EXPANSION AND ELECTRICAL CONDUCTIVITY OF MONTMORILLONITE IN AMMONIA ATMOSPHERE*

by

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ABSTRACT

THE EXPANSION of montmorillonite at various relative pressures of ammonia up to saturation was shown to be markedly affected by the kind of ion present on the exchange complex. A 12.3 Å spacing was obtained with Li-, Na-, K-, Mg- and Ca-montmorillonites at low relative pressures. This spacing was maintained up to saturation for the K and Mg systems and apparently represents one layer of ammonia in the interlamellar spaces. For Li-, Na- and Ca-clay, two layers of ammonia were formed at higher relative pressures. In the cases of Cu- and Co-montmorillonite, rational spacings at 12.8 and 15.1 Å respectively were obtained at low relative pressures and were maintained to saturation. The results are interpreted in terms of co-ordination complex formation.

Electrical conductance studies showed exponential increases in conductivity as the relative pressure of ammonia increased. The apparent activation energies showed decreases with increase in relative pressure for all systems except Co- and Mg-clay, which remained rather constant over the pressure range studied. The results indicated that both expansion and electrical conductivity were influenced by the formation of the ammonium ion and by the co-ordinating power of the exchangeable cation.

INTRODUCTION

INVESTIGATIONS on the expansion of montmorillonite at various relative pressures of water vapor have shown that the kind of ion present on the exchange complex is a major factor influencing the amount of swelling (Hendricks, Nelson and Alexander, 1940). The electrical conductivity of montmorillonite at various relative pressures of water vapor has been interpreted by Oster and Low (1963) in terms of exchange cation movement and the temperature dependence of the conductivity as reflecting the activation energy for such movement. Since water and ammonia have a number of similarities with respect to their properties as solvents, an attempt is being made in this work to study the expansion and electrical conductivity

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of montmorillonite in an ammonia atmosphere over a range of relative pressures approaching saturation. Earlier work has shown that montmorillonite will expand in ammonia atmosphere, but it was done at room temperatures and pressures not exceeding one atmosphere; thus, the relative pressure was quite low. No results for the electrical conductivity of montmorillonite in ammonia were found.

EXPERIMENTAL PROCEDURES

Material and sample preparation

For this study, the American Petroleum Institute reference sample montmorillonite no. 25 from Upton, Wyoming, was used. The homo-ionic Li-, Na-, K-, Mg-, Ca- and Co-clays were prepared by saturating the colloidal fraction ($<2\mu$) with normal chloride solutions of the respective cations. This treatment was repeated three times, and after each saturation the clay was washed with distilled water until peptization was approached. Finally, the clay suspension was purified by dialysis and, when the electrical resistance of the equilibrium solution was similar to that of distilled water, it was stocked in plastic bottles.

Clay plugs were used for conductivity measurements and were prepared by the following method. The dry clay obtained by freeze-drying the suspension was ground and equilibrated in a medium of 35 per cent relative humidity. An amount equivalent to 500 mg. of oven-dried clay (105°C) was pressed to a thickness of 0.2 ± 0.01 in. in a cylindrical stainless steel die of 0.39 in. interior diameter. The resulting plugs, containing equivalent amounts of ions, were sufficiently rigid to be handled safely. A thin, homogeneous layer of carbon black was spread on the flat surfaces of the clay plugs before putting them in the conductance cell, in order to ensure good electrical contact with the platinum electrodes.

Clay films, prepared by evaporating the dilute clay suspension in aluminum dishes, were used for X-ray diffraction and infrared absorption measurements. These films, containing about 3 mg. of dry clay per cm^2, were very thin, translucent and homogeneous and could be easily removed from the aluminum surface.

Conductance cell and conductivity measurements

The conductance cell had to satisfy three major requirements: nonreactivity to ammonia, vacuum tightness and operation at low temperature, near the boiling point of NH_3, in order to allow conductivity measurements at different relative pressures ranging from zero to unity. Multicompartment nylon conductance cells described elsewhere by Cloos and Mortland (1964) were used. The cell constants were determined with 0.1 N solution of KCl, the electrodes being kept at equal distance by a small plastic cylinder.

The experiments were run in duplicate in two identical cells immersed in a cooling alcohol bath and connected to a vacuum system as shown by Fig. 1.

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Before putting in the first increment of ammonia, the cells were evacuated at room temperature for three days and then brought to equilibrium with the bath temperature controlled to ± 0.1°C. The electrical leads immersed in alcohol were insulated by a 2-3-mm thick paraffin layer in addition to their own plastic insulation. An adsorption isotherm was determined at -36.2°C: and desorption isotherms were determined at three different temperatures, $-36.0°$, $-32.0°$ and -29.0°C. Conductance measurements were taken at equilibrium, which was supposedly reached when the ammonia pressure remained constant for several hours.

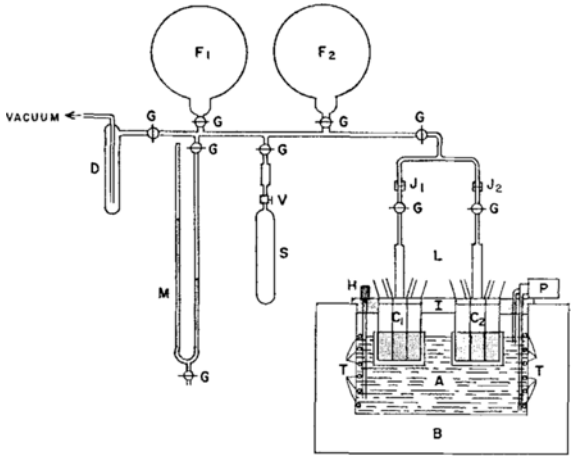

FIG. 1. System used to make conductivity measurements on montmorillonite pellets.

D	Trap immersed in liquid nitrogen	H	Heating element
M	Mercury manometer	B	Low temperature bath
F_1 F_2	Flasks for storing gaseous ammonia	A	Methanol
S	Steel bottle containing anhydrous ammonia	L	Platinum leads
C_1 C_2	Multicompartment nylon conductance cells	T	Circulation tubes of refrigerating gas
P	Circulation pump	I	Insulating cover (Styrofoam)
		J_1 J_2	Ball and socket joint
		G	Stopcock (vacuum)
		V	Metal valve

Low conductance, i.e. high resistance measurements generally present two main difficulties. An alternating-current conductivity bridge has capacitance effects, while direct-current devices have the problem of electrode polarization. Therefore, in this study, the measuring device having a variable alternator, described previously by Cloos and Mortland (1964), was used to reduce to a minimum both sources of error.

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X-ray diffraction and infrared absorption

The X-ray data were obtained with a Norelco diffractometer, to which a furnace constructed by R. L. Stone Co. was attached and modified for low temperature work. The sample holder could be cooled to −40°C by means of nitrogen gas cooled in liquid nitrogen with a heat exchanger. The clay film, contained in this chamber, was exposed to increasing relative pressures of ammonia, and X-ray patterns were recorded. Then the system was allowed to heat up to room temperature and finally degassed for 15 min with a mechanical vacuum pump.

The clay film was removed and immediately put into a Beckman IR7 infrared spectrometer. After recording the initial spectra, the films were subjected to varying heating and rehydration treatments as noted in the figures, and the spectra again recorded.

EXPERIMENTAL RESULTS

X-ray Diffraction Studies

Figs. 2, 3 and 4 show the relationship of the (001) spacing of montmorillonite to the relative pressure of NH_3. The influence of the exchangeable cation on the expanding properties of the clay mineral is obvious. When transition

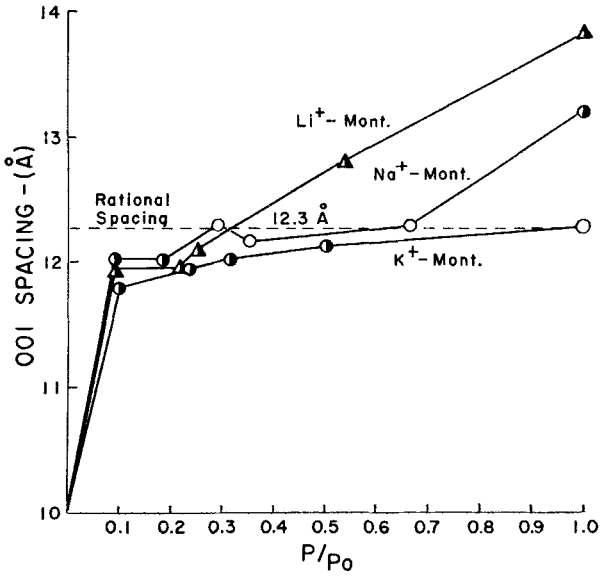

FIG. 2. Effect of relative pressure of NH_3 on the (001) spacing of montmorillonite saturated with Li^+, Na^+ or K^+. Open symbols represent rational non-interstratified systems, and half-shaded symbols indicate presence of random interstratification.

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metal ions, such as Co^{++} or Cu^{++} are the saturating cations, the clay expands at a low relative pressure to a definite spacing that is maintained rather uniformly throughout the whole pressure range. This was about 15.1 Å for cobalt and 12.8 Å for copper. There was some evidence, based on the appearance of random interstratification, that at saturation the Cu-clay was beginning to expand from 12.8 Å toward some higher level.

All the alkali metal and alkaline earth saturated montmorillonite clays gave evidence of some expansion; however, there were differences in magnitude. For example, Mg- and K-saturated montmorillonite never exceeded a spacing of 12.3 Å even at saturation, while Ca-, Li- and Na-montmorillonite

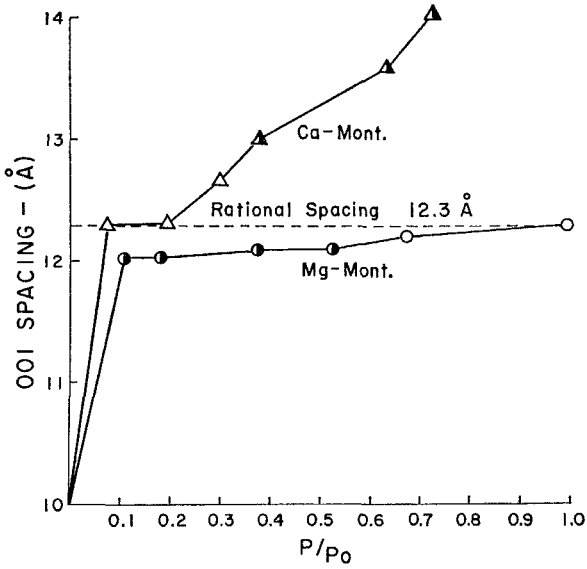

FIG. 3. Effect of relative pressure of NH_3 on the (001) spacing of montmorillonite saturated with Ca^{++} or Mg^{++}. Open symbols represent rational non-interstratified systems, and half-shaded symbols indicate presence of random interstratification.

expanded to higher levels by the time saturation was approached. The spacing of 12.3 Å undoubtedly represents one layer of ammonia molecules in the interlamellar positions of the clay mineral; and the spacing at about 15 Å, indicated at higher relative pressures for the Ca, Li and Na, represents two layers of ammonia, although the latter was observed only in interstratified systems. As evidenced by the presence of ordered or randomly interstratified systems, in both Ca- and Na-montmorillonite, a rather stable homogeneous one-ammonia layer system was established, which after increasing pressure began to yield a two-layer system. In the case of Li-clay, however, a stable one-layer system was never established and a continuous swelling of the

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clay occurred over the whole pressure range. For Mg- and K-montmorillonite, the most stable form was apparently one layer of ammonia (12.3 Å), both systems giving rational spacings near saturation. From the data presented here for the alkali metals and alkaline earths over the pressure range 0 to saturation, the ability of montmorillonite to expand depends on the saturating cation in the following series Ca > Li > Na > Mg = K.

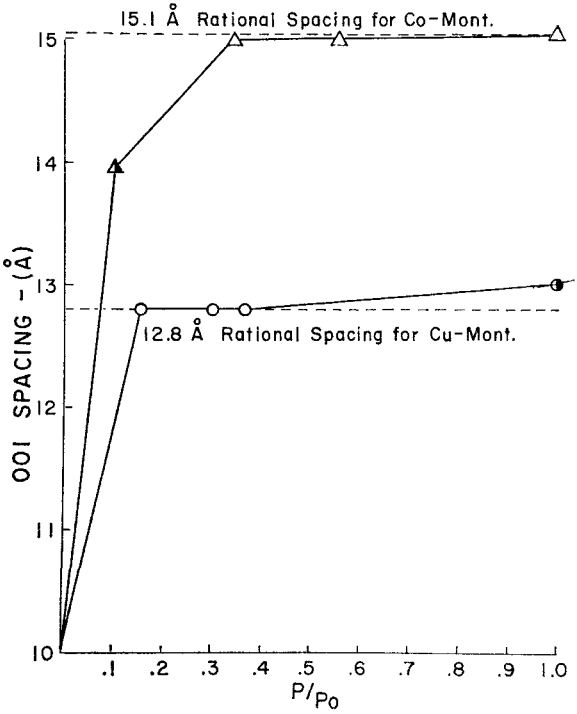

FIG. 4. Effect of relative pressure of NH_3 on the (001) spacing of montmorillonite saturated with Co^{++} or Cu^{++}. Open symbols represent rational non-interstratified systems, and half-shaded symbols indicate presence of random interstratification.

The results for the Cu and Co systems can be interpreted in terms of co-ordination reactions. Noting that the spacing of Cu-montmorillonite (12.8 Å) is different than any other and recalling the properties of Cu, it may be reasonable to assume the formation of Cu–NH_3 co-ordination, which results in a spacing higher than that of the alkaline earths and alkali metals. A co-ordination complex may also be expected for the Co system. The difference in spacing between Cu- and Co-montmorillonite may be explained on the basis of their co-ordination numbers, Cu probably being 4 and Co 6, and the geometry of the resulting complex ion. The Cu complex would probably be

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planar, while the Co would tend to be octahedral. Such a difference in co-ordination number and resulting geometry could easily explain the observed differences in lattice spacing. This explanation is supported by infrared absorption data, in which the symmetric deformation band of co-ordinated NH_3 was observed for the Co-montmorillonite at 1368 cm^{-1} and for Cu-montmorillonite at 1255 cm^{-1}. The beginning of further expansion of the Cu-montmorillonite at saturation probably represents the introduction of a layer of NH_3 in the silicate interlamellar surfaces in addition to the co-ordinated NH_3.

The type data obtained here for alkaline-earth and alkali-metal ions on montmorillonite in ammonia are not greatly different from those obtained for similar systems at various water-vapor pressures. Apparently one or two layers of NH_3 may be introduced between the aluminosilicate sheets depend-

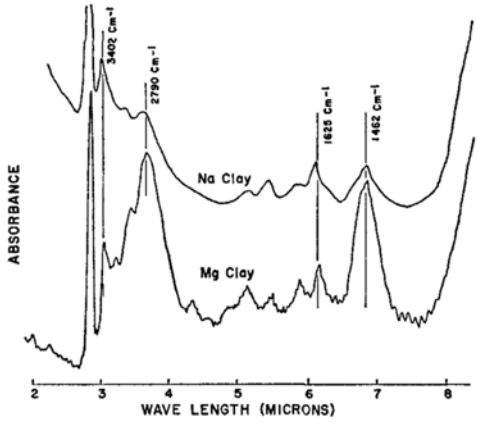

FIG. 5. Infrared spectra of Na- and Mg-montmorillonite in one atmosphere of NH_3 at room temperature (Russell and Farmer, unpublished).

ing upon the relative pressure (P/P_0) and the ammoniation (analogous to hydration) properties of the particular ion. Another factor here may be the specific influence of the silicate sheet itself on certain ions, thus changing ammoniation properties of these ions from those that exist in nonclay systems. For example, according to Sidgwick (1950) the co-ordination number of NH_3 with KCl is zero and with $MgCl_2$ it may be 2, 4 or 6. In the expansion of K- and Mg-montmorillonite, they behave similarly, having a maximum of 12.3 Å at $P/P_0 = 1$. Undoubtedly the formation of NH_4^+ to varying degrees depending upon the nature of the metal ion present also has an effect on the observed expansion.

Fig. 5 shows the infrared spectra obtained by Russell and Farmer*

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(unpublished) of Na- and Mg-montmorillonite in one atmosphere of NH_3 at room temperature. The formation of large quantities of NH_4^+ is made evident in the Mg system by the strong deformation band at 1462 cm^{-1} as well as by the N–H stretchings at 2790 cm^{-1}. These positions represent the hydrogen bonded condition of the NH_4^+ with NH_3. These results confirm those of Mortland *et al.* (1963) who showed NH_4^+ ion formation in base saturated montmorillonite as a result of proton donation by residual water molecules to ammonia.

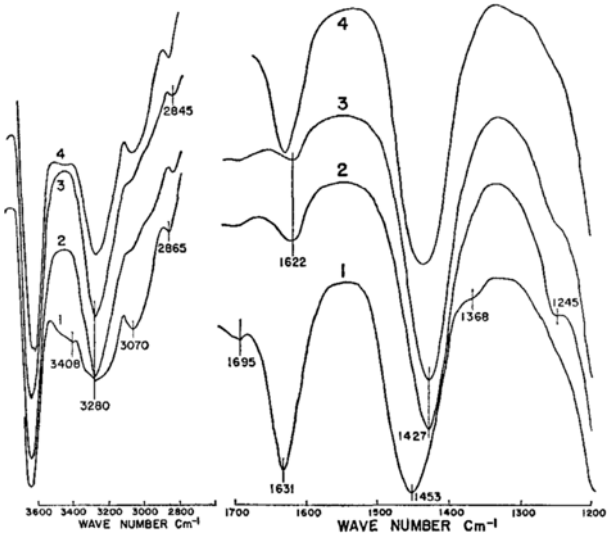

FIG. 6. Infrared spectra of Co^{++}-montmorillonite film after exposure to liquid NH_3 then degassed with a mechanical vacuum pump.

1. Initial scan
2. After heating 30 min at 105°C
3. After heating 2 hr at 105°C
4. Exposure to air 5 days.

Infrared Studies

Figs. 6, 7 and 8 show the infrared spectra of the ammonia-clay systems after exposure to a saturation pressure of NH_3 ($P/P_0 = 1$) followed by freezing out NH_3 and degassing for 15 min with a mechanical vacuum pump. The NH_3 observed on the spectra is therefore adsorbed on the clay by bonds stronger in energy than ordinary Van der Waal bonds. The presence of the NH_4^+ ion in varying amounts is indicated in each metal-clay system by the deformation band at 1427 cm^{-1}. In most systems in the initial scan, this bond is perturbed to higher wave numbers around 1460 cm^{-1} by the interaction with NH_3. However, when the NH_3 is removed or reduced in quantity by heat treatment, the band shifts to 1427 cm^{-1}. The presence of co-ordinated NH_3 is indicated in the initial scan of the cobalt-clay system by the symmetric deformation

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band at 1368 cm^{-1} and in the copper-clay system at 1255 cm^{-1}. In the cobalt-clay system, this band is typical for Co^{III} ammine complexes. Upon heat treatment, the co-ordinated NH_3 band shifted to 1245 cm^{-1}, a position

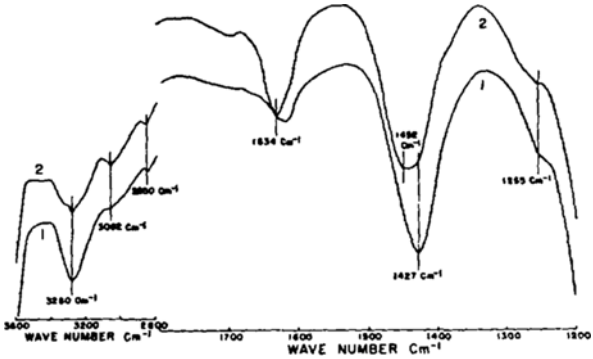

FIG. 7. Infrared spectra of Cu^{++}-montmorillonite film after exposure to liquid NH_3 then degassed with a mechanical vacuum pump.

1. After heating at 105°C for 1 hr
2. Initial scan

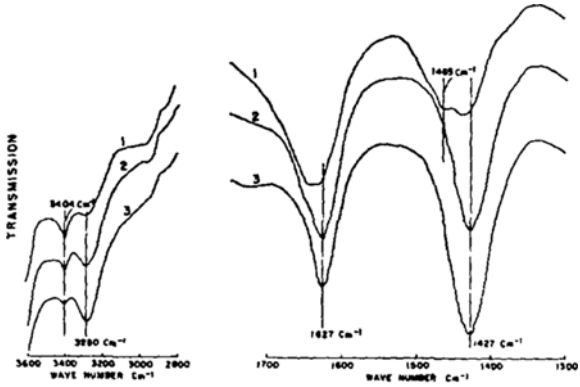

FIG. 8. Infrared spectra of Li^{+}-montmorillonite film after exposure to liquid NH_3 then degassed with a mechanical pump.

1. Initial scan
2. After heating 105°C for ½ hr
3. After heating 105°C for 2½ hr

characteristic of Co^{II} ammine complexes. Thus an oxidation reduction reaction is indicated. In the other metal-ion–montmorillonite systems, this band is obscured by the broad absorption of the Si—O bonds in the 1300–900 cm^{-1} region. Russell and Farmer (personal communication) have been able to find

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co-ordinated NH_3 on Li-, Ca- and Mg-saponite, by observing the deformation band at 1130, 1185, and 1218 cm^{-1} respectively. The peak located at 3404 cm^{-1} can be attributed to the NH stretching of NH_3, and that at 3280 cm^{-1} to the NH stretching of the NH_4^+ ion. In all cases except the Li-clay system, which will be discussed later, the 3404 cm^{-1} band of NH_3 disappears upon heat treatment. In most of the spectra taken immediately after exposure to NH_3, small bands appear at about 2860 and 3070 cm^{-1}. This may be attributed to NH stretch bands of the NH_4^+ ion, which is perturbed or affected by the NH_3. As the NH_3 is removed, this band always disappears and the unperturbed NH stretching of NH_4^+ ion at 3280 cm^{-1} is enhanced. When the films are then placed in the air and allowed to hydrate, similar bands are observed, which are again NH stretching of the perturbed NH_4^+ ion but this time by interaction, probably hydrogen bonding, with water. Also, the deformation band shifts toward higher wave numbers upon hydration, again indicating a hydrogen bonding between the NH_4^+ ion and H_2O.

In the spectra for Li-clay, it will be noted that NH_3 persisted in the clay film as indicated by the presence of the 3404 cm^{-1} band of NH_3 even after heating at 105°C for 2½ hr. While Li ion is known to form more stable co-ordination compounds with NH_3 than the other alkali-metal ions, it is not certain that such a complex would be stable under the above conditions, although co-ordinated NH_3 was seen to persist in Co- and Cu-clay under heat treatment. Another explanation for the maintenance of NH_3 in the Li-clay film is that some of the Li ions have penetrated into the clay lattice and taken up positions in the empty holes of the dioctahedral mineral in a fashion similar to that described by White (1955) for dioctahedral micas in molten Li salts and by Greene-Kelly (1953) for Li-montmorillonite heated to 200°C. The negative charge in the octahedral layer is thus compensated for by the Li, and the mineral loses its ability to swell. Ammonia molecules may then be trapped in the cavities formed by the hexagonal network of oxygen atoms in the mineral's interlamellar surfaces, hence their persistence even after heat treatment.

Conductivity Studies

The logarithms of the conductivity of the clay plugs containing various cation saturations are shown in Fig. 9 as a function of the relative pressure of NH_3. Smooth S-shaped curves were obtained. Above a relative pressure of 0.5, the order of magnitude of specific conductance is Na>Li>Mg>Ca>K>Co. At the lowest level of relative pressure ($P/P_0 = 0.032$) the order was Na>Mg>Li>K>Co>Ca. If a voltage, E, is impressed through electrodes at the base and top upon a cylinder of length l and cross-sectional area a, the current I through a solution with a specific conductance L will be:

$$I = ELa/l = 10^{-3}EaF/l \; \Sigma \, C_i \, \alpha_i \, u_i \, Z_i \qquad (1)$$

where F is the faraday, C is the ionic concentration and subscript i indicates any of the ionic species present, α is the fraction of ions carrying current, u the

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ionic mobility and Z is the ionic valence. The following equation:

$$L = 10^{-3} FB \Sigma C_i \alpha_i u_i Z_i \tag{2}$$

shows the relationship between specific conductance L and ionic mobility u, B being a geometry correction factor for the clay system.

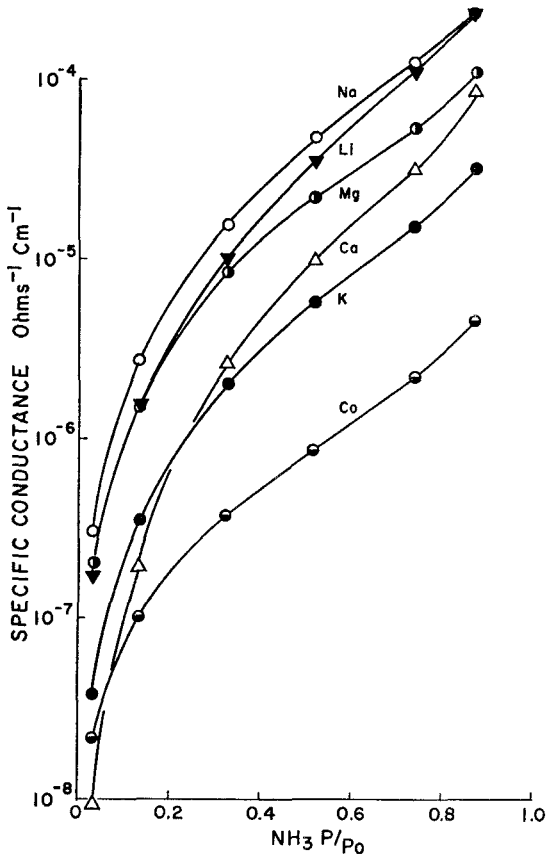

FIG. 9. Specific conductance of montmorillonite pellets as a function of relative pressure of NH_3 at $-36.2°C$

The system through which electrical current will flow is a cylindrical close-packed clay pellet with electrodes at the base and top of the cylinder. The clay itself in such a system is fixed and the current must be carried by exchangeable ions and free salts if such were present in the pores. Great pains were taken to purify the clay systems of free salts, and thus their contribution was extremely minor in these experiments.

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In order for an ion on the clay to move in the electrical field, bonds must be broken before moving from one equilibrium position to another. The energy required to surmount this energy barrier is equivalent to the activation energy. The mobility of ions then in the pores of the clay pellet depends upon the magnitude of the activation energy, E.

$$u = Ae^{-E/RT} \tag{3}$$

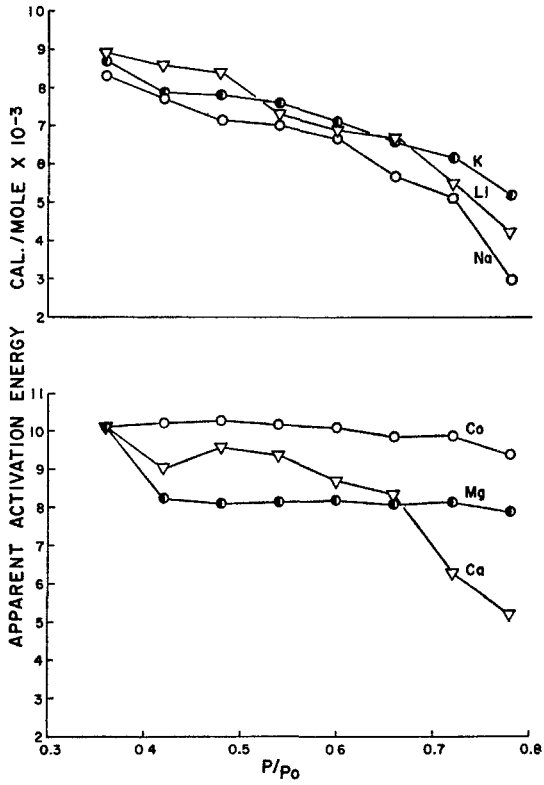

FIG. 10. Apparent activation energies of ion mobility in montmorillonite pellets as a function of relative pressure of NH_3.

where A is a constant related to the entropy of activation and the distance between equilibrium positions of the ion. The apparent mobility U equals the right-hand side of equation 3 multiplied by αB in accordance with Low's (1958) development and the following equation is obtained:

$$\ln U = \ln (\alpha BA) - E/RT \tag{4}$$

from which the activation energy for ion movement may be obtained by

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plotting the logarithm of the apparent mobility versus the reciprocal of temperature and obtaining the slope of the line. Since apparent mobility is directly related to specific conductance, the activation energy may be determined by plotting the logarithm of the specific conductance L versus the reciprocal of temperature and determining the slope. Implicit in this is the assumption that only the exchangeable cations are conducting electricity.

The results of the activation energy calculations are given in Fig. 10. The calculated activation energies for the Co-clay system showed no significant change over the whole relative pressure range 0.36 to 0.78 averaging around 10 kcal per mole. For all the other systems, there was a tendency for the activation energy to decrease as relative pressure increased.

The assumption that, when NH_3 is absorbed on the clay, only the exchangeable cations are available for the conductance of electricity is not valid. Infrared data clearly indicate the formation of the NH_4^+ ion even on base saturated montmorillonite. The NH_4^+ ion may arise from one or both of two ways—from the dissociation of liquid NH_3,

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

and by reaction with residual water in the clay lattice:

$$NH_3 + (H_2O)_r \rightarrow NH_4^+ + OH^-$$

The latter reaction would be shifted to the right if the residual water $(H_2O)_r$ in the interlamellar surfaces of montmorillonite is more highly dissociated than ordinary water, as has been indicated by Mortland *et al.* (1963). While the order of magnitude of the dissociation constant of NH_3 in the first reaction is 10^{-33}, it is quite possible that the polarization forces of the exchangeable cations on the clay surface augmented by the clay matrix itself would increase the dissociation constant in the same way as has been suggested for water. At any rate, since the existence of NH_4^+ ions on the clay surface has been proved by infrared absorption, this ion must be considered in any discussion of electrical conductance in clay-ammonia systems. The metal cations cannot be assumed to be the only carriers of electricity. Thus, if the specific conductance L resulted from the mobility of three ion species—for example, the exchangeable metal ion and the ions formed from the second of the two NH_3 reactions described above—the following equation would result:

$$L = 10^{-3}\,F\,B\left(C_M\,\alpha_M\,Z_M\,A_M\,e^{-\frac{E_M}{RT}} + C_{NH_4}\,\alpha_{NH_4}\,A_{NH_4}\,e^{-\frac{E_{NH_4}}{RT}} + C_{OH}\,\alpha_{OH}\,A_{OH}\,e^{-\frac{E_{OH}}{RT}}\right) \tag{5}$$

It will be noted then that each different ion will make its own contribution to the specific conductance in accordance with its concentration (C), fraction carrying current (α), valence (Z), and activation energy (E). Any determination of E using the specific conductance data, as has been done here, must give

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only an apparent activation energy. The conduction contributed by the ammonium ion is thought to be as by the whole ion and not by proton jumping from one ammonia molecule to another, as has been shown for hydronium-water systems.

The apparent activation energy data presented here indicate little variation in this value, regardless of the saturating metal cation, at the lowest relative pressure studied, i.e. 0.36. It may be that the NH_4^+ ion is primarily responsible for electrical conductance at this pressure. At this point, residual water has been consumed and NH_4^+ formation completed. Upon increasing relative pressure, however, a marked effect of the saturating metal cation may be noted. As already mentioned, Co-clay had little change in the apparent activation energy over the whole relative pressure range included in the study. Mg-clay, after an initial drop from about 10 to 8 kcal, remained at about that level. In the Ca-, K-, Na- and Li-clays, however, the apparent activation energy decreased as relative pressure increased.

The viscosity of the ammonia layer through which the ions must move should be a major factor affecting activation energy, ionic mobility, being inversely related to viscosity of the medium. This would be expected to be affected by the nature of the exchangeable cation, since they have varying abilities to co-ordinate or solvate with the NH_3 molecules. The clay lattice itself might exert an organizing effect on the NH_3 molecules. Also the degree of expansion of the clay lattice is a function of the exchangeable cation and of relative pressure as shown in the section on X-ray diffraction. The magnitude of expansion would probably influence the NH_3 configuration within the clay lattice and hence the viscosity. The interplay of three factors: (1) the ability of the metal cation to co-ordinate with NH_3, (2) the magnitude of the clay lattice expansion, and (3) the amounts of NH_4^+ formation, must affect the apparent activation energies obtained. In the cobalt system, the co-ordinating effect of this ion was of paramount importance, creating a network of octahedrally co-ordinated NH_3 molecules. Such a medium must be a great deal more viscous than ordinary liquid NH_3 would be. The movement of the cobalt through this system might explain the observed activation energy. It would seem, however, that even higher activation energies should be required for the cobalt to break the strong co-ordinating ligands and move as a free ion to other octahedral positions. Another explanation might be the movement of the complex ion. The possibility of some ions moving in the solvated state in clay systems may be worthy of consideration. In the Mg-clay system, the apparent activation energy was also relatively constant at about 8 kcal. In this system the co-ordinating effects of the Mg ion are not nearly so great as the Co, but the degree of lattice expansion is limited to one layer of NH_3 molecules; thus the effect of the clay lattice itself on the viscosity of NH_3 would be greater than in the Co-clay system. In addition, large quantities of NH_4^+ are present in the Mg system, confounding the interpretation of the electrical results. In the Ca-clay system, the clay lattice begins to expand to two layers of NH_3 as relative pressure is increased. The

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resulting organizing effect of the clay lattice on the two layers of NH_3 might be less than when there is only one layer, hence the viscosity might be less, with an observed lowering of the apparent activation energy. The results for the alkali metal ion-clay systems indicate a general decrease in the apparent activation energy with increase in relative pressure of NH_3. Again the interplay of co-ordination effects by the metal ion, the presence of NH_4^+ ion and lattice expansion have their impact upon the results. Li ion has probably the greatest affinity for co-ordination or solvation with the NH_3 but balanced against this is the continuous lattice expansion. Na ion has intermediate co-ordinating effect and the Na-clay lattice also expands to two NH_3 layers. K ion has little co-ordinating effect but only one layer of NH_3 molecules penetrates the interlamellar surfaces of the K-clay.

The ability of different ions to co-ordinate with NH_3 is dependent upon the strength of the electrostatic field around the central cation and upon the total dipole moment of the co-ordinated ammonia. On the other hand, the total dipole moment of the ammonia depends upon its permanent dipole moment, P, and the induced moment, P'. In turn the induced moment, P', is determined by the strength of the inducing electrostatic field, E, and the electronic polarizability, a, of the ammonia:

$$\text{Total Moment} = P + P' = P + aE \tag{6}$$

An important point here is that the inducing electrostatic field, E, around the central cation may be affected to some degree by the force field exerted by the clay lattice itself on the cation, just as it is known that the type anions affects the energy of formation of some co-ordination compounds. Thus, the co-ordination properties in the metal-ion–clay system may be a great deal different than when the metal ion is in simpler systems.

CONCLUSION

The expansion property of montmorillonite in NH_3 was greatly affected by the nature of the exchangeable cation. A 12.3 Å spacing was obtained with alkali-metal and alkaline-earth cations at low relative pressures of ammonia, which represents a monolayer of ammonia molecules in the interlamellar spaces. This spacing was maintained up to saturation pressure in the case of K- and Mg-montmorillonite. For Li-, Na- and Ca-montmorillonite, two layers of ammonia were formed at higher relative pressures. In the cases of Cu- and Co-montmorillonite, stable, rational spacings at 12.8 and 15.1 Å respectively were obtained at low relative pressures and were maintained to saturation. These results were explainable in terms of a fourfold planar co-ordination complex in the case of Cu and a sixfold octahedral co-ordination complex for the Co montmorillonite.

Electrical conductance studies were made on the same systems that were examined with X-ray diffraction except for Cu-clay. Exponential increases in

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conductivity were observed in all cation-clay systems as relative pressure increased. Activation energy calculations showed a continuous decrease as relative pressure increased for the alkali-metal ion-clay systems and for Ca-clay. In the case of Mg- and Co-clay, activation energies remained rather constant over the whole pressure range studied. Results indicated that the formation of ammonium ion, the presence of which has been proved by infrared absorption, must be taken into account in interpreting the conductance and expansion data. The co-ordinating power of the exchangeable cation may be another major factor in influencing the electrical conductivity and expansion properties of montmorillonite in ammonia atmosphere.

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