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UREA COMPLEXES WITH MONTMORILLONITE: AN INFRARED ABSORPTION STUDY*

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ABSTRACT: Urea was observed to become protonated in H-, Fe-, and Al-montmorillonite films and to form hemisalts when urea was present in excess of the number of available protons. The fully protonated urea disappeared upon dehydration, then the original protonated condition was re-established by rehydration. This completely reversible reaction indicates the importance of water in the protonated form. Indications were that urea will coordinate through the carbonyl group to the metal ion in Cu (II), Mn (II), and Ni (II) montmorillonite. Urea may be bonded to the metal ion in Mg-, Ca-, Li-, Na-, and K-montmorillonite by coordination and possibly by ionization of the N–H bond. The importance of ion-dipole interaction in urea complexes with montmorillonite is suggested. Decomposition of urea to ammonium ions was observed mainly in the Cu-montmorillonite system.

The mechanisms of interaction between clays and organic compounds have been reviewed recently by Greenland (1965). The nature of the interaction between urea and silicate mineral surfaces has been judged by Mitsui & Takatoh (1963) to be primarily through hydrogen bonds arising between the carbonyl and amino groups of the urea and exposed hydroxyl groups and oxygen atoms of the silicate surface. However, since minerals such as montmorillonite possess a high cation exchange capacity which may be neutralized by hydrogen or metal ions, protonation of the urea might be expected in the first case and ion-dipole interaction in the second. The work reported here concerns the nature of the interaction between urea and montmorillonite particularly as related to the kind of the exchangeable cation.

METHODS

The montmorillonite used in this study was H-25 from Upton, Wyoming, supplied by Wards Natural Science Establishment. Homoionic clays were prepared by the

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same techniques employed by Farmer & Mortland (1965). Fresh H-montmorillonite was prepared by passing suspension of the Na-clay through a column of H-IR120 resin.

Fresh, reagent grade urea was used to prepare a standard solution and aliquots of this were added to 50 mg clay suspensions. Three levels of urea were used in preparing urea-clay complexes—one-half the cation exchange capacity (C.E.C.) (50 m-moles urea per 100 g of clay), amount equal to the C.E.C. (100 m-moles urea per 100 g of clay), and twice the C.E.C. (200 m-moles urea per 100 g of clay). After the urea-clay systems were equilibrated overnight, the suspensions were poured into small dishes of aluminium foil and the water evaporated away. The resulting thin clay films (2.5 mg/cm²) could be readily stripped from the aluminium. Infrared spectra were obtained by mounting the clay films at right angles to the beam of a Beckman IR-7 spectrophotometer. Thus infrared spectra were obtained on self-supporting clay films treated with urea.

REACTIONS OF UREA WITH ACID MONTMORILLONITE SYSTEMS

Figs. 1 and 2 show the spectra of urea absorbed on H-, Fe-, and Al-saturated montmorillonite. The features of these spectra are quite similar and are compared with those of urea hydrochloride in Table 1. These spectra are quite different from others obtained in the course of this work and protonation of the urea is indicated. In accordance with the ideas of Janssen (1961) and of Cook (1964) that the oxygen of the carbonyl is protonated in urea salt formation, assignments of the various absorption bands have been made.

The main evidence for protonation of the urea is the formation of a broad band centred at about 2600 cm⁻¹, which is attributed to the OH stretching vibration of the protonated carbonyl, and the concomitant appearance of a band centred at 1360 cm⁻¹, which is assigned to the hydrogen deformation mode, δ OH. These two bands are shown in the dehydration study below, to be associated in that when the molecular form of urea is formed from the cationic, both of these bands disappear. Upon reconstitution of the cationic form, they both reappear. In accordance with the arguments of Janssen (1961), the band at about 1708 cm⁻¹ is assigned to the CN stretching and the band at 1565 cm⁻¹ to the CO stretching vibration. The assignments made here are very similar to those which Kutzelnigg & Mecke (1961) made on the urea salt of PtCl₆²⁻, 2H₂O.

The observed NH stretch frequencies are generally at a higher level for the urea cation in montmorillonite than for urea or urea-HCl in paraffin mull as reported by Spinner (1959). This may be interpreted as resulting from a relatively greater freedom of some of the NH₃ groups in the interlamellar spaces of the clay and a lowered intermolecular and/or environmental interaction.

The effects of concentration of urea in H-clay are shown in Fig. 1. Great changes are observed in progressing from 50 (spectrum 1) to 200 m-moles/100 g (spectrum 3). One of the major alterations is the great increase in background in the 1700–1200
Urea complexes of montmorillonite
cm$^{-1}$ region as concentration increased; the increase in background probably extends to even smaller wave numbers, the absorption in the Si–O region interfering below 1200 cm$^{-1}$. All three of the spectra have the same baseline in that they were adjusted to 98% transmission at 2000 cm$^{-1}$; they are thus directly comparable. This phenomenon is attributed to the formation of a salt of the type, base/acid ratio = 2; this involves the formation of strong, possibly symmetrical hydrogen bonds such as

$$(\text{H}_2\text{N})_2\text{C}:\text{O} \ldots \text{H}^+ \ldots \text{O}:\text{C(NH}_2)_2$$

These bonds are characterized by a strong broad absorption. Many compounds of this type are now known as for example acetamide hemichloride described by Albert & Badger (1958). Additional evidence that the hemisalt formation has taken place is that the bond at 2600 cm$^{-1}$ (Fig. 1), attributed to the OH stretch of the protonated urea, disappears at higher levels of urea and that the absorption in the infrared by the higher urea level in this region of the spectrum is much less than that of the lower level. Simultaneously, the band at 1360 cm$^{-1}$ assigned to the OH deformation mode disappears, although in this region it could be masked by the strong broad

**Fig. 2.** Infrared spectra of urea in (1) Al, (2) Fe, (3) Mn, (4) Ni, (5) Cu-montmorillonite at concentrations of 50 m-moles urea/100 g of clay in the Al and Fe systems and 100 m-moles urea/100 g of clay for the Mn, Ni and Cu-clays.
absorption. Such changes in the OH stretching and deformation vibrations would be expected in going from the 1:1 salt, where there is a proton for every urea molecule, to a 2:1 salt, where two urea molecules share a proton and are in a sense in competition for it. The spectra of urea hemisalts in montmorillonite are very similar to those, obtained by Kutzelnigg & Mecke (1961), of the urea hemisalt, [(urea)$_2$H$_2$], PtCl$_6$.

The H-clay film (spectrum 1, Fig. 3) containing 50 m-moles of urea/100 g was evacuated (0.1 torr) and heated (90° C) for 1 hr in a brass cell fitted with NaCl windows. It was then cooled, and a spectrum obtained. Spectrum 2 in Fig. 3 shows the results of this treatment. The OH stretching and deformation bands at 2600 and 1360 cm$^{-1}$ have disappeared and the strong CN stretching band at 1710 cm$^{-1}$ evident in spectrum 1 has greatly diminished. The band appearing at 1432 cm$^{-1}$ is allocated to NH$_4^+$ deformation indicating a small amount of urea decomposition. After allowing the film to be exposed to the atmosphere for 1 hr, spectrum 3 was obtained, which was identical to spectrum 1 in every detail with the exception of the convexity at 1432 cm$^{-1}$ from NH$_4^+$+. These results indicate that the protonation in the urea-clay systems involves a hydrated proton, which gives up water on heating and evacuation. One or both of the following reactions may occur up dehydration:

$$\text{Urea H}_3\text{O}^+ [\text{Clay}^-] \rightleftharpoons \text{Urea} + \text{H-Clay} + \text{H}_2\text{O}$$

$$2 \text{Urea H}_3\text{O}^+ [\text{Clay}^-] \rightleftharpoons (\text{Urea})_2 \text{H}_2\text{O}^+ [\text{Clay}^-] + \text{H-Clay} + \text{H}_2\text{O}$$

Upon addition of H$_2$O to the dehydrated phase, hydrated proton is again generated and the cationic urea formed. Thus, the affinity of the clay for the naked proton

<table>
<thead>
<tr>
<th>Urea–HCl$^*$</th>
<th>Exchangeable ion on montmorillonite</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>Al</td>
</tr>
<tr>
<td>3360</td>
<td>3470m</td>
<td>3475m</td>
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<tr>
<td>3165</td>
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<td>3385m</td>
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<td>1565s</td>
<td>1565s</td>
</tr>
<tr>
<td>1550</td>
<td>1475</td>
<td></td>
</tr>
<tr>
<td>1407</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1317</td>
<td>1360m(br)</td>
<td>1360w(br)</td>
</tr>
</tbody>
</table>

s, Strong; m, medium; w, weak; sh, shoulder; br, broad.

* Absorption bands taken from Spinner (1959); assignments made by M. Mortland.
may be greater than that of urea, but when the proton is present as oxonium (H$_3$O$^+$) size considerations may restrict its close approach to the negative charge arising within the octahedral layer of the mineral and the urea can compete successfully for it. Since the dehydration experiment was carried out at 90°C, complete removal of H$_2$O was probably not accomplished so the second of the reactions above may be the more likely. Some spectral features of the dehydrated phase were similar to those of the hemisalt systems. The H$_3$O$^+$ may occupy exchange sites or arise from ionization of water associated with aluminium ions which in turn may have been released from the lattice by acid decomposition. These results with urea contrast with those obtained for ammonium or ethylammonium saturated montmorillonite both of which maintain their protonated form under similar conditions described above because of their greater basicity.

It is noteworthy that both Al- and Fe-montmorillonite were able to protonate the urea molecule. They apparently are able to provide a sufficiently acid system through the ionization of associated water molecules to allow cation formation by the urea. None of the other metal cation-montmorillonite systems studied here permitted the protonation of urea to occur, coordination of the urea to the metal cation being the main adsorption mechanism.
Urea complexes of montmorillonite

COORDINATION OF UREA IN METAL ION-MONTMORILLONITE SYSTEMS

The structure of urea involves resonance between the following three forms:

\[
\begin{align*}
&\text{I} & \text{II} & \text{III} \\
\text{O} = \text{C} & \text{NH}_2 & \text{NH}_2 & \text{NH}_2 \\
\text{NH}_2 & \text{O} = \text{C} & \text{NH}_2 & \text{NH}_2 \\
\end{align*}
\]

The observed values of the interatomic distances indicate a 20% double-bond character for the CN bonds and 60% for the CO bonds according to Pauling (1960). When the formation of oxygen-to-metal bond occurs, the contribution of structure I will decrease and this will result in more double bond character for the CN bond and more single bond character for the CO bond. The result of this is to decrease the CO stretching frequency and to raise the CN stretching frequency. On the other hand, coordination with metal ions through the nitrogen as well as the oxygen atoms may occur according to Penland et al. (1957). In this case the contributions of structures II and III will decrease with a resulting increase in the double-bond character of the CO bond and with an increasing single bond character of the CN bond. The CO stretching frequency will thus increase and the CN stretching frequency will decrease.

Complexes with Li-, Na-, K-, Ca-, and Mg-montmorillonite

Penland et al. (1957) reported that urea coordinated through the nitrogen in both Pd(II) and Pt(II) urea complexes. This type of bonding will enhance structure I of urea and as Table 2, column 1, shows the absorption bands are affected as follows: an increase of the CO stretching frequency to greater than 1700 cm\(^{-1}\), a decrease of the NH (coordinated) bending frequency to less than 1600 cm\(^{-1}\), and a decrease of the CN stretching frequency to about 1400 cm\(^{-1}\). Fig. 4 shows the spectra of urea complexed with Li-, Na-, K-, Ca-, and Mg-montmorillonites. Bands appearing in these spectra have some similarities to those from Pd(NH\(_2\)CO NH\(_2\))\(_2\)Cl\(_2\) (Table 2); assignments are therefore made on the basis of coordination of urea to the metal ion through nitrogen atoms. The bands appearing around 1730 cm\(^{-1}\) seem too high in frequency to be assigned to a C:N vibration and they have been assigned to a C:O frequency; this implies that coordination is through the nitrogen of the urea. A number of contradictions and inconsistencies exist that oppose this interpretation. For example, the bands appearing at 1330-1350 cm\(^{-1}\), which are assigned to a CN stretching of coordinated urea, are about 50 cm\(^{-1}\) lower than those from the Pt(II) and Pd(II) complexes of Penland et al. (1957). Also the CN
stretching and NH₂ bending frequencies of coordinated urea in the K-clay system are relatively more intense than those of any of the other systems—a rather unlikely situation in that potassium should be the least effective of these ions in co-ordination reactions. In addition, the CN stretching frequencies of uncoordinated urea vary considerably in the range 1450–1480 cm⁻¹.

Another possible interpretation of these results is that bonding through the nitrogen might occur by ionization of the N–H bond, the metal ion taking the place of the hydrogen ion. Freeman, Smith & Taylor (1961) found a similar ionization of biuret in alkaline systems. Acetamide can form the sodium salt by ionization of the amide hydrogen; the infrared spectra of such salts have been reported by Kutzelnigg & Mecke (1962). If a similar mechanism exists in the urea systems, the band at 1350 cm⁻¹ might be assigned to NH deformation frequency. The bands assigned to 'uncoordinated' urea in Table 2 may in fact reflect some ion–dipole interaction and this could account for their observed variability of frequency (particularly in the 1440–1480 cm⁻¹ region) with different systems. The urea in these systems would then be considered to exist in two forms: (1) anionic, and (2) com-
plexed (ion–dipole). According to Pfeiffer (1927), complexes such as [urea,NaCl, H₂O] and 6 urea,MgBr₂ are known.

The above discussion suggests that an unambiguous interpretation of the infrared absorption results is not possible. However, it is obvious that urea exists in some form of complex and that the kind of exchangeable cation on the clay influences the nature of these complexes. Thus interaction between urea and the exchangeable metal ion plays a role in the adsorption of that compound on the montmorillonite surface. Ledoux & White (1966), whilst studying kaolinite–urea complexes, assigned a weak band at 1725 cm⁻¹ to CO stretching. Compared with the corresponding band in the pure urea spectrum, it was displaced to greater frequencies owing to weaker hydrogen bonding, which in the kaolinite complex occurred between silicate OH groups and carbonyl groups of urea instead of between adjoining urea molecules as NH…O:C. Another interpretation might be that this is the CO stretching vibration displaced to greater frequencies by interaction of the urea with metal ions as suggested here for montmorillonite.

The infrared spectrum of urea in KBr shown in Fig. 4 and the second column of Table 3 differs in some respects from those reported in the first column and by other workers, Laulicht et al. (1965), Mitsui & Takatoh (1963), and Spinner (1959) for example. The differences are the band at 1446 cm⁻¹ instead of about 1468 cm⁻¹ and a band around 1605 cm⁻¹, which exists only as a weak shoulder in this spectrum. The concentration of urea was 0.4 mg/600 mg KBr. When the author prepared a pellet containing 1.2 mg/600 mg KBr, spectra similar to those reported by the other

| TABLE 2. Absorption bands in the spectra of some urea coordination complexes in montmorillonite |
|---------------------------------|------------------|------------------|------------------|------------------|------------------|
| Pd(NH₂CONH₂)₂Cl₄*               | Exchangeable ion on montmorillonite | Assignments |
| Mg                             | Ca               | Li               | Na               | K                |
| 3390 3510m                      | 3515m            | 3510s            | 3510s            | 3510s            |
| 3290 3390m                      | 3390m            | 3400s            | 3390s            | 3385s            |
| 3140 3230m(sh)                  | 3240m(sh)        | 3250w(sh)        | 3240w(sh)        | 3200w            |
| 3030 1736m                      | 1731(m(sh))      | 1722m            | 1720w(sh)        | 1718w(sh)        |
| 1615 1668s                      | 1668s            | 1670s            | 1674s            | 1670s            |
| 1585 1588w(sh)                  | 1600(m(sh))      | 1598(m(sh))      | 1595(m(sh))      | 1590(m(sh))      |
| 1480 1440s                      | 1474             | 1460s            | 1450s            | 1460s            |
| 1400 1350w                      | 1350w            | 1340w            | 1350w            | 1330w            |

* Taken from Penland et al. (1957).
workers was obtained (column 1, Table 3), that is a band appeared at 1468 cm\(^{-1}\) and a distinct peak at 1605 cm\(^{-1}\) was observed. At the very low level of urea a complex may be formed with an impurity in the KBr. When the level of urea used exceeded the amount necessary to react with the impurity, the 'normal' spectrum in KBr resulted. An impurity which might exist in KBr could be NaBr. The author prepared urea–NaBr pellets and found quite a different spectrum from that in KBr. Two very sharp bands appeared at 1620 and 1640 cm\(^{-1}\) with a shoulder on the high frequency side of the 1640 cm\(^{-1}\) band. A sharp band at 1455 cm\(^{-1}\) also appeared and marked differences were noted in the NH stretching region compared with the KBr system. It is suggested therefore that spectral variations observed between different samples of urea and KBr are likely to be due to an impurity in the spectroscopically 'pure' KBr, perhaps NaBr, that interacts with the urea.

**Complexes with Cu (II), Mn (II), and Ni (II) montmorillonite**

The infrared absorption spectra of urea complexed with Cu (II), Mn (II), and Ni (II) montmorillonite appears in Fig. 2 and the principal bands with their assignments in Table 3. The absorption bands of Cu\([OC(NH_2)_2]Cl_2\) reported by Penland et al. (1957) are also given for comparison. The spectra of complexes formed when urea is adsorbed by these three systems bear considerable resemblance to those reported by Penland et al., and this indicates that oxygen-to-metal bonds are present in the montmorillonite complexes. The infrared bands observed at about 3500 and 3400 cm\(^{-1}\) are NH stretching vibrations which are at significantly higher frequencies (as in all the systems in this work) than those of urea in KBr (Table 3) or in paraffin mull (Spinner, 1959). This suggests a relatively greater freedom of the NH\(_2\) groupings on the interlamellar surfaces of montmorillonite and a minimum of intermolecular and environmental interaction at least in comparison with the KBr and paraffin mull preparations. The bands observed around 1640 cm\(^{-1}\) can be assigned to NH bending vibrations, the positions of which are relatively unchanged from those of the free molecule. The CO stretching frequency appears around 1590 cm\(^{-1}\) and the CN stretching frequency at about 1490 cm\(^{-1}\) as the structures II and III are enhanced by coordination through the carbonyl group. A comparison of the main bands given by the Cu (II) urea complex of Penland et al. (1957) with those of the Cu (II)-montmorillonite–urea system indicates relatively good agreement. Infrared absorption studies by Tahoun & Mortland (manuscript in preparation) on tertiary amide complexes with montmorillonite show the CO stretching frequency to have been displaced to even lower frequencies by coordination through the carbonyl group. There is no amide II band to confuse the situation in such systems.

The three divalent transition metal ion complexes had traces of uncoordinated urea appearing even at the lowest level of urea (50 m-moles/100 g, a 1:1 ratio of urea to M\(^{2+}\) ions). When the urea level was raised to a 2:1 ratio, a little more uncoordinated urea appeared in all three systems, and when increased to a 4:1 ratio, considerable uncoordinated urea was present as indicated principally by the CN stretching band near 1450 cm\(^{-1}\). The X-ray diffraction patterns of systems
TABLE 3. Absorption bands in the spectra of some urea coordination complexes in montmorillonite

<table>
<thead>
<tr>
<th>Urea*</th>
<th>Urea†</th>
<th>Cu[OC(NH₂)₂]₅Cl₂⁺ Exchangeable ion on montmorillonite</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu (II)   Ni (II)  Mn (II)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3425      3500s  3505s  3510s vNH</td>
<td></td>
</tr>
<tr>
<td>3450s</td>
<td>3440s</td>
<td>3355s      3390s  3400s  3395s</td>
<td></td>
</tr>
<tr>
<td>3350s</td>
<td>3350s</td>
<td>3265w 320w</td>
<td></td>
</tr>
<tr>
<td>3265w</td>
<td>3260w</td>
<td>3275 3265w(sh) 3260w(sh) 3260w(sh)</td>
<td></td>
</tr>
<tr>
<td>1682s</td>
<td>1670w</td>
<td>1655 1640s(br) 1658s 1635s(sh) 1637s(br) Mostly NH bending</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1630s 1622s 1620 NH₄+ scissoring</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1605s 1605sh Mostly CO stretching</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1468s 1447s 1485 1498s 1483m 1490s vCN</td>
<td></td>
</tr>
<tr>
<td>1158w</td>
<td>1163w</td>
<td>1160 NH₂ rocking</td>
<td></td>
</tr>
</tbody>
</table>

* KBr pellet. Spectrum obtained by author. Assignments made in accordance with observations by Laulitch et al. (1965) on normal solid urea.
† KBr pellet, spectrum appearing in Fig. 4 (apparent impurity altering urea spectrum somewhat).
‡ Taken from Penland et al. (1957).

containing a 4:1 ratio of urea to metal ions indicated a homogenous system (by rationality of 00l reflections and by the symmetry of the 001 peak) of basal spacing of 13.8 Å for the Cu (II), Ni (II), and Mn (II) systems and of basal spacing of 14.3 Å for the Ca and Mg systems. Two factors may account for this difference; first, the mechanism of coordination may be different for these two types of compounds, and second, differential tendencies toward octahedral, tetrahedral, or planar coordination could also be important.

STABILITY OF UREA–MONTMORILLONITE COMPLEXES

For the most part, the urea complexes were quite stable and storage for 3 months in a desiccator unaffected their infrared spectra. An exception to this was the Cu (II) montmorillonite where a significant amount of NH₄⁺ was observed after 3 months by the appearance of the μ₄ deformation vibration of NH₄⁺ ion at 1437 cm⁻¹. This was most pronounced in the film containing the lowest level of urea (50 m-moles/100 g clay). The decomposition of urea in the copper system probably goes by the following reactions:

\[
\text{Cu \ O} \text{C(NH}_2\text{)}_2^{2+} [\text{Clay}^-] + \text{H}_2\text{O} \rightarrow \text{Cu (NH}_2\text{)}_2^{2+} [\text{Clay}^-] + \text{CO}_2,
\]
\[
\text{Cu (NH}_2\text{)}_2^{2+} [\text{Clay}^-] + 2\text{H}_2\text{O} \rightarrow \text{Cu (OH)}_2 + 2\text{NH}_4^+ [\text{Clay}^-].
\]
After the above observations were made, several of the urea–montmorillonite complexes were heated in air at 70 °C for 16 hr, and then scanned for evidence of NH₄⁺ formation. The Cu (II) system showed large quantities of NH₄⁺ formed and, with the lowest urea level, only a small amount of complexed urea remained. The Ni (II) system also had formed NH₄⁺ and about half of the urea had disappeared, but the Mn (II) system was relatively stable showing a small but definite amount of NH₄⁺ formation. As noted previously in the dehydration study of urea complexed with H-montmorillonite, a small amount of NH₄⁺ was formed on heating, but there was no evidence for urea decomposition before heating. The alkali metal and alkaline earth systems did not show significant NH₄⁺ formation in the heating experiment. From these results, it appears that the copper ion, particularly, catalyses the decomposition of urea on the montmorillonite surface.

GENERAL DISCUSSION

Mechanisms of bonding of urea in montmorillonite are varied and depend to some degree upon the nature of the cation satisfying the cation exchange sites of the mineral. The work reported here indicates perhaps some interaction between the urea and the silicate itself, mainly hydrogen bonding between some NH₂ groups and the oxygens of the silicate sheet, which is indicated by a NH stretching band in the region 3200–3275 cm⁻¹; urea in KBr has however weak bands in this position. Another possibility might be that this band could be the overtone of the —NH₂ bending frequency in the 1600–1650 cm⁻¹ region. Other strong NH stretching vibrations around 3500 and 3400 cm⁻¹ suggest considerable freedom of other NH₂ groups. This is in contrast with the conclusions of Mitsui & Takatoh (1963) who concluded that the adsorption of urea by bentonite (montmorillonite) was due chiefly to hydrogen bonding. These workers drew this conclusion from their observation that the NH stretching vibration of urea was at a lower frequency in the montmorillonite than in the pure form. Actually, they report NH stretching vibrations of 3500 and 3400 cm⁻¹ for urea alone, and 3490 and 3400 cm⁻¹ for urea in bentonite. This could hardly be considered a significant decrease. In spectra of urea in KBr in this work and in paraffin mull reported by Spinner (1959), the NH stretching vibrations are generally at lower frequencies than when the urea is in the montmorillonite. Thus a greater freedom of the amide group is indicated when it is in the montmorillonite than when it is in the solid state where considerable interaction between adjoining molecules occurs. This is confirmed by Ledoux & White (1966) for formamide and urea intercalated in kaolinite. Thus urea within the interlamellar regions of montmorillonite displays a monomeric condition with a minimum of intermolecular interaction. Mitsui & Takatoh (1963) do not say what kind of exchangeable cation was on the montmorillonite, but the results reported here indicate that the nature of the ion present is extremely important in determining the kind of complex formed between the urea and the mineral. Their spectra were obtained by incorporating the urea–clay systems in KBr disks, but the work reported here
was performed on self-supporting clay films which eliminates any possible effect of the KBr on the urea spectrum. Kohl & Taylor (1961) have suggested hydrogen bonding between carbonyl groups of organic molecules and OH groups of montmorillonite as the mechanism of adsorption of such materials. The author submits that ion-dipole interaction between the oxygen of the carbonyl and the exchangeable metal cations may be a much more important mechanism of interaction in many compounds.

It is of interest to note that protonation of urea, for example in the preparation of its chloride, requires very strong acidity—dry hydrogen chloride being passed through a suspension of urea in dry ether. Yet, protonation readily occurred in the H-montmorillonite and even in the Fe- and Al-montmorillonite, thus indicating an extremely acidic environment at the mineral surface. Studies by Tahoun & Mortland (in preparation) on primary, secondary, and tertiary amides complexed with H- and Al-montmorillonite also show protonation and the formation of hemi-salts when the amount of amide exceeded the amount of protons available. Hemisalts of various amides and other compounds have been reported by several workers (as for example, Hadzi, Novak & Gordon, 1963; Albert & Badger, 1958; Cook, 1964; Kutzelmigg & Mecke, 1961, who reported hemisalts of urea). The residual water in the Mg- and Ca-montmorillonite is sufficiently dissociated to protonate NH₃ as shown by Mortland et al. (1963) and ethylamine by Farmer & Mortland (1965), but it is not sufficiently acidic to protonate the urea or amide molecules.

The disappearance of the urea cation upon dehydration and the reconstitution of the cation upon rehydration shows the importance of water in the protonation mechanism on the montmorillonite surface. Cook (1964), whilst studying the anhydrous and hydrated N,N-dimethylacetamide salts of H₅SbCl₆, showed that the OH stretching of the protonated carbonyl appeared at 2515 cm⁻¹ in the hydrated salt and at 3360 cm⁻¹ in the anhydrous salt. He concluded that this difference arose from the much greater basicity of the water molecule in CO⁺—H . . . OH₂ compared with the SbCl₆⁻ in CO⁺—H . . . Cl₆Sb⁻. In his systems the carbonyl is protonated in all cases. In the work reported here, however, the evidence suggests that as soon as the water is removed, the bare protons so formed attached themselves to the silicate sheet.

It is difficult to give a rigorous account to support the suggestion that both oxygen to metal and nitrogen to metal bonds may occur depending on the kind of exchangeable ion. Penland et al. (1957) give no explanation for their results. The bonding through the nitrogen might occur either by coordination or perhaps, as noted earlier, by the N–H bond ionizing in Li⁺, Na⁺, K⁺, Ca⁺, and Mg-montmorillonite and the metal ion taking the place of the hydrogen atom. It may be recalled that the three divalent transition metal ions, which coordinate with urea through the carbonyl group, have unfilled d orbitals; it is therefore assumed that they will bond with urea by electron pair donation. The alkali and alkaline earth metal ions, however, have these orbitals completely filled and so their bonds with the nitrogen or oxygen differ. Ion-dipole interaction, probably some hydrogen bonding, and Van der Waals forces lend stability to the urea-montmorillonite complexes. Protonation of the
urea in acid montmorillonite indicates that electrovalent bonds are of importance in such systems.

Attempts were made to use the pleochroism of the urea-montmorillonite complex in order to obtain information on molecular orientation. The method used to prepare the clay films results in orientation of the (001) planes of the clay mineral predominantly in the plane of the film. The 3500 (asymmetric NH stretching) and the 1640 (NH$_2$ bending) cm$^{-1}$ bands showed slight pleochroic behaviour because their intensity increased by about 10% when the clay film was placed at an angle of 45° to the infrared beam. This suggests that the NH$_2$ group, while not being perpendicular to the silicate sheets, may be inclined at some angle to them. If they were perpendicular, a much greater increase in intensity would be expected. No other bands changed their intensities.

REFERENCES