ALCOHOL–WATER INTERACTIONS ON MONTMORILLONITE SURFACES. I. ETHANOL*

by

R. H. DOWDY† and M. M. MORTLAND

Department of Soil Science,
Michigan State University, East Lansing, Michigan

ABSTRACT

INFRARED spectroscopic, X-ray diffraction and gravimetric techniques were used to study the vapor phase adsorption of ethanol on homoionic Cu-, Al-, Ca-, Na-, and NH_4-montmorillonite films. Equilibration of these films with ethanol vapor at a relative pressure of unity reduced the water content to less than 0.7% (300°C). As dehydration proceeded, the infrared absorption bands of the residual water were observed. Apparent differences between different cation saturations are reconciled by a consideration of the different types of ion–dipole interactions involved. Adsorption isotherms and X-ray diffraction results substantiated the interpretations of the infrared data. Prolonged evacuation did not remove all of the adsorbed ethanol as shown by spectroscopic and gravimetric techniques. Cu-, Al- and Ca-montmorillonite retained 4.5, 7.9, and 4.5 molecules per ion, respectively, while Na- and NH_4-clays retained less than one molecule per cation. Ethanol loss occurred rapidly at 40% relative humidity except in the Cu-system where 70 hr were required for complete replacement. These differences indicate that the adsorption and retention of alcohol by montmorillonite is affected by the saturating cation and that alcohol and water compete for the same adsorption sites. Ion–dipole type interactions should thus be considered in adsorption mechanisms of alcohol on montmorillonite.

INTRODUCTION

SIMPLE monohydric alcohols, such as methanol and ethanol, are routinely used in research involving clay minerals, often with little regard to their affect upon the clay surfaces, the ions satisfying the cation exchange sites on the surfaces, and the water associated with these surfaces. MacEwan (1948) noted that normal monohydric alcohols would extract interlamellar water from halloysite and montmorillonite and concluded that the adsorbed layers were extremely labile and liquid in nature. This suggests a two-dimensional interlamellar liquid, the same conclusion suggested by Martin

* Published with the approval of the Director of the Michigan Agricultural Experiment Station as Journal Article Number 3936.

† USDA, ARS, SWCRD, Soil Science Department, University of Minnesota, St. Paul, Minnesota.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

(1962) for adsorbed water. Glaeser (1954) observed that adsorption and retention of methanol and ethanol on Ca- and Na-montmorillonite were a function of the exchangeable cation.

Many investigators have proposed O—H···O—clay type hydrogen bonds as the mechanism responsible for interlamellar retention of polar, non-ionic molecules. Using this approach, Emerson (1957) and Brindley and Ray (1964) have presented models for the molecular orientation of normal monohydric alcohols in the interlamellar space of montmorillonite that satisfies experimental X-ray data and known van der Waals dimensions and bond angles.

The purpose of this investigation was to study the vapor adsorption and retention of ethanol on homoionic Al-, Cu-, Ca-, Na-, and NH_4-montmorillonite surfaces and its interaction with residual water adsorbed on those surfaces.

METHODS AND PROCEDURES

Materials and Sample Preparations

A sample of Wyoming bentonite, H-25, was used in this study. Homoionic suspensions were prepared by treating the $<2.0\ \mu$ fraction with appropriate chloride solutions in excess of the exchange capacity. After flocculation, the supernatant was decantated and the procedure repeated twice. The suspensions were washed free of excess salts with distilled water as confirmed by a negative $AgNO_3$ test.

Thin self-supporting clay films (2 mg/cm^2) were prepared by evaporating a freshly prepared suspension in aluminum foil dishes. Copper films were prepared by using aluminum dishes lined with a polyethylene film. Absolute ethyl alcohol was used.

Apparatus

The system used in this study was situated in a constant temperature room (20°C and 40% relative humidity) and connected to a two-stage rotary vacuum pump. It contained four basic interconnecting components: (1) a vapor source, (2) a detachable IR cell for spectroscopic examination, (3) a specimen holder for X-ray examination, and (4) a calibrated quartz helix balance from which clay films were suspended to obtain sorption data. Infrared spectra (4000 to 600 cm^{-1}) were recorded by a Beckman IR7 spectrophotometer fitted with a NaCl prism and grating. The clay films were positioned at right angles to the incident radiation. The evacuable brass cell used to support the clay films for IR scanning was capable of heating the film to 100°C. X-ray data were obtained with a Norelco diffractometer equipped with an evacuable chamber capable of heating a clay specimen to 1100°C.

Adsorption—Desorption

Portions of similar clay films were placed in the IR and X-ray sample holders and suspended from the quartz helix. A moisture determination was

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

made on a fourth portion. After degassing (partial dehydration) the Al-, Cu-, and Ca-films for 10 min and the Na- and NH_4-films for 5 min against a liquid N_2 cold trap, the system was exposed to successively increasing vapor pressures of ethanol. A 2-hr equilibration period was used at each level, except at saturation pressure when 4 hr were allowed for equilibration. Lack of change in the distension of the quartz helix indicated that equilibrium was reached during the first hour. Initially, after degassing, and after equilibration at each pressure, appropriate measurements were taken, including X-ray and IR scans.

The samples were then degassed for 10 hr; periodically, the evacuation was interrupted to collect appropriate data. At this point, films in the X-ray and IR cells were further evacuated while being heated to 80°C, scanned, then heated to 100°C for 20 min during evacuation, and once again were scanned. After degassing, the films were allowed to rehydrate in the atmosphere of approximately 40% relative humidity. Periodically, the films were scanned until the ethanol had been replaced by water, as indicated by IR data.

State of Hydration

Since the experimental weight data for sorbed material were net values representing the algebraic sum of sorbed water and ethanol, it was necessary to separate the net values into their respective components. This was accomplished by taking identical homoionic clay films and placing a portion in the IR cell, another on the quartz helix, and making a moisture determination on a third portion. Then by continuous evacuation, interrupted periodically for simultaneously scanning the 1650–1600 cm^{-1} deformation region of water and taking the necessary weight data from the quartz helix, it was possible to plot peak intensity versus water content. Since water retained in the air-dried state exists as two different types (Russell and Farmer, 1964), it was necessary to plot the integral intensity rather than optical density. The origin is considered a point on such curves and is based on the assumption that dehydration of montmorillonite is complete at 300°C. In this respect, all weights for water and ethanol presented in these studies are expressed on a 300°C oven-dried basis.

RESULTS AND DISCUSSION

Infrared Studies

The infrared absorption frequencies of ethanol are given in Table 1, as well as the band assignments for the vibrational modes. Assignment of the O—H in-plane deformation vibration was a point of uncertainty for a number of years. However, Krimm *et al.* (1956) have shown that the broad doublet in liquid ethanol with maxima at 1410 and 1330 cm^{-1} is due to a mixing of C—H and O—H bending modes. Upon dilution, less interaction occurs and

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

TABLE 1.—INFRARED ABSORPTION FREQUENCIES OF ETHANOL

Infrared bands (cm^{-1})	Mode	References
3680 (vapor)	OH stretch	Plyler (1952)
3500–3000 (liquid)	OH stretch	Coburn and Grunwald (1956)
2984	asym. CH_3 stretch	
2936	asym. CH_2 stretch	Drushel *et al.* (1963)
2898	sym. CH_3 stretch	
1923 (vapor)	CO + CC stretch	Plyler (1952)
1467	CH_2 scissoring	
1456	asym. CH_3 bend	Drushel *et al.* (1963)
1398	sym. CH_3 bend	
1410–1330 (liquid)	OH in-plane	
1243 (vapor)	deformation	Krimm *et al.* (1956)

these bands separate into a 1384 cm^{-1} bending and a 1250 cm^{-1} O—H deformation band.

When Cu-montmorillonite, containing 5% water, was exposed to increasing pressure of ethanol, the water of hydration was replaced as shown by the decrease in absorbance of the 1632 cm^{-1} deformation vibration (curves B and C, Fig. 1). The moisture content was reduced to 0.6% at $P/P_0=1$ for ethanol. The reduction of absorbance of the 1632 cm^{-1} band was accompanied by a splitting of the band with a maximum at 1598 cm^{-1} and a shoulder near 1640 cm^{-1}. Such splitting is indicative of the presence of two types of water on hydrated Cu-montmorillonite. These two species of water could be thought of as: (1) molecules coordinated directly to the cation, and (2) molecules in an outer coordination sphere or loosely adsorbed on the clay surface. The latter group are less energetically bound and predominate in the air-dried state giving rise to the 1632 cm^{-1} maximum (curve A, Fig. 1). In the dehydrated state a portion of the directly coordinated water remains and is responsible for the 1598 cm^{-1} band. Why the maximum should occur at this low frequency is not directly apparent. This is very close to the 1595 cm^{-1} deformation band of free, unassociated water molecules. However, hexagonal ice has been reported to have a deformation band near 1585 cm^{-1} (Haas and Hornig, 1960) and certain hydrated salts, such as $CuCl_2 \cdot 2H_2O$, have been reported to have bending modes of water at frequencies as low as 1550 cm^{-1} (Rundle *et al.*, 1955). Evidence that the 1598 cm^{-1} species of water is not independent of the Cu-ion resides in the fact that such a band does not exist for dehydrated Na- and NH_4-systems where water–ion interactions are considerably weaker. Therefore, it appears reasonable to conclude that this residual water is quite energetically bound to the Cu-ion and that in the combined electric field of the cation and clay lattice, the ν_2 bending vibration is much more anharmonic in nature, as suggested by Hornig *et al.* (1958) for the ν_2 mode in crystalline water.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

Curve E, Fig. 1, shows the retention of ethanol, against 10 hr of degassing and heating to 100°C under vacuum, by the persistency of C—H vibrations in the 3000–2900 cm^{-1} stretching and 1480–1400 cm^{-1} deformation regions. The EtO—H bending of adsorbed ethanol shifted to 1265 cm^{-1} from its unperturbed vapor phase position of 1242 cm^{-1}. This is a shift in the direction and of the magnitude expected for ethanol molecules coordinated through their oxygen atom. The C—H stretching vibrations of adsorbed ethanol are very similar to those found in the pure liquid or gaseous states, and, hence, fail to support the hypothesis that C—H···O-clay type interactions are important in the adsorption of non-ionic polar organic materials on clay surfaces (Bradley, 1945).

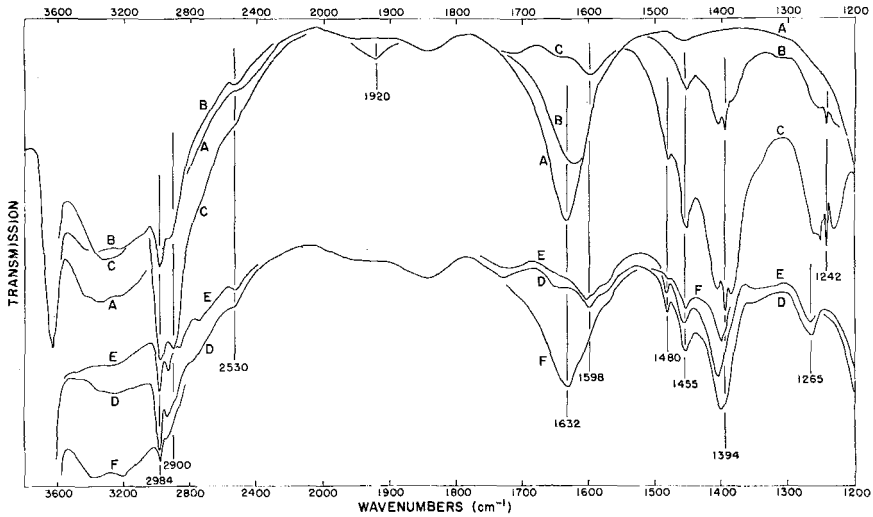


FIG. 1. Infrared spectra of Cu-montmorillonite: A, air-dried; B, exposed to 0.15 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hr after EtOH saturation; E, degassed 10 hr after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 24 hr after EtOH saturation, degassing, and heating.

The rehydration of ethylated Cu-montmorillonite upon exposure to 40% relative humidity for 24 hr is shown in curve F, Fig. 1. The replacement was essentially complete in 70 hr as indicated by the disappearance of the 1400 cm^{-1} CH_3 deformation band, which proved to be the most sensitive vibration to the presence of ethanol in the systems studied. Thus, it is apparent that the adsorption–desorption of ethanol on Cu-montmorillonite is a reversible process.

In contrast to Cu-montmorillonite, the 1635 cm^{-1} deformation vibration

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

of water was shifted to a higher frequency when Al-montmorillonite, containing 7.6% water, was exposed to increasing vapor pressures of ethanol (curves A, B, and C, Fig. 2). This is in agreement with the principle that H-bonding increases the frequency of bending vibrations. The deformation band is much broader than was observed in the case of residual water on Cu-films. An explanation of these apparent anomalies probably lies with the different types of coordination habit of the two species. All residual water molecules remaining on Cu-montmorillonite, having a square planar coordination, will be exposed to identical force fields of lower intensity than will be

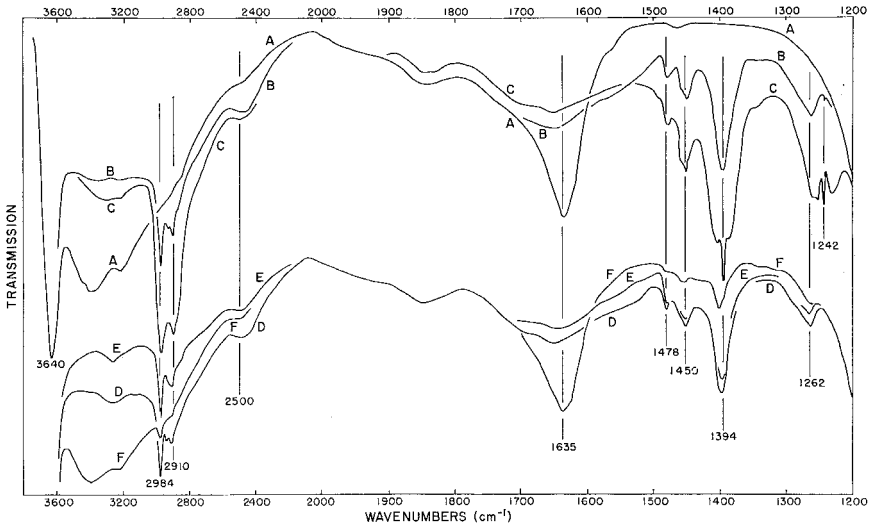


FIG. 2. Infrared spectra of Al-montmorillonite: A, air-dried; B, exposed to 0.15 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hr after EtOH saturation; E, degassed 10 hr after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 1 hr after EtOH saturation, degassing, and heating.

true of octahedral Al-complexes. However, due to the greater three-dimensional character of the Al-complex, the residual water molecules will be placed at higher intensity levels in the electric field of the clay lattice. In addition to this, the water molecules will be exposed to differing intensity levels in the force field because of distortions in the octahedral complex introduced by the spontaneous hydrolysis of adsorbed $Al(-OH_2)_6^{3+}$ (Jackson, 1963).

The quantity of ethanol retained against evacuation and heating was essentially the same for Al and Cu-montmorillonite, as suggested by the absorbance of the CH_3 deformation vibration (curve E, Figs. 1 and 2). However, only 2 hr were required for the replacement of adsorbed ethanol by atmospheric moisture in the Al system as compared to the 70 hr required for EtOH—Cu complexes. As mentioned above, the differential force fields

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

exerted on various ligands of the $Al(OH)_x(H_2O)_{6-x}^{(3-x)+}$ complex would be expected to distort the complex and thus allow more rapid exchange.

Ca-montmorillonite, initially containing 5.8% water, was more completely dehydrated at an ethanol pressure of $P/P_0=1$, than were the Cu- and Al-systems. This is explained by the lower hydration energy of calcium which allows easier replacement of the water associated with the cation. All traces of ethanol were gone after exposure to the atmosphere for 1 hr. The only significant difference between infrared data for Ca- and Na-montmorillonite was that the water deformation band for Na-films was not shifted to a higher frequency upon dehydration.

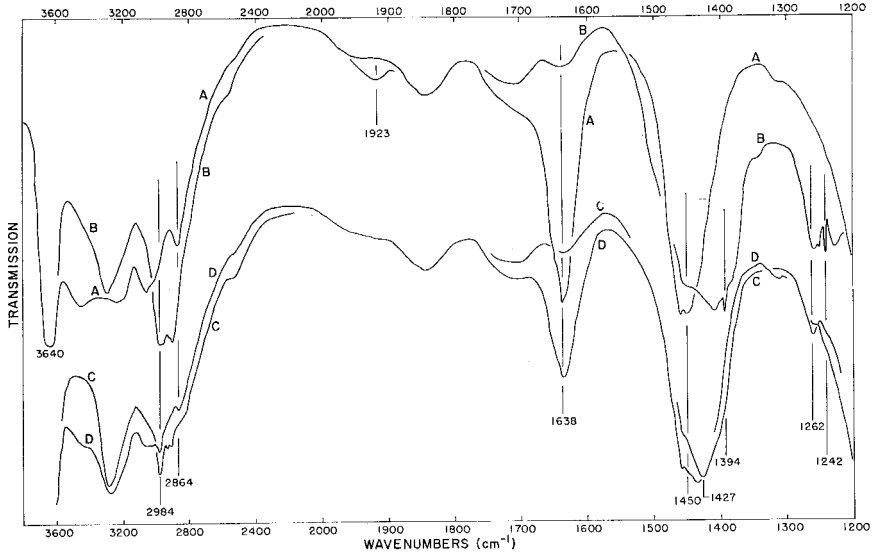


FIG. 3. Infrared spectra of NH_4-montmorillonite: A, air-dried; B, exposed to 1.0 relative pressure EtOH; C, degassed 1 hr after EtOH saturation; D, exposed to atmosphere for 1 hr after EtOH saturation, degassing 10 hr, and heating to 100°C while degassing.

Since infrared spectroscopic data have shown that NH_4—H_2O interactions do occur on montmorillonite surfaces, it was considered informative to study this system in the same way as the metallic cation systems. This interaction can be seen by noting that the NH_4^+ band centered at 1450 cm^{-1} (curve A, Fig. 3) normally vibrates at 1427 cm^{-1} in the unperturbed state. Upon degassing the ethylated film, the 1427 cm^{-1} band can be observed (curve C, Fig. 3). The positioning of the NH_4^+ deformation band at 1427 cm^{-1} and the NH stretching at 3280 cm^{-1} when the clay film was ethylated suggests that little EtOH—NH_4 interaction occurs.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

X-ray Studies

The X-ray data are presented in Fig. 4 where the half-shaded symbols represent the relative pressure regions where symmetrical first-order diffraction peaks were observed. These tracings approached rationality, but strictly rational 00*l* reflections were seldom observed.

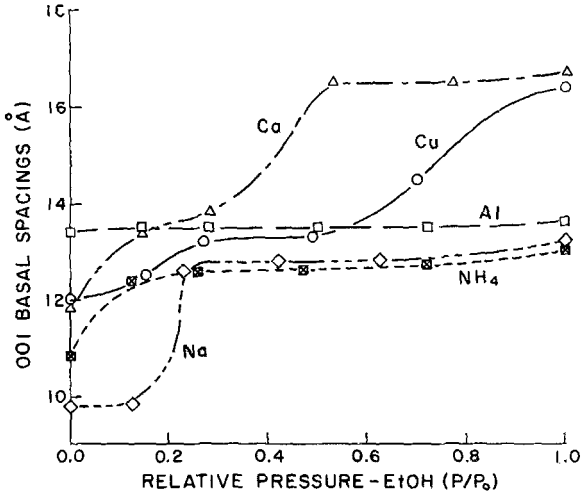


FIG. 4. The 001 basal spacing as a function of the relative pressure of EtOH for homoionic montmorillonite.

For Cu-montmorillonite, the initial adsorption involved expansion to 13.3 Å, followed by a rather stable 001 basal spacing where exchange of ethanol for water is occurring in the inner coordination sphere of the Cu-ion. The final stage of adsorption is characterized by a further weakening of electrostatic binding forces with a resultant expansion to 16.5 Å. The 13.3 Å basal spacing is in very close agreement with results of Brindley and Ray (1964) where it is described as a single layer of ethanol between adjacent Ca-montmorillonite platelets. If the CCO plane of the ethanol molecule lies parallel to the oxygen surface of the clay structure as might be expected in a square planar Cu—EtOH complex, the maximum layer spacing required for the molecule is theoretically 13.6 Å in the *c*-direction using known bond distances and van der Waals radii. However, by proper geometrical packing a "contact shortening" of 0.4 Å can be achieved at each organic/silicate interface (Brindley and Hoffmann, 1962). Hence, it is obvious that a Cu—EtOH coordination complex with the CCO plane parallel to the lattice surface is geometrically feasible and will explain the types of X-ray data which have been used to propose alcoholic—OH···O–clay type bonding for alcohol adsorption on montmorillonite surfaces (Emerson, 1957; Brindley and Ray, 1964).

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

The symmetrical 001 basal spacing of 16.5 Å is also in agreement with the 16.6 Å spacing reported by Brindley and Ray (1964) for a double layer EtOH—Ca-montmorillonite complex. In light of the preceding discussion, the transition from 13.3 to 16.5 Å might be visualized as a result of the rotation of the square planar complex from a parallel position to one essentially at right angles to the silicate surface. This is accompanied by the approach of an ethanol molecule on each side to form a distorted octahedral Cu—EtOH coordination complex.

Ca-montmorillonite, like the Cu-system, expanded to 16.5 Å, but at a lower relative pressure of ethanol. In fact, only a slight inflection occurred at 13.4 Å in the plot of 001 basal spacing versus relative pressure (Fig. 4). This is expected since calcium does not have a preferred coordination habit that would give rise to a stable 13.4 Å basal spacing. In this respect, the ethylation of Ca-montmorillonite closely follows its hydration pattern (Mering, 1946). Mering observed that Ca-montmorillonite did not form a one-layer hydration complex, but expanded to a two layer complex as soon as the octahedral hydration sphere of the Ca-ion was complete. At $P/P_0 = 1$, the Ca-clay appeared to be expanding still further as indicated by the asymmetry of the diffraction peak.

In contrast to the Cu- and Ca-clays, Al-, Na-, and NH_4-montmorillonite did not expand beyond 13.6 Å. The greater nuclear charge of the Al-ion and its spontaneous hydrolyzing character in clay systems restricted further expansion. On the other hand, in the delicate energy balance that exists in the interlamellar space, the energy of interaction between the Na- and NH_4-ions and adsorbate is not sufficient to overcome the attractive forces binding the platelets together.

Adsorption Isotherm Studies

The adsorption isotherms for ethanol on the montmorillonites studied are presented in Fig. 5. Theoretically, this is a combination isotherm with increasing P/P_0 of ethanol and decreasing P/P_0 of water. However, P/P_0 of water is slight with respect to P/P_0 of ethanol. The striking feature of the Cu-montmorillonite isotherm is the linear relationship which exists between the amount of ethanol adsorbed and relative pressure. This linear relationship indicates that the sum of the forces involved in the adsorption process, must vary in a similar manner over the entire pressure range. However, the components of total force do vary from one region of the isotherm to another and include such components as the cationic hydration energy, Coulombic type forces, and/or van der Waals type attractions.

The isotherms for Al-, Ca-, Na-, and NH_4-montmorillonite (Fig. 5) exhibited a decrease in slope in the 0.2–0.8 relative pressure region. However, the positioning and extent of the "plateau" was a function of the saturating cation and coincided closely with the pressure region where the 001 basal spacing exhibited greatest stability (Fig. 4). Ca-montmorillonite, with its greater interlamellar volume, exhibited greater total adsorption.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

Vapor adsorption may be divided into three stages. Initially, ethanol is adsorbed on the bare clay surfaces. Once the relative pressure of ethanol reaches a critical level and overcomes the ion–water binding energy of the

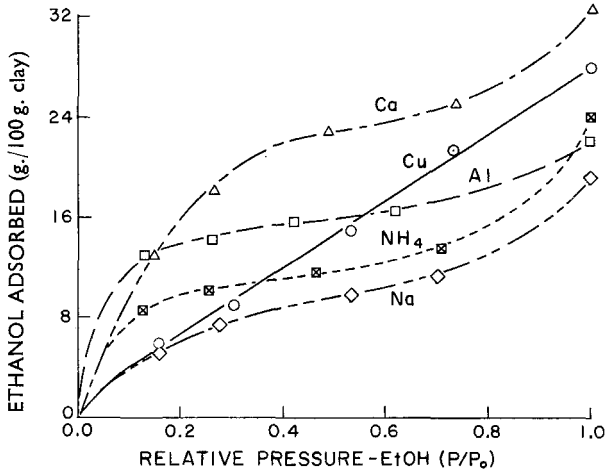


FIG. 5. The EtOH adsorption isotherms for homoionic montmorillonite.

hydration sphere, there is an exchange of ethanol for water of hydration. Finally, as $P/P_0 \rightarrow 1$, adsorption is characterized by a filling of voids in the interlamellar spaces created by expansion between the clay platelets.

Stability Studies

The plot of ethanol retained versus evacuation time (Fig. 6) shows the relative stability of the clay–cation–ethanol complexes. It will be noted that polyvalent cationic systems retain appreciably more ethanol than the monovalent systems. Cu-clay retained 4.5 molecules/ion after 10 hr of evacuation, which is very close to its preferred coordination number. Al- and Ca-montmorillonite retained approximately 7.9 and 4.5 molecules/ion, respectively, while Na- and NH_4-systems, which do not show strong cation–adsorbate interaction, retained < 1.0 molecule/ion.

Even though the ethanol–cation–clay complexes were stable to evacuation against a liquid N_2 cold trap, infrared data showed that the ethanol was completely replaced when the clay films were exposed to 40% relative humidity. Replacement of ethanol by water occurred rapidly except in the Cu-montmorillonite system which required approximately 70 hr. Once the initial rapid loss of ethanol had occurred, its desorption from Cu-clay appeared to follow a diffusion process until exchange with water was essentially complete (Dowdy, 1966).

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

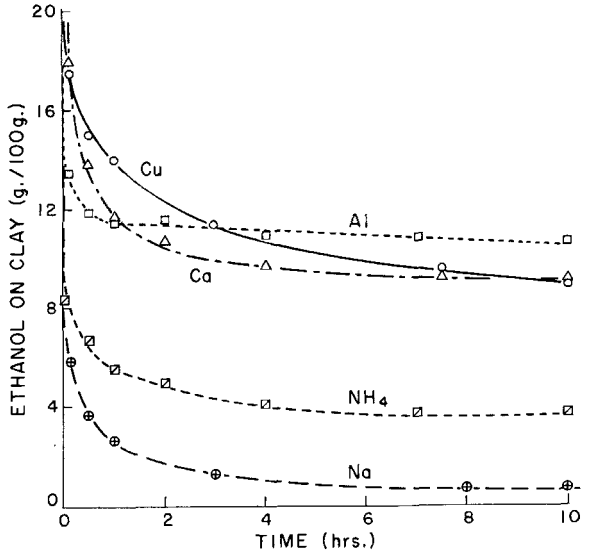


FIG. 6. Adsorbed EtOH as a function of the evacuation time for homoionic montmorillonite.

GENERAL DISCUSSION AND SUMMARY

Infrared data have shown that adsorbed water is replaced by ethanol on homoionic montmorillonite surfaces. As dehydration occurred with increased ethanol pressure, the 1632 cm^{-1} deformation band of the water on Cu-montmorillonite split into a shoulder at 1640 cm^{-1} and a maximum at 1598 cm^{-1}. This is evidence of two types of adsorbed water. The 1598 cm^{-1} absorbing species is the more strongly bound and is thought to be coordinated directly to the Cu-ion. On the other hand, the deformation band of water was displaced to a higher frequency as Al- and Ca-montmorillonite were dehydrated. These apparent anomalies were reconciled by a consideration of the different types of coordination habits of the respective cations. In contrast to the polyvalent cationic systems, the position of the water deformation band was unchanged in Na- and NH_4-montmorillonite, which suggests that forces other than ion–dipole interactions are predominant in these systems during dehydration–ethanol adsorption. This low ion–dipole interaction is in accord with the known complexing abilities of these two ions.

The ethylated clay complexes were stable to evacuation. The Cu-system retained 4.5 molecules/ion, which is close to its preferred coordination number, while Na- and NH_4-clays, which do not exhibit strong coordination, retained less than one molecule/cation. Rehydration occurred rapidly upon exposure of the ethylated complexes to 40% relative humidity, except for the Cu-montmorillonite system which required approximately 70 hr.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

The results of these studies clearly demonstrate the influential nature of the exchangeable cation in the adsorption–desorption of ethanol on homoionic montmorillonite surfaces. This agrees with the established fact that the water content of clay, under a given set of conditions, is directly related to the properties of the saturating cation. However, numerous differences of opinion exist as to the influential nature of the saturating cation upon the adsorption of non-ionic polar organic molecules on clay surfaces. Hoffman and Brindley (1961) noted, ". . . that for several substances the exchangeable inorganic cation has no significant influence on the organic adsorption, at least for the ions Na^+, Ca^{2+}, and Mg^{2+}". On the other hand, Glaeser (1954) noted that Ca-montmorillonite retained more methanol and ethanol than did Na-montmorillonite.

No evidence was found to support the hypothesis that C—H···O–clay type interactions are important in the adsorption of ethanol on clay surfaces (Bradley, 1945). The C—H stretching vibrations were not observed to shift to a lower frequency upon adsorption, which would occur if C—H···O–clay bonds existed. Direct evidence of organic–metal interactions were obtained in another series of studies where infrared bands attributable to the O—H stretching modes of ethylene glycol coordinated directly to the Cu-ion were observed (Dowdy and Mortland, 1966).

Ethanol and water compete for ligand positions around the exchangeable metal ions. Ethanol is thus an effective dehydrating agent of various homoionic montmorillonites. It is pointed out that the X-ray data for ethanol adsorption can be explained by coordination type complexes without having to inject O—H···O–clay type bonds. One of the strongest, though indirect proofs that cation–dipole interactions are of major importance, is the differential response of various homoionic montmorillonites to the sorption of ethanol. Acceptance of this thesis requires a break with traditional use of such terms as "monomolecular layers". For such terms to be meaningful, as Quirk (1955) stated, they ". . . must have some significance for the same surface irrespective of the cation".

REFERENCES

BRADLEY, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids: *Jour. Amer. Chem. Soc.* **67**, 975–81.

BRINDLEY, G. W., and HOFFMAN, R. W. (1962) Orientation and packing of aliphatic chain molecules on montmorillonite. Clay–organic studies VI: *Clays and Clay Minerals*, Proc. 9th Conf., Pergamon Press, New York, 546–56.

BRINDLEY, G. W., and RAY, S. (1964) Complexes of Ca-montmorillonite with primary monohydric alcohols (Clay–organic studies VIII): *Amer. Min.* **49**, 106–15.

COBURN, W. C., Jr., and GRUNWALD, E. (1958) Infrared measurements of the association of ethanol in carbon tetrachloride: *Jour. Amer. Chem. Soc.* **90**, 1318–22.

DOWDY, R. H. (1966) *Alcohol–Water Interactions on Montmorillonite Surfaces.* Ph.D. Thesis, Michigan State University.

DOWDY, R. H., and MORTLAND, M. M. (1966) Alcohol–Water interactions on montmorillonite surfaces. II. Ethylene glycol (manuscript in preparation).

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press

DRUSHEL, H. V., SENN, W. L., Jr., and ELLERBE, J. S. (1963) Effect of structure on the methyl and methylene group absorptivities in aliphatic alcohols: *Spectrochim. Acta* **19**, 1915–30.

EMERSON, W. W. (1957) Organo–clay complexes: *Nature* **180**, 48–9.

GLAESER, RACHEL (1954) Complexes organo–argileus et rôle des cations exchangeables: Thèse (Paris).

HAAS, C., and HORNIG, D. F. (1960) Inter- and intramolecular potentials and the spectrum of ice: *Jour. Chem. Phys.* **32**, 1762–9.

HOFFMANN, R. W., and BRINDLEY, G. W. (1961) Adsorption of ethylene glycol and glycerol by montmorillonite: *Amer. Min.* **46**, 450–2.

HORNIG, D. F., WHITE, H. F., and READING, F. P. (1958) The infrared spectra of crystalline H_2O, D_2O, and HDO: *Spectrochim. Acta* **12**, 338–49.

JACKSON, M. L. (1963) Aluminum bonding in soils: a unifying principle in soil science: *Soil Sci. Soc. Amer. Proc.* **27**, 1–10.

KRIMM, S., LIANG, C. Y., and SUTHERLAND, G. B. B. M. (1956) Infrared spectra of high polymers. V. Polyvinyl alcohol: *Jour. Poly. Sci.* **22**, 227–47.

MACEWAN, D. M. C. (1948) Complexes of clays with organic compounds. I. Complex formation between montmorillonite and halloysite and certain organic liquids: *Trans. Faraday Soc.* **44**, 349–67.

MARTIN, R. T. (1962) Adsorbed water on clay: a review: *Clays and Clay Minerals*, Proc. 9th Conf., Pergamon Press, New York, 28–70.

MERING, J. (1946) On the hydration of montmorillonite: *Trans. Faraday Soc.* **42B**, 205–19.

PLYLER, E. K. (1952) Infrared spectra of methanol, ethanol, and *n*-propanol: *Jour. Res. Nat. Bur. Standard* **48**, 281–6.

QUIRK, J. P. (1955) Significance of surface area calculated from water vapor sorption isotherms by use of the B.E.T. equation: *Soil Sci.* **80**, 423–30.

RUNDLE, R. E., NAKAMOTO, K., and RICHARDSON, J. W. (1955) Concerning hydrogen positions in aquo–complexes–$CuCl_2 \cdot H_2O$: *Jour. Chem. Phys.* **23**, 2450–1.

RUSSELL, J. D., and FARMER, V. C. (1964) Infrared spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Min. Bull.* **5**, 443–64.

https://doi.org/10.1346/CCMN.1967.0150131 Published online by Cambridge University Press