 mixture of the amide and hydrochloric acids, or to account for bond lengths in the solid compound as revealed X-ray and neutron diffraction analyses. In the work reported here, it is definite that the hemisalt of amides were formed on the surface of the acidified montmorillonite when excess amide was present, and the intense background absorption observed is similar to that reported in the literature.

Farmer and Mortland (1965) found that a hemisalt for ethylamine was formed on the surface of montmorillonite. In such compound a symmetrical hydrogen bond extends between two nitrogen atoms of two ethylamine molecules. This might suggest that, in amide hemisalts the bond could extend between two nitrogen atoms too. But this is not the case for two reasons. First, the nitrogen atom is not

protonated and therefore the prescribed bond cannot exist. Second, the carbonyl group in amides greatly diminishes the basicity of the nitrogen atom in the molecule so that its ability to form such strong hydrogen bond is certainly impaired (Cannon, 1955; Mizushima et al., 1955; and Bellamy and Pace, 1963).

White (1955), suggested the following structure for the amide hemisalt:



This proposed structure suggests N-protonated of amides and also requires the presence of two bonds between the two molecules. That N-protonation of amides does not take place has been outlined previously. Also, the fact that N,N-diethylacetamide should not be capable of forming the hemisalt, and since it does, this structure is discredited. So it seems that the following structure for amide hemisalt (acetamide taken as an example) is the only valid choice, which incidentally is in agreement with that proposed by Pauling (1960) and Kutzelnigg and Mecke (1962). It should be noticed that the order of the C-O and C-N bonds is approximately 1.5 to account for resonance.



The data of this work suggest a differential effect for the acidifying agent on the surface of montmorillonite in promoting the formation of amide hemisalt; the hydrogen system is more efficient than those of Al or Pt-system. Coordination of some amide molecules through the carbonyl group to Al^{+3} or Pt^{+4} undoubtedly causes the differential effect to appear.

Amides as coordinating agents

Theoretical considerations

Since amides have two basic centers, the mechanism of donor action is of special interest. It has been mentioned previously that the structure of amides is described in terms of delocalization of the \mathcal{T} electrons of the O-C-N system which is pictorially expressed in terms of resonance. It was also mentioned that the resonance structures, for a tertiary amide for example are:



The question as to the location of the coordination site of an amide is not as controversial as it was in the case with protonation. Actually, with the exception of Martinette et al. (1959) whose evidence is rather guestionable, it seems that there is an agreement on a carbonyl coordinate bond. The basis of this is two-fold. First, as Archambault and Rivest (1958) put it, the formation of a coordinated link through the free electron pair of nitrogen would result in the loss of the resonance energy of the parent base which amounts to 21 kcal/mole while the formation of an oxygen-metal bond is expected to increase the contribution of the dipole structure. The second is advanced by Bull et al. (1963), where they observed through construction of typical compounds using molecular models, that appreciable steric interaction occurs if coordination takes place through the nitrogen whereas much less interaction is indicated by models if coordination is through the oxygen.

Since amides contain two donor groups, the question might arise concerning the possibility of a chelate structure. But Archambault and Rivest (1958) exclude such possibility on the reasonable basis that, such structure would represent a four atom ring which is very seldom obtained.

The experimental evidence for O-coordination is established by infrared spectroscopy. The spectra of the

complexes show a considerable shift of the carbonyl group absorption to a lower frequency. This has been observed by most workers. Cotton (1960), in an extensive review of the effect of coordination on the stretching modes of the ligands, concludes that coordination shifts the stretching bands to a lower wave length because it causes the drainage of electrons from the donor atom towards the metal ion, and consequently decreases the force constant of the bond which binds it to the parent molecule.

A vigorous treatment of this problem would have to use the principles of quantum mechanics which are rather involved. Nevertheless, an approximation utilizing the Simple Valence Force Field (SVFF) could yield a simple physical picture. Based on SVFF, it might be possible to treat the vibrations of any two connected atoms in complicated molecules separately, and thus derive a set of simple equations relating their vibrations with the force constant of the bond (Cotton 1960). The simplest form of such equations is:

$$v = \frac{1}{c} \left(\frac{k}{4\pi^2 \mu}\right)^{\frac{1}{2}}$$
 (1)

where:

v = the frequency of the vibration given in cm⁻¹ c = the velocity of light k = the force constant of the bond μ = the reduced mass of the vibrating atoms.

Qualitative as it might seem, the equation shows clearly how coordination of a donor atom to a metal ion, which decreases it force constant, should shift its stretching frequency to a lower wave length.

The infrared data in lending evidence to the O-coordination argument, offers a powerful proof to the validity of resonance theory regarding amide structure, and therefore discrediting Spinners's concept. This is based on the fact that if O-coordination was predominant, the relative contribution of structure (B) increases, which means that the double bond character of the CN bond increases, thus increasing its force constant, and consequently, the C-N stretch should shift to a higher frequency. Actually, this has been observed for amide coordination complexes by many workers among them Archambault and Rivest (1958), and Kutzelnigg and Mecke (1962).

Coordination on the surface of montmorillonite:

Table 4 shows that acetamide was coordinated to copper on montmorillonite and the spectrum of the complex is almost identical to that given by Kutzelnigg and Mecke (1962) with the exception of Amide II and NH stretching bands.

Ledoux and White (1965) found that the NH stretching of formamide was shifted to a higher frequency when the liquid was intercalated on kaolinite. The reason for this is the breaking down of the intermolecular hydrogen bonds in the amide liquid and the formation of a weaker hydrogen bond between the amide and the clay mineral surface. The same observation is reported in this work. However, the reason is different in both cases. For formamide

	Daild assignment	NH stretching	C=O stretching	NH deformation	C-H assymmetric deformatio	C-H stretching
D	Ca-mont.	3500 3382	1659	1608	1468	1407
on i do comolo	Cu-mont.	3490 3452 3368	1661	1576	1471	1416
nd positi		3373 3260	1664	1590	~•	1412
Bal		3330 3160	1681	1610	1458	1399

The main features in the spectra of acetamide and its complexes Table 4.

^aThe data for acetamide and its Cu-complex are taken from Kutzelnigg and Mecke (1960) with the exception of the assignment of the band at 1399 cm⁻¹ which is taken from Bellamy (1958).

^bThe data for the dehydrated 0.5 symmetry level.

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intercalated on kaolinite, there are very few exchangeable ions in the media to initiate reactions more important than hydrogen bonding. On the other hand, acetamide adsorbed on the surface of montmorillonite, there exists a coordination complex. Thus, at least at the low levels of amide, the amino group of the amide has more freedom to vibrate, and therefore, shifting the NH stretch to a higher frequency.

The second difference between Cu-acetamide spectrum on montmorillonite and the Cu-acetamide complex of Kutzelnigg and Mecke is the position of Amide II band; it is at a lower frequency in the montmorillonite complex. According to Bellamy (1958) the Amide II band of primary amides is almost pure NH deformation, and according to Mortland et al. (1962), the symmetric deformation band of NH₃ shifts to a higher frequency upon coordination. But since the amide group of acetamide was free in the montmorillonite complex due to the "relative dilution," the NH deformation is found at a lower frequency. This is not taken to mean that Kutzelnigg and Mecke's complex was a N-coordination complex, rather, it was intermolecular hydrogen bonded through the amino group.

The coordinate bond between acetamide and the exchangeable sodium or calcium ions was not as strong as with copper ions. Actually, their spectra were similar to that of solid acetamide of the emodification. However, as could be seen from Table 4, the Ca-complex shows the presence of free

NH stretching, a shift of Amide I band to a lower frequency, and a slight shift of the C-N band to a higher frequency indicating a rather weak O-coordinate link.

This conclusion regarding the bond strength is based on the work of Suzuki et al. (1960). They found that when N-methylacetamide is dissolved in benzene it forms a complex with benzene in which the NH stretch is a little lower than that of the monomer in dilute solution of CCl4. This complex may be considered to be formed by hydrogen-bondlike interaction between the NH group of N-methylacetamide and the π electrons of the benzene ring. In different solvent containing phenyl group, the position of the NH maximum depends on the electron density in the phenyl group of the solvent. When the \mathcal{T} electron density in the benzene ring of the solvent is lowered by substituting halogen atoms for hydrogen atoms, the maximum of the NH band shifts toward higher frequency. On the other hand, when the \mathcal{T} electron density in the benzene ring in the solvent is elevated by substituting the hydrogen atoms with alkyl group, the maximum of the NH band shifts toward a lower frequency.

Upon coordination of amides to a given metal ion through the carbonyl group, the relative displacement of Amide I band to a lower wave length was found to be in the following order: tertiary > secondary > primary. The main features of the spectra of pure N-ethylacetamide and its complexes of copper and calcium ions on the surface of

montmorillonite is reported in Table 5. From the table it could be seen that the shift in C=O stretching in the Cu^{+2} and Ca^{+2} complexes was 29 and 13 cm⁻¹, respectively. Due to the fact that the spectrum of N, N-diethylacetamide is not resolved, a corresponding table could not be constructed. Nevertheless, it was noted that its C=O stretching frequency was shifted upon coordination by about 50 cm^{-1} to the right. This seems to indicate that the amide-metal ion bond increases in strength with the order: tertiary > secondary > primary. However, the mass of the amide might exert some effects. According to Bellamy (1958), it is an oversimplification to consider any single motion of a pair of atoms of the CO-NH system in isolation. Now, to qualitatively deduce the effect of the mass upon the position of the band, the simplest way to do this is to make use of the equation (1) mentioned previously. It might be reasonable to conceive that k for the C=O group in the system C=O . . . M^{+n} , where M^{+n} is the metal ion, is about equal in primary, secondary, and tertiary amides. In this case, it is evident from the equation that the frequency is inversely proportional to the reduced mass of the vibrating atom. Since the carbon atom of the carbonyl group is attached to a nitrogen atom to which two hydrogen atoms are attached; primary amide, one hydrogen atom and one alkyl group; secondary amides, two alkyl groups; tertiary amides, the relative position of the Amide I band is at a lower frequency

Band iquid amide ^a 500 390	position Amide c Cu-mont. 3455 3285 3130	omplexes ^b Ca-mont. 3410 3315 3120	Band assignment NH stretching
550	1621	1637	Amide I band
555	1561 1490	1578 1548	Amide II band
174	1477	1476	CH ₃ (Č) assymmetric bending
167	1452	1461	CH ₂ sissoring
145	1437 1413	1440 1420	CH ₃ (N) bending ?
573	1387	1379	CH ₃ (C) bending
557	1356	1356	CH ₃ (C) symmetric bending
200	1336 1289	1336 1289	Amide III band

^aThe data are taken from Beer et al. (1958) with the exception of the two bands at 1477 and 1357 cm⁻¹ which are taken from Nakanishi (1962).

^bThe data for the hydrated 2.0 symmetry complex.

in tertiary amide complex than that of a secondary amide, which in turn is at a lower frequency than that of a primary amide.

The coordination number of the exchangeable cation plays a prominant role in determining the amount of amide which is chemically adsorbed. It has been observed that calcium-amide complex invariably gave a greater 001 spacing than that of the corresponding Cu-amide complex. This was to be expected in accordance with the fact that the calcium complexes are usually octahedral while those of the copper frequently are square planar. It should be emphasized however, that exception to this rule is possible since the strength of the amide-metal ion bond is not comparable in both cases. However, the interlamellar space of the clay mineral might impose some limitations and restrict the coordination requirement of the metal ion, thus affecting the number of amide molecules which are chemically bonded to the metal ion. Without such limitation the metal ion might react with amides to give a complex in which the number of amide molecules in the complex exceeds the coordination number. Cook (1960) was able to prepare a crystal of Mg⁺² -N,N-dimethylformamide complex whose amide to metal ion ratio was 12:1. However, he believes that it seems most unlikely that this could be a Mg^{+2} with 12 coordination number, rather, it is more likely that it is a six coordinated Mg^{+2} with six further N, N-dimethylformamide molecules not interacting with the cation, but incorporated in the crystal lattice. His evidence for this is the fact that the 12:1 complex rapidly reduces to a 6:1 complex whose stability is somewhat between those of Mg $(NH_3)_6^{+2}$ and Mg $(H_2O)_6^{+2}$.

Significance of coordination in clay mineral reactions:

It seems then that the exchangeable cation can and does effect the nature of interaction between clay minerals and organics through the formation of a coordinate bond. Actually, many adsorption studies could be more vigorously interpreted in terms of this kind of interaction than others that are frequently invoked. For example, Kohl and Taylor (1961) in studying the status of adsorbed diethylketone on Ca-saturated bentonite, found that the C=O stretching of the adsorbed ketone was at 1684 cm⁻¹ compared with 1709 cm⁻¹ for the liquid. They interpreted this result in terms of a hydrogen bond between the carbonyl group of the ketone and the hydroxyl group on the broken edges of the clay. Certainly, the possibility of a coordination complex formation between the ketone and the calcium ions lends a more reasonable interpretation.

Orientation of the amide-montmorillonite complexes

The usefulness of infrared spectroscopy in studying the orientation of adsorbed molecules on the surface of

clay minerals is bound up with two facts. First, is that the method of preparation of films leads to a well-oriented sample with the 001 planes of the clay mineral predominantly in the plane of the film. Second, is that absorption bands with a component perpendicular to the clay sheet should be enhanced in intensity when the film is positioned at an angle to the infrared beam. The theoretical reasons for the second fact are rather involved but they could be summarized as follows: an infrared beam is an electromagnetic wave with which a magnetic field is associated. This magnetic field is perpendicular to path of the wave. On the other hand, the vibtation of atoms within a given molecule creates a magnetic field the direction of which depends on the mode of vibration. Now, a vibration with a dipole component parallel to the beam does not interact with the magnetic field as does a vibration mode with a dipole component perpendicular to the beam. The extent of this interaction is reflected by the intensity of the absorption band.

The data of this work showed that band intensities of the vibrations involving the C=O or the N-H groups did not change much when the film was tilted at a 45° angle to the beam. The only reasonable orientation consistent with this observation is the one in which the amide molecule lies flat in the interlamellar space of the clay mineral with its plane in the 001 plane of the silicate sheet.

A powerful proof to the validity of this postulated orientation is the change in intensity of the band near 1465 cm⁻¹ (CH₂ sissoring) in N-ethylacetamide with changing the incidence angle. In the postulated orientation the CH₂ group in the amide is displaced such that the bisector of the H-C-H angle, along which the dipole change of the sissoring vibration, is at 90° with respect to the long axis of the molecules. Therefore, such a dipole change would be almost parallel to the beam if its incidence angle makes 90° with the film. Then, as the incidence angle decreases, the interaction between the dipole moment of the sissoring atoms and the magnetic field of the beam increases, and consequently the intensity of the absorption band subsequently increases. Actually this was the case: the intensity of the 1465 cm^{-1} increased by almost 100 percent when the incidence angle decreased from 90 to 45° .

Ledoux and White (1965), in studying the orientation of formamide intercalated between kaolinite surfaces by using the same technique (changing the incidence of the beam), found that the relative intensity of the C=O stretching increased while that of NH deformation decreased when the incidence angle was decreased from 90 to 45° . Hence they conclude that the transition moment of the C=O vibration is perpendicular or nearly perpendicular to the 001 plane of kaolinite. Actually, this is a rather questionable conclusion. According to Serratosa et al. (1962) and Farmer and Mortland (1965), bands with dipole change perpendicular to the plane of the clay sheets would show a three or fourfold increase in intensity by decreasing the incidence angle. Such was not the case in the work reported by Ledoux and White.

The usefulness of infrared studies in studying the lay-out of individual adsorbed molecules seems to be impaired at a higher percentage of surface coverage, and particularly if the complex was not symmetric. Nevertheless, the orientation of the complex as a whole could be deduced from the infrared data. Such case could be illustrated by the data of N-ethylacetamide which were reported in Fig. 15. The structure of the complex seems to exhibit three orientations depending on the amount of amide in the complex.

1. Amide is present in amounts at or below the coordination requirement of the cation: Since the amide is coordinating through the carbonyl groups, the final structure would provide greater freedom to the NH groups. The following structure is consistent with this, as it gives a free NH of the trans-form.



2. Amide is present in amounts exceeding the coordination requirement of the cation. Here the suggested structure has to show both free and bonded amide of the trans-form as indicated below:



3. Amide is present in excessive amounts. The structure here is essentially that of stage 2 to which bonded amide molecules of the cis-form are added. Two molecules of such bonded amide are shown:



This structure has two advantages: It offers the possibility of forming two hydrogen bonds for every two molecules, and the alkyl groups are directed such as to form hydrogen bonds with the oxygen of the silicate sheets.

The stability of amide-montmorillonite complexes:

The stability of any system is a function of its free energy. If the system reaches a minimum free energy level such that for any change it might undergo, the change in its free energy is zero it could be described as a stable system. A direct corollary of this is that, such system could be described to be in a state of equilibrium, where the forward rate of a reaction in the system is equal to the backward rate.

The stability of the amide-montmorillonite complexes is a very complicated phenomena. However, two parameters could be singled out as the most important: the nature of the bond between the amide and the clay mineral, and the quantity of the amide present in the complex. It should be emphasized that these two factors are not independent of each other but they mutually interact, and it might be considered that they represent two interdependent variables of which the stability of the complex is a function.

The nature of the bond depends on the kind of forces involved in complex formation. Generally, four types of these forces could be recognized. First, coordination where the amide molecule is held to the clay surface through a coordinate link to the exchangeable ion. Second, electrostatic forces where the amide after being protonated, is held as an exchangeable ion. Third, is hydrogen bonding

where the amide molecule is hydrogen bonded to the hydration water, to the silicate sheet, or both. Fourth, is van der Waals-London dispersion forces. The quantity of the amide in the system plays a significant role in determining the predominant bond in the complex and subsequently, in determining its stability. Yet, the nature of the bond does not completely lose its independence. This could be made clear if the Cu-montmorillonite complex is contrasted with that of Al-montmorillonite. For the former system, in the very low levels of amide coordination requirement of the metal ion is not satisfied and therefore, water is a part of the complex. Due to the asymmetry of such complex, it might be less stable than a system where all the ligands are the same. By increasing the amide level, water is displaced and the coordination requirement of the metal ion is satisfied forming a more stable complex. Any excess amide beyond this limit would be held through hydrogen bonds and van der Waals-London dispersion forces and, therefore, the stability of the complex is impaired. On the other hand, the relation of water to the stability of the Al-montmorillonite complex display a different role. At very low levels of the amide, protonation is almost complete, and consequently, the amide cation is very strongly held to the clay surface. As the amide level progressively increases, amide held by coordination predominates. With further increases of the amide level, hydrogen bondings and van der Waals-London forces predominate.

The nitrogen analysis data reveals a linear relationship between the amide content of the complex and time. That is to say, the decomposition of the complex is apparently zero order reaction and, therefore, the following equation could be derived:

$$\frac{d[A]}{dt} = -k$$

which upon integration yields

[A] = -kt + constant

where

- t = time
- k = the decomposition rate constant.

So it seems that the kinetic of decomposition is independent of the amide concentration. This seems to contradict the fact that amide molecules held by coordination or as exchangeable ions are more strongly held to the clay than if hydrogen bonding was the only force involved. Such contradiction could be resolved if it is assumed that diffusion is the rate determining step in the decomposition of the complex. But since there are two diffusing materials; water into the complex and amide out of the complex, the question as to which rate is the most important could be involved.

Actually, the data reported here, seem to suggest that the presence of a coordination center in the interlamellar space initiates a stable orientation. Some of the amide molecules in excess of coordination requirement of the metal ion are certainly hydrogen bonded to the amide molecules which are acting as ligands. Another set of hydrogen bonds extends between the "secondary coordinated" molecules and some more of the free molecules, which in turn are hydrogen-bonded to the silicate sheet. Therefore, there is a hydrogen-bond network extending from the silicate sheet through the adjacent amide molecules to the coordination center. Such coordination-hydrogen bond network was stable against vacuum for one week but was not stable in atmosphere for the same period. The reason for this is that water in the atmosphere competes with the amide for adsorption sites, and it seems that once the network is ruptured in one place, its stability is greatly reduced. It was found that the difference in stability of the complex in vacuum and atmosphere was in the order of: acetamide > N-ethylacetamide > N,N-diethylacetamide. This indicates a bond strength with the reverse order. But it also indicates that the molecular size of the molecules might have had something to do with their diffusion rate.

It should be emphasized that the composition of amidemontmorillonite complexes in atmosphere reaches a limit where the complex might be very stable. This is indicated

by the fact that acetamide and N-ethylacetamide complexes left in the atmosphere for a period of six months, showed amide contents up to 100 millimoles per 100 gm. clay. Since the infrared spectra of these complexes did not show any sign of disintegration, it is concluded that the complex did not suffer any chemical or biochemical transformation.

SUMMARY

In studying the nature of interaction between amides and montmorillonite, it was found that the exchangeable ion on the clay plays a significant role in determining the nature and the extent of the interaction. For the acidified (H, Al, or Pt) clay, protonation of amides took place. On the basis of protonation studies reported in the literature, it was concluded that the pH of these systems is definitely lower than 0.8.

Since amides contain two basic sites, protonation could occur through either the oxygen atom or through the nitrogen atom. However, the supporting evidence for both cases reported in the literature, as well as the data of this work were critically evaluated, and it was concluded that oxygen protonation is the predominant case.

At fairly high levels of amides, it was found that the hemisalt formation took place. The evidence for this was supplied by infrared data in terms of the intense background absorption in the 1700-1100 cm⁻¹ region. The structure of the hemisalt was found to consist of two amide molecules where their carbonyl groups share a proton through a symmetrical hydrogen bond.

Within a series of acidified clay, the extent of protonation was differentially affected by the source of protons,

the ability of the exchangeable ion for coordination, and the order of the amide. It was found that monoprotonation or hemisalt formation of a given amide was greater in the hydrogen system where coordination potentials are kept at a minimum if compared with the aluminum or platinum systems. On the other hand, the absolute reactivity of a given system which accounts for protonation and coordination potentials, was modified by the order of the amide since the basicity of amides follows the order: tertiary > secondary > primary.

On the surface of Cu-, Ca-, or Na-montmorillonite, the nature of the interaction indicates the formation of a coordination complex. Due to internal energy and structural considerations, the complex was expected to involve an oxygen-metal ion coordinate link. Such expectation was verified by the infrared data in terms of the shift of Amide I band to a lower frequency.

As was the case with protonation, the extent of coordination on the surface of montmorillonite is differentially affected by the exchangeable ion and the order of the amide. Within a given amide complex, coordination was most pronounced with Cu-montmorillonite. Clearly, this is bound up with the fact that copper is a transitional metal whose ion could form a strong coordinate bond. On the other hand, the strength of the bond is affected by the order of amide. Since due to the inductive effects of the alkyl groups, the lone pair electrons on the oxygen atom is more available for bond formation. The extent of coordination in a given system was found to be in the order: tertiary > secondary > primary. The experimental evidence for such order was furnished in terms of the relative position of the Amide I band of the complex compared with the pure amide.

Amide adsorption from the vapor phase proved to be a diffusion controlled process where the amount of adsorbed amide increased by increasing the treatment time. At short exposure periods, a more or less complete one layer of the amide was taken up by the clay, whereas at extended exposure periods, up to three layers of the amide were adsorbed. The order of the amide, however, was a significant factor in determining the relative difference between a given two exposure intervals. Such effect was attributed to the difference in dipole moments and molecular sizes of the amides.

At any rate, the three-layer complex is not stable; one layer is lost within 24 hours of complex formation. The remaining two layers decompose with a rate which seems to be a function of two variables: the nature of bond between the amide and the clay, and the presence of water as a displacing agent. The first variable involves the order of the amide and the exchangeable ion as both determine the strength of the bond. The second variable was verified by observing the rate of complex decomposition in atmosphere against that of a vacuum. It was found that the complex is

more stable in vacuum than in atmosphere. The experimental evidence for this was furnished by determining the amide content of the complexes, X-ray diffraction through observing the complexes, and infrared spectroscopy through observing the relative intensity of absorption bands. It should be stated however, that the relative difference between the stability of the complex in vacuum and atmosphere was affected by the order of the amide giving rise to the sequence: primary > secondary > tertiary. Also it was affected by the exchangeable ion in the order: $Al^{+3} > Cu^{+2} > Ca^{+2} > Na^{+}$.

The greater stability of the complex in vacuum compared with that of the atmosphere offered a reasonable explanation as to why amides could not be adsorbed from aquaous solution. In such environment, water is in such excess that the competition of amide molecules for adsorption sites on the clay surface is very much impaired. On the other extreme of the experiment, when amides were adsorbed from the vapor phase during extended exposure periods, amides were held by the clay in such quantities as to impair the ability of water to compete for adsorption sites. The persistence of a considerable amount of amide in complexes left in the atmosphere for a period of six months justifies this conclusion.
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