

ALCOHOL-WATER INTERACTIONS ON
MONTMORILLONITE SURFACES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
Robert Hedley Dowdy
1966



This is to certify that the

thesis entitled

Alcohol-Water Interactions on
Montmorillonite Surfaces

presented by

Robert Hedley Dowdy

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Soil Science

A handwritten signature in cursive script, likely of a major professor.

Major professor

Date April 1, 1966

ROOM USE ONLY

on hom

red sp

niques

reason

an ins

faces,

surfac

search

the qu

the 16

dehydr

pressu

24 hou

to exc

possib

of eth

atmosph

ABSTRACT

ALCOHOL-WATER INTERACTIONS ON MONTMORILLONITE SURFACES

by Robert Hedley Dowdy

Vapor phase adsorption of ethanol and ethylene glycol on homoionic montmorillonite surfaces was studied by infrared spectroscopy, x-ray diffraction and gravimetric techniques. These two compounds were chosen for the following reasons: a) their polar, non-ionic properties; b) to gain an insight into their interactions with montmorillonite surfaces, the exchangeable cations, and residual water on these surfaces; and c) their extensive use in soils and clay research. Calibration techniques are outlined for estimating the quantity of adsorbed water at any given time by use of the $1650-1600\text{ cm}^{-1}$ deformation band of water.

The homoionic montmorillonite surfaces were essentially dehydrated by equilibration with ethanol vapor at a relative pressure of unity or with ethylene glycol vapor at 115°C for 24 hours. Adsorption of these two compounds is reversible to exchange with water at 40% relative humidity with the possible exception of Al-glycol complexes where a low level of ethylene glycol appears to remain in equilibrium with atmospheric moisture. However, the adsorption-desorption of

both a

satur

of cor

Cu-mor

trolle

obeys

tions

ethyla

than C

in the

satur

is the

lonite

stretc

to sup

are in

molecu

ethyla

type c

both ethanol and ethylene glycol is a function of the saturating cation with respect to time, quantity, and type of complexes formed. The rate of loss of ethanol from Cu-montmorillonite during rehydration is a diffusion controlled process, and replacement of ethylene glycol by water obeys the conditions of second order chemical kinetics.

The lack of uniformity in the shifting of O-H vibrations (stretching and bending) of adsorbed ethanol and ethylene glycol suggest that cation-dipole type bonds, rather than O-H...O-clay type interactions, are of primary importance in the binding of these compounds on montmorillonite surfaces saturated with polyvalent ions. The most direct proof of this is the 2750 and 2650 cm^{-1} adsorption bands in the Cu-montmorillonite system which are directly attributable to the O-H stretching modes of coordinated glycol. There was no evidence to support the hypothesis that C-H...O-Clay type interactions are important in the adsorption of non-ionic polar organic molecules on the surfaces.

It is pointed out that the x-ray data for ethanol and ethylene glycol systems can be explained by coordination type complexes as easily as by O-H...O-clay type bonds.

ALCOHOL-WATER INTERACTIONS ON
MONTMORILLONITE SURFACES

By

Robert Hedley Dowdy

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Soil Science

1966

10-1-1948

ACKNOWLEDGEMENTS

The author wishes to thank Drs. R. L. Cook, B. G. Ellis, E. C. Doll, J. B. Kinsinger and R. S. Bandurski who, as members of his guidance committee, offered helpful suggestions during the course of study. To Dr. M. M. Mortland, the author wishes to express his sincere gratitude for his guidance and continued encouragement throughout this study.

He appreciates the Graduate Assistantship offered to him by Michigan State University, enabling him to complete this study.

To his wife, Annette, he expresses his thanks for her encouragement during his course of study.

INTROD

LITERA

METHOD

RESULT

GENERA

CONCLU

LITERA

APPEND

TABLE OF CONTENTS

	Page
INTRODUCTION	1
LITERATURE REVIEW.	3
Adsorption of water.	5
Adsorption of organic molecules.	10
Monohydric alcohols.	12
Dihydric alcohols.	16
METHODS AND PROCEDURES	20
Materials and sample preparations.	20
Apparatus.	21
Infrared spectroscopy.	23
X-ray diffraction.	23
Procedures	23
Ethanol adsorption-desorption.	23
Glycol adsorption-desorption	24
Determination of state of hydration.	25
RESULTS AND DISCUSSION	29
Ethanol adsorption-desorption studies.	29
Hydrated Cu-montmorillonite.	31
Hydrated Al-montmorillonite.	40
Hydrated Ca-montmorillonite.	45
Hydrated Na-montmorillonite.	48
Hydrated NH ₄ -montmorillonite	51
Deuterated ethanol studies	54
Acetaldehyde adsorption.	60
General considerations	62
Glycol adsorption-desorption studies	70
Cu-montmorillonite	70
Al-montmorillonite	76
Ca-montmorillonite	78
General considerations	81
The 1575 cm ⁻¹ band	88
The 1480-1400 cm ⁻¹ band.	90
GENERAL DISCUSSION AND SUMMARY	94
CONCLUSIONS.	102
LITERATURE CITED	104
APPENDIX	112

TABLE

1. Infr
etha
2. Infr
C₂H₅
3. Infr
ethy
4. A co
tech
tent

LIST OF TABLES

TABLE	Page
1. Infrared frequencies of pure and adsorbed ethanol.	30
2. Infrared frequencies of liquid and adsorbed C ₂ H ₅ OD and CH ₃ CD ₂ OH.	57
3. Infrared frequencies of liquid and adsorbed ethylene glycol.	71
4. A comparison between infrared and gravimetric techniques for determination of the water content of homoionic montmorillonite.	113

LIST OF FIGURES

FIGURE	Page
1. Schematic diagram of the system used for studying the adsorption of ethanol vapor on thin clay films.	22
2. Relationship between the water adsorbed on homoionic montmorillonite (300° basis) and the area of the 1650-1600 cm ⁻¹ deformation band of water.	27
3. Infrared spectra of ethanol-Cu-montmorillonite complexes.	32
4. A: 001 spacing <u>vs.</u> relative pressure of ethanol for Cu-montmorillonite. B: Ethanol adsorption isotherm for Cu-montmorillonite.	36
5. Infrared spectra of ethanol-Al-montmorillonite complexes.	41
6. A: 001 spacing <u>vs.</u> relative pressure of ethanol for Al-montmorillonite. B: Ethanol adsorption isotherm for Al-montmorillonite.	44
7. Infrared spectra of ethanol-Ca-montmorillonite complexes.	46
8. A: 001 spacing <u>vs.</u> relative pressure of ethanol for Ca-montmorillonite. B: Ethanol adsorption isotherm for Ca-montmorillonite.	47
9. Infrared spectra of ethanol-Na-montmorillonite complexes.	49
10. A: 001 spacing <u>vs.</u> relative pressure of ethanol for Na-montmorillonite. B: Ethanol adsorption isotherm for Na-montmorillonite.	50
11. Infrared spectra of ethanol-NH ₄ -montmorillonite complexes.	52

LIST OF
FIGURE

12. Ad
Po
13. A:
B:
14. In
af
15. In
exp
16. Var
the
lon
17. Ads
tio
18. Abs
etha
ethy
19. Log
mont
20. Infr
comp
21. Adso
atmo
22. Infr
compl
23. Adso
pheri
24. Infr
comple
25. Adso
atmosph

LIST OF FIGURES - Continued

FIGURE	Page
12. Adsorbed ethanol as a function of ($\log \log P_0/P + 2$) for NH_4 -montmorillonite.	53
13. A: 001 spacing <u>vs.</u> relative pressure of ethanol for NH_4 -montmorillonite. B: Ethanol adsorption isotherm for NH_4 -montmorillonite	55
14. Infrared spectra of Al- and Cu-montmorillonite after exposure to $\text{C}_2\text{H}_5\text{OD}$ and $\text{CH}_3\text{CD}_2\text{OH}$	58
15. Infrared spectra of Cu-montmorillonite after exposure to ethanol and acetaldehyde	61
16. Variation in water content as a function of the relative pressure of ethanol for montmorillonite	63
17. Adsorbed ethanol as a function of the evacuation time for homoionic montmorillonite.	66
18. Absorbance of the CH_3 deformation band of ethanol as a function of rehydration time for ethylated, homoionic montmorillonite	67
19. $\log (1 - A/A_0)$ as a function of time for Cu-montmorillonite.	69
20. Infrared spectra of glycol-Cu-montmorillonite complexes.	72
21. Adsorbed glycol as a function of time of atmospheric exposure for Cu-montmorillonite.	75
22. Infrared spectra of glycol-Al-montmorillonite complexes.	77
23. Adsorbed glycol as a function of time of atmospheric exposure for Al-montmorillonite	79
24. Infrared spectra of glycol-Ca-montmorillonite complexes.	80
25. Adsorbed glycol as a function of time of atmospheric exposure for Ca-montmorillonite.	82

LIST OF FIGURES - Continued

FIGURE	Page
26. Curves showing variation of (001) spacing as a function of the mole ratio of glycol:water for homoionic montmorillonite.	83
27. Reciprocal concentration of adsorbed glycol as a function of time of atmospheric exposure for homoionic montmorillonite.	87
28. Infrared spectra of Cu-montmorillonite after exposure to D ₂ O vapor.	89
29. Absorbance of the 1575 cm ⁻¹ deformation band of water as a function of the absorbance of the 1480-1400 cm ⁻¹ carbonate absorption band for Cu- and Al-montmorillonite	93

F
tific r
plines.
represe
mass, s
surface
of grea
part of
laborat
the cla
reactio
as ion
can be
ethanol
often w
and the
surface
and gly
surface
minerals
red spec
it was c

INTRODUCTION

Reactivity at the clay surface is an area of scientific research being actively pursued in numerous disciplines. Since clay surfaces are dynamic in character and represent one of the major reactive components of the soil mass, studies of reactions and interactions between clay surfaces and inorganic and organic substances have been of great importance to soil science. Water is an integral part of these surfaces under natural conditions and in most laboratory systems. Since water is an active component of the clay system, its behavior during physical and chemical reactions must be known and understood before such phenomena as ion exchange, hydration, pH, and adsorption of organics can be explained. The use of simple alcohols, such as ethanol, is common in research involving clay minerals; often with little regard to its affect upon the clay surface and the ions satisfying the cation exchange sites on the surface. The di- and trihydric alcohols, ethylene glycol and glycerol, respectively, are routinely used in specific surface determinations and x-ray identification of clay minerals. With the relatively recent introduction of infrared spectroscopy as a tool in the study of surface chemistry, it was considered useful to attempt elucidation of the

questions:

1) H₂O

by

2) H₂O

c

With

interact w

complex sy

vironment

of decompo

and polyhy

hydrates.

a) the ro

aggregati

questions:

- 1) How are these simple alcohols adsorbed and retained by clay surfaces; and
- 2) How does the interaction of these alcohols with clay surfaces affect the residual water?

With a better understanding of how these simple alcohols interact with clay surfaces, it will be possible to study more complex systems. Such a system might be the plant root environment which contains organic materials in various states of decomposition, including degraded nucleic acids, proteins, and polyhydric polymeric "alcohols" such as the complex carbohydrates. This would lead to a better understanding of:

- a) the rooting habits of plants and b) the phenomena of soil aggregation.

The
phenomenon
face of cl
of these r
Thermodyn
taneously
the total
the solid
or liquid

The
ways. To
One appro
tractive
exists a
tion pot
remove a
from the
molecule
theory v
occurri
product
complex
ation i

LITERATURE REVIEW

The reactivity of clay surfaces is a well established phenomenon. It is well verified that as the specific surface of clay minerals increases, the ability and tenacity of these minerals to adsorb substances are greatly enhanced. Thermodynamically, the free energy of a system will spontaneously seek a minimum. Hence, when adsorption occurs, the total free energy of the surface is reduced by replacing the solid-gas or solid-liquid interface with a liquid-liquid or liquid-gas interface.

Theories of adsorption have been grouped in various ways. Toth (1955) has outlined three different approaches. One approach is the potential theory which postulates attractive forces producing an adsorption potential which exists at a finite distance from the surface. This adsorption potential is defined as the amount of work required to remove a molecule from this area to an infinite distance from the surface and predicts an adsorption layer several molecules in thickness. Another approach is the chemical theory which considers adsorption as a chemical reaction occurring on the surface of the adsorbent. The reaction product will be the most insoluble or least dissociable complex obtainable in the given system. The third consideration is the electrical theory approach which treats the

adsorbent as a charged species that will attract an approaching dipole. By this theory the energy of adsorption decreases rapidly with distance from the surface, but extends into the multimolecular layer range.

A somewhat more meaningful classification is to divide adsorption into the two categories of physical adsorption and chemical adsorption or simply chemisorption. This has been done by Barrow (1961) for the adsorption of gases on solids in the following manner:

Physical adsorption	Chemisorption
Heat of adsorption less than about 10 kcal/mole	Heat of adsorption greater than about 20 kcal/mole
Adsorption is appreciable only at temperatures below the boiling point of the adsorbate	Adsorption can occur at high temperatures
The incremental increase in the amount adsorbed increases with each incremental increase in pressure of the adsorbate	The incremental increase in the amount adsorbed increases with each incremental increase in pressure of adsorbate
The amount of adsorption on the surface is more a function of the adsorbate than the adsorbent	The amount of adsorption is characteristic of both adsorbate and adsorbent
No appreciable activation energy is involved in the adsorption process	An activation energy may be involved in the adsorption process
Multilayer adsorption occurs	Adsorption leads to, at most, a monolayer

Although most adsorption processes involve either physical adsorption or chemisorption, it should be pointed out that often both types of adsorption occur in experiments designed

to establish the relationship between the amount of gas adsorbed on an adsorbent and the equilibrium vapor pressure in the system. Adsorption onto clay minerals involves both of these phenomena. The various types of molecular adsorption on clay minerals have been presented in considerable detail by Marshall (1964).

Adsorption of water.

The fact that the surfaces of clay minerals adsorb and retain water has been well established. This subject has been reviewed from time to time as new findings are reported. Probably, the most thorough and comprehensive review of the state of adsorbed water has been presented by Martin (1962). Early, Bouyoucos (1936) attempted to characterize the hygroscopic moisture in soils. He observed that 95 per cent ethanol will extract all water from bentonite that is removed by heating to 110°C and concluded that hygroscopic water exists as physically adsorbed water. Since 95 per cent ethanol will not extract water from hydrated CuSO_4 , but heating to 110°C will remove 37.8 per cent of this water, Bouyoucos concluded that ethanol will not remove chemically bound water. Marshall (1936) summarized earlier research of Nagelschmidt, who noted that the first few molecules of water adsorbed on dehydrated montmorillonite expand the clay platelets by considerably more than the volume of water adsorbed. Marshall then hypothesized: 1) the first few water molecules congregate around the cations or oxygen atoms holding the layers

together, and 2) the number of molecules entering the first stages of adsorption will be approximately proportional to the base exchange capacity.

Hendricks and colleagues (1940) were one of the first to carefully study the hydration of montmorillonite as affected by various saturating cations. Observing the low temperature endothermic peak obtained from differential thermal analysis (D.T.A.) data for Ca-montmorillonite, they noted a double peak at relative humidities less than 40 per cent. They concluded that the higher temperature portion of the doublet is due to the hydration of the cation. This was confirmed by peak area calculations showing that the water content attributed to this portion was essentially the same as that required for the hexahydrate of the calcium ion. The lower portion of the peak occurred at a temperature 40°C lower and was attributed to water lost from the clay surface not contiguous to the exchangeable cation. At relative humidities of 40 per cent and greater, the dual peak develops into a triplet with the third portion being attributed to an additional layer of water. Magnesium and other alkaline earth salts of montmorillonite exhibited a similar behavior. To study the affect of exchangeable cations and cation exchange capacity upon free energy, heats of reaction, and entropy changes occurring during water vapor adsorption, Barshad (1960) used homoionic samples of three different bentonites saturated with various cations. He concluded that

the magnitude of change in these thermodynamic quantities is much greater for the interaction of water with the exchangeable ion than for the interaction of water with the oxygen surfaces.

The presence of residual water in montmorillonitic and vermiculitic clays above temperatures of 110°C has been rather elegantly shown by use of infrared spectroscopy. Fripiat et al. (1960) have followed the dehydration of homo-ionic montmorillonites and vermiculites with infrared and x-ray techniques. Even though $d(001)$ spacings collapsed to less than 10Å at 150°C , these workers observed "free water" at temperatures up to 400°C . This residual water was thought to occupy the empty hexagonal holes in the surface oxygen sheets of the lattice. Dehydration of the clay system was shown to be a function of both the cation and type of mineral. It was also shown that dehydroxylation of the clay lattice is initiated before dehydration is complete, showing the extreme affinity of the exchangeable cation for water of hydration. Using thinner clay films, Russell and Farmer (1964) have obtained similar results with the exception that the residual water was lost at somewhat lower temperatures. However, they noted a better correlation between firmly held water and the exchangeable cation than was noted by Fripiat et al. (1960). Further evidence that residual water exists on base saturated clay minerals and that its reactivity is a function of the exchangeable cation is presented by Mortland et al. (1963).

1911

1912

Studying ammonia adsorption, these researchers noted the conversion of adsorbed ammonia to ammonium at temperatures up to those of lattice dehydroxylation. They noted that residual water was the only source of protons in base saturated systems. Turning to water vapor adsorption on colloidal size material, Benesi and Jones (1959) observed that a monolayer did not form on a silica gel. Therefore, capillary condensation occurred prior to the formation of a true monolayer. They also concluded that water vapor was physically adsorbed since the fundamental ν_2 vibration of adsorbed water was very similar to that of liquid water. Studying Na-zeolite, Szymanski et al. (1960) obtained similar results when the relative humidity was greater than 30 per cent. However, when the relative humidity was less than this, the fundamental 1640 cm^{-1} absorption band shifted to 1690 cm^{-1} showing the water to be strongly associated with the adsorption sites (Na^+ ions).

Mering (1946) noted the stepwise hydration of montmorillonite and pointed out that the equilibrium water content at a given relative humidity was a function of the saturating cation. From x-ray data he observed that Ca-montmorillonite forms a two layer hydration complex as soon as the octahedral hydration sphere of the calcium ion is satisfied (18% relative humidity); whereas, Na-montmorillonite will form a complete monomolecular layer of water between the platelets. He suggests that the first layer of water in

Na-montmorillonite may be hexagonal in nature, but doubts that the silicate lattice possesses much "organizing action." The x-ray and water adsorption data of Mooney et al. (1952) showed that changes of slope in the adsorption isotherm and changes in the number of layers of water between platelets occurred simultaneously. As others have done, Puri and Murari (1964) attempted to calculate the surface area of soils and clays from a single point on the water isotherm. They concluded that a relative pressure of 0.53 was required to form a monolayer of water, a value essentially twice that noted by others (Quirk, 1955). Noting considerable data that suggests the amount of water adsorbed by various clays is dependent upon the saturating cation, Quirk (1955) quite appropriately stated that when ". . . polar molecules are being adsorbed by clays it does not seem valid to speak of a monolayer." In a series of papers, Orchiston (1953, 1954, 1955, 1959) noted that the adsorption isotherms were sigmoidal in form indicating a multimolecular adsorption of a physical nature. He proposed the following mechanism for water vapor adsorption on clays: a) first, water clusters around the active adsorption sites (exchangeable cation); b) these clusters grow, finally running together to approximate "monolayer" coverage, with some multilayering around the active sites; and c) condensation occurring with further adsorption. At this point, the heat of adsorption approaches the heat of liquidification. Gillery (1959) studied the

desorption of water from Na- and Ca-saturated montmorillonids. His results were very similar to those already discussed except that he observed a stable one-layer (12.3 Å) Ca-saturated species at 5 per cent relative humidity. Considering the rates of adsorption of water vapor on degassed Arizona bentonite, Anderson and Sposito (1963) concluded that water was probably being chemisorbed onto the exchangeable cation.

In conclusion, it appears well verified that some type of stepwise hydration of expanding alumino-silicates does occur as water is adsorbed on dry clay. Also, it is obvious that the hydration of clays is a function of the exchangeable cation, particularly that moisture retained against heating to 100°C. It is this water that has proved to be so chemically reactive.

Adsorption of organic molecules.

Since it is not the intent of this study to consider the adsorption of ionic species, this review will not consider the vast amount of literature concerning the adsorption of ionic or easily ionizable organic molecules. For the most part, they are adsorbed by straight-forward Coulombic forces. Adsorption of nonionic organic molecules is more complex and not as well understood. The forces involved in adsorption of undissociated molecules are principally H-bonding and van der Waals type forces. One of the more extensive series of studies on the adsorption and retention of nonionic organics on montmorillonite has been conducted by Brindley

and his colleagues. Using Na-, Ca-, and Mg-montmorillonite, they (Brindley and Ruston, 1958) noted no difference in the adsorption of the polyethylene glycol ester of oleic acid from aqueous suspension. It was concluded that the adsorption processes were the same for all three species. An aliphatic chain, 5-6 carbon atoms in length, was required to initiate adsorption of the various alcohols, glycols, acetones, and ketones from aqueous suspensions (Hoffmann and Brindley, 1960). Adsorption increased with increasing chain length and CH activity. CH activity is increased by increasing the number of electron withdrawing groups adjacent to a methylene group. From x-ray data and molecular models, Brindley and Hoffmann (1962) concluded that polar aliphatic molecules are oriented with the plane of the carbon chain parallel to the silicate surface. This would be anticipated from the tetrahedral coordinating nature of carbon, if the assumption is made that the polar group is bonded to the clay surface. Aliphatic molecules without polar groups appeared to have the plane of the carbon atoms perpendicular to the silicate surface. The reason for this orientation was not clear unless it would provide a more favorable organic-organic interaction.

Infrared spectroscopy (IR) was used by Tensmeyer et al. (1960) to study the fundamental vibrations of ketones adsorbed on Ca-montmorillonite. Two observations were made with respect to adsorbed ketones: a) no change in peak position



was observed between the adsorbed and nonadsorbed states, and b) spectra of adsorbed, one layer complexes were very similar to those of the solid material, suggesting solidification at temperatures above the normal melting point. Therefore, adsorption of ketones is physical in nature and organic-organic interactions are the predominant forces involved. The extinction coefficient of all vibrations decreased exponentially with increased surface coverage, save the 2913 cm^{-1} symmetrical methylene stretching vibration (Hoffmann and Brindley, 1961b). Folman and Yates (1959) also noted little change in the apparent extinction coefficient of the C-H stretching vibration of acetone adsorbed on porous silica glass. The absence of change in the extinction coefficient with increasing surface coverage can be considered evidence that CH groups are not directly involved in adsorption mechanism.

Monohydric alcohols.

Normal monohydric alcohols longer than ethanol will extract interlamellar water from halloysite and montmorillonite (MacEwan, 1948). Nonpolarizable molecules will not form layer complexes since the energy liberated by adsorption is insufficient to overcome the Coulombic attraction between the saturating cation and the clay surfaces. MacEwan (1948) concluded that the adsorbed layers were extremely labile and liquid in nature for the following reasons: a) close packing of the molecules is not required to fit x-ray data;

b) ease exchange of one complex for another by simply washing with another miscible liquid; and c) no simple integral number of molecules existed per unit cell as expected in a crystalline system. This suggests a two-dimensional liquid, the same conclusion suggested by Martin (1962) for adsorbed water. Working with vermiculite and three montmorillonites, Barshad (1952) found that interlayer expansion was greatly dependent upon the extent of dehydration prior to contact with n-alcohols, acetone and ether. Expansion also decreased with decreasing lattice charge. Glaeser (1954) studied the vapor phase adsorption of methanol, ethanol, acetone, and water on Ca- and Na-montmorillonite. She observed that the amount of adsorption and the ability to retain these compounds was a function of the exchangeable cation. Two lines of proof were presented: 1) the higher the ionization potential, the greater the adsorption, because of the increased ability of the ion to capture d-orbital electrons of oxygen and hence complex organics; and 2) the greater the exchange capacity, the greater the adsorption, because of the presence of more cations. She concluded that C-H...O-clay bonds (discussed later) were not sufficient to explain the differences observed. Barrer and MacLeod (1954) studied the vapor adsorption of ethanol, water, ammonia and pyridine on degassed montmorillonite. The first additions were adsorbed on the external surfaces. At a given threshold pressure, the penetration forces of the molecule overcome the attractive

forces between lamellae allowing interlamellar adsorption. Finally, as $P/P_0 \rightarrow 1$, capillary condensation occurs and the amount sorbed tends to increase without limit. If adjacent layers are held apart by tetra-alkyl ammonium ions, interlamellar sorption occurs with the first additions of gas (Barrer and Reay, 1957). Since intermolecular O-H...O bonding occurs in liquid alcohols, Emerson (1957) suggests that O-H...O-clay bonds would be more reasonable than C-H...O bonds for interlamellar adsorption. The O-H...O bond must be linear and should have a tetrahedral angle since the surface oxygens are already tetrahedrally bonded to two silicon atoms. Using van der Waals dimensions and known bond angles, the observed and calculated d-spacings for such a configuration are in good agreement. For one layer complexes, the d-spacing for methanol was 12.7 Å and for higher polyvinyl alcohols, the value was 13.6 Å. These values are essentially the same as those observed by Brindley and Ray (1964) for primary monohydric alcohols ranging in length from two to eighteen carbon atoms, as well as earlier values reported by MacEwan (1948), Barshad (1952), and Glaeser (1954). Using Ca-montmorillonite and x-ray diffraction techniques, Brindley and Ray (1964) observed that the d-spacing for a one layer alcohol complex at temperatures above its melting point was larger than that observed for temperatures below the melting point. The observed phenomena were reversible and suggested that re-orientations occur in organic-clay complexes

as a fun
ations t
from the
configur

Gr
pressure
evacuati
observed
aluminum

CH

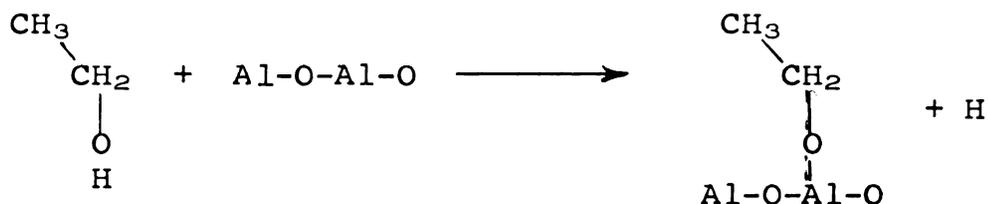
If equili
than 160°
and 1488
symmetric
according



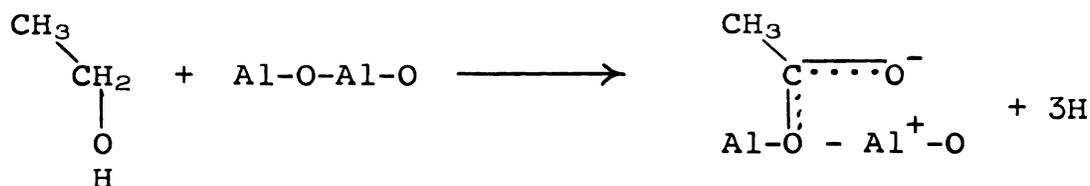
These resu
C¹³ isotope
results wer
groups of r

as a function of temperature. They propose various configurations to fit the observed x-ray data, which differ slightly from the Emerson model, but maintain the same O-H...O-surface configuration.

Greenler (1962) exposed Al_2O_3 to ethanol vapor at a pressure of 25 mm. Hg. After equilibration at 35°C and evacuation, a series of IR absorbing vibrational bands were observed that correspond very closely to the spectrum of aluminum ethoxide and suggested the reaction:



If equilibration is carried out at temperatures greater than 160°C , two new bands appear in the IR spectrum at 1572 and 1466 cm^{-1} which were assigned to the asymmetric and symmetric vibrations of "acetate-like" surface compounds according to the equation:



These results were confirmed by use of deuterated (OD) and C^{13} isotopes of ethanol and exposure to D_2 gas. The same results were presented by Boreskov et al. (1964). Both groups of researchers obtained similar results for $\text{Al}_2\text{O}_3\text{-MeOH}$

interacti
surface c

Dihydric a

Bras

base excha

and expel

the uncert

distance f

of a surfa

a strong C

for variou

expected,

are imposs

C-H...O-su

ing energy

However, T

proof of C

montmorillo

glycol. A

of the symm

with no sho

not shift.

Brindley (1

wardite rema

length incre

dimensional

interactions. Uvarov (1963) postulated the same Al-O-C₂H₅ surface compound using a surface deuterated alumina.

Dihydric alcohols.

Bradley (1945) observed that glycols do not enter into base exchange, but can be adsorbed from dilute solutions and expel interlamellar water from montmorillonite. Admitting the uncertainties of Fourier sketches, he noted that the distance from the center of the aliphatic chain to the center of a surface oxygen is about 3.3-3.6 Å. This is too long for a strong O-H...O-surface bond and does not vary significantly for various glycols and polyglycols where such would be expected, nor with their dimethyl ethers where such bonds are impossible. For these reasons, he concluded that C-H...O-surface bonds are important and comparable in bonding energy to O-H...O bonds in natural water systems. However, Tettenhorst et al. (1962) could not observe any good proof of C-H...O-surface interactions from IR studies of montmorillonite-polyalcohol complexes, including ethylene glycol. A slight decrease in the intensity and broadening of the symmetrical CH₂ vibration suggests a weak C-H...O bond with no shortening of the bond, since the peak position did not shift. Studying six different dihydric alcohols, Brindley (1956) noted that the 001 lattice spacings of allevardite remained essentially constant even though the chain length increased from two to twelve carbon atoms. A one-dimensional Fourier synthesis showed the plane of the carbon

atoms of ethylene glycol to be perpendicular to the basal plane of the lattice.

Ethylene glycol has been used extensively for specific surface determinations because of its apparent ability to form a monomolecular film on clay surfaces. All of these procedures and modifications of the one proposed by Dyal and Hendricks (1950) have involved calibration techniques between the cross-sectional area of the molecule and the surface area of known specimens. One of the major problems involved has been that of controlling the vapor pressure at levels low enough to obtain only monolayer coverage on the clay surface. This aspect, as well as various procedures, has been recently reviewed by Mortland and Kemper (1965).

In ethylene glycol-water-montmorillonite systems Mackenzie (1948) observed a constant 17.1 \AA basal spacing over a wide range of glycol:water ratios. Similarly, Tettenhorst et al. (1962) observed that the basal spacings obtained with ethylene glycol- or glycerol-montmorillonite complexes were independent of the initial water content.

Morin and Jacobs (1964) have also shown no difference in the amount of ethylene glycol adsorbed by clays when the initial moisture content ranged from 1 to 12 per cent. On the other hand, Martin (1955) observed a 56 per cent increase in the ethylene glycol adsorbed by a Ca-montmorillonite dried over P_2O_5 compared to that adsorbed by a moist sample. He concluded that clay has the same affinity for ethylene glycol

as for wa

samples w

Ho

montmoril

glycerol

drying be

alcohols.

with Na,

amount of

pendent o

montmoril

clusion, v

cations we

In c

(1352) obs

ethylene g

bentonite

samples as

Dyal and He

ethylene gl

of the sate

led Quirk

by ethylene

other polar

on the clay

D.T.A. data

as for water and that the reduced glycol retention in moist samples was a result of fewer "free" adsorption sites.

Hoffman and Brindley (1961a) have shown that Mg-montmorillonite will adsorb very little ethylene glycol or glycerol from aqueous solutions but forms complexes upon drying because the water evaporates much faster than the alcohols. They also reported that montmorillonite saturated with Na, Ca, or Mg showed no significant differences in the amount of organics adsorbed. Hence, adsorption is independent of the exchangeable cations for these homoionic montmorillonites. MacEwan (1948) had reached the same conclusion, while agreeing with others that the exchangeable cations were influential in clay-water complexes.

In contrast to these findings, Bower and Gschwend (1952) observed considerable variation in the amount of ethylene glycol retained by different homoionic Wyoming bentonite systems. This variation was observed for preheated samples as well as those not heated prior to adsorption. Dyal and Hendricks (1952) also found that the amount of ethylene glycol adsorbed by Wyoming bentonite was a function of the saturating cation. It was this type of results that led Quirk (1955) to conclude that surface areas determined by ethylene glycol retention may be in error since it, like other polar molecules, tends to be adsorbed around cations on the clay surface. Recently, McNeal (1964) concluded from D.T.A. data of glycolated montmorillonite systems that ethylene

glycol re

and hence

montmorill

water-mon

ation of

cation ma

the glyco

the clay

that the

to two mo

two molec

These resu

who noted

with the c

Work

ethylene g

lonite, Ju

adsorbed on

montmorillo

In co

tion and re

alcoholic g

able cation

some data t

water is in

the adsorpt

on clay sur

glycol retention is dependent upon the saturating cation and hence, is held at various energy levels. The glycol-montmorillonite D.T.A. tracings were similar to those for water-montmorillonite complexes, suggesting that the association of these two polar molecules with the exchangeable cation may be similar. If he made the assumption that all the glycol retained in Na-systems was adsorbed directly on the clay surfaces, then from retention data he calculated that the "excess" glycol present in the Ca-systems amounted to two molecules per calcium ion. He concluded that these two molecules were associated directly with the calcium ion. These results are in agreement with those of Mortland (1954) who noted that the total specific surface correlated well with the cation exchange capacity of both soils and clays.

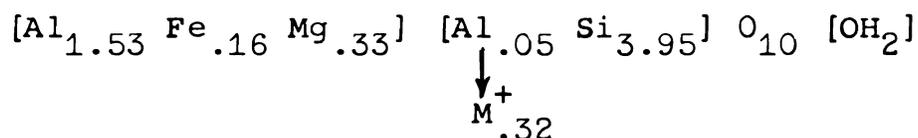
Working with vapor adsorption of the bromide analog of ethylene glycol, ethylene dibromide, on dehydrated montmorillonite, Jurinak (1957) showed that ethylene dibromide is adsorbed only on the external surfaces of Mg-, Ca- and Na-montmorillonites when compared to ethylene glycol retention.

In conclusion, it appears very likely that the adsorption and retention of simple organics, possessing functional alcoholic groups, is in some way influenced by the exchangeable cation and/or the force fields of these ions, despite some data to the contrary. Whether the presence of adsorbed water is influential, and in what way it may be involved in the adsorption and retention of mono- and dihydric alcohols on clay surfaces is even less clearly defined.

METHODS AND PROCEDURES

Materials and sample preparations

The montmorillonite used in these studies was H-25 from the John C. Lane Tract, Upton, Wyoming, and was supplied by the Ward's Natural Science Establishment. This was a subsample of the Wyoming bentonite recently characterized by Ross and Mortland (1966). From chemical analyses, they calculated the formula to be:



Homoionic clays were prepared by treating the < 2.0 μ fraction with appropriate chloride salt solutions in excess of the cation-exchange capacity. After flocculation, the supernatant was removed and the procedure repeated three times. The suspensions were then washed five times by centrifugation to remove excess salts. They were then considered free of excess salts as confirmed by a negative AgNO₃ test for chlorides in the supernatant. Dialyzing against distilled water was avoided since infrared (IR) results indicated that slight dissolution of the clay lattice occurred before the resistance of the dialyzate reached that of distilled water.

The
prepared
pension
Copper f
with a p
may reduc
never sto
were prep

The
stored ov
Anhydrous
chemical
England N
grade obt
less than
"glycol."

Apparatus

A so
adsorption
which was
connected
components
support cla
specimen h
a calibrat
suspended

Thin self-supporting clay films (~ 2 mg./cm²) were prepared by evaporating 10 ml. of a freshly prepared suspension of appropriate density in aluminum foil dishes. Copper films were prepared by using aluminum dishes lined with a polyethylene film. To minimize side reactions, that may reduce the purity of the films, clay suspensions were never stored for longer than two months and fresh films were prepared immediately prior to use.

The ethyl alcohol (ethanol) used was absolute and was stored over anhydrous MgCO₃ in an air-tight container. Anhydrous CH₃CH₂OD and D₂O were obtained from the Volk Radiochemical Co., while CH₃CD₂OH was obtained from the New England Nuclear Corp. The ethylene glycol used was reagent grade obtained from the J. T. Baker Chemical Co. It contained less than 0.08% water and will simply be referred to as "glycol."

Apparatus

A schematic diagram of the system used in the ethanol adsorption studies is presented in figure 1. This system, which was situated in a constant temperature room (20°C) and connected to a rotary vacuum pump, contained four basic components: 1) a vapor source, 2) a detachable IR cell to support clay films for spectroscopic examination, 3) a specimen holder for x-ray diffraction examination, and 4) a calibrated quartz helix balance from which clay films were suspended to obtain sorption data. Manometer readings as

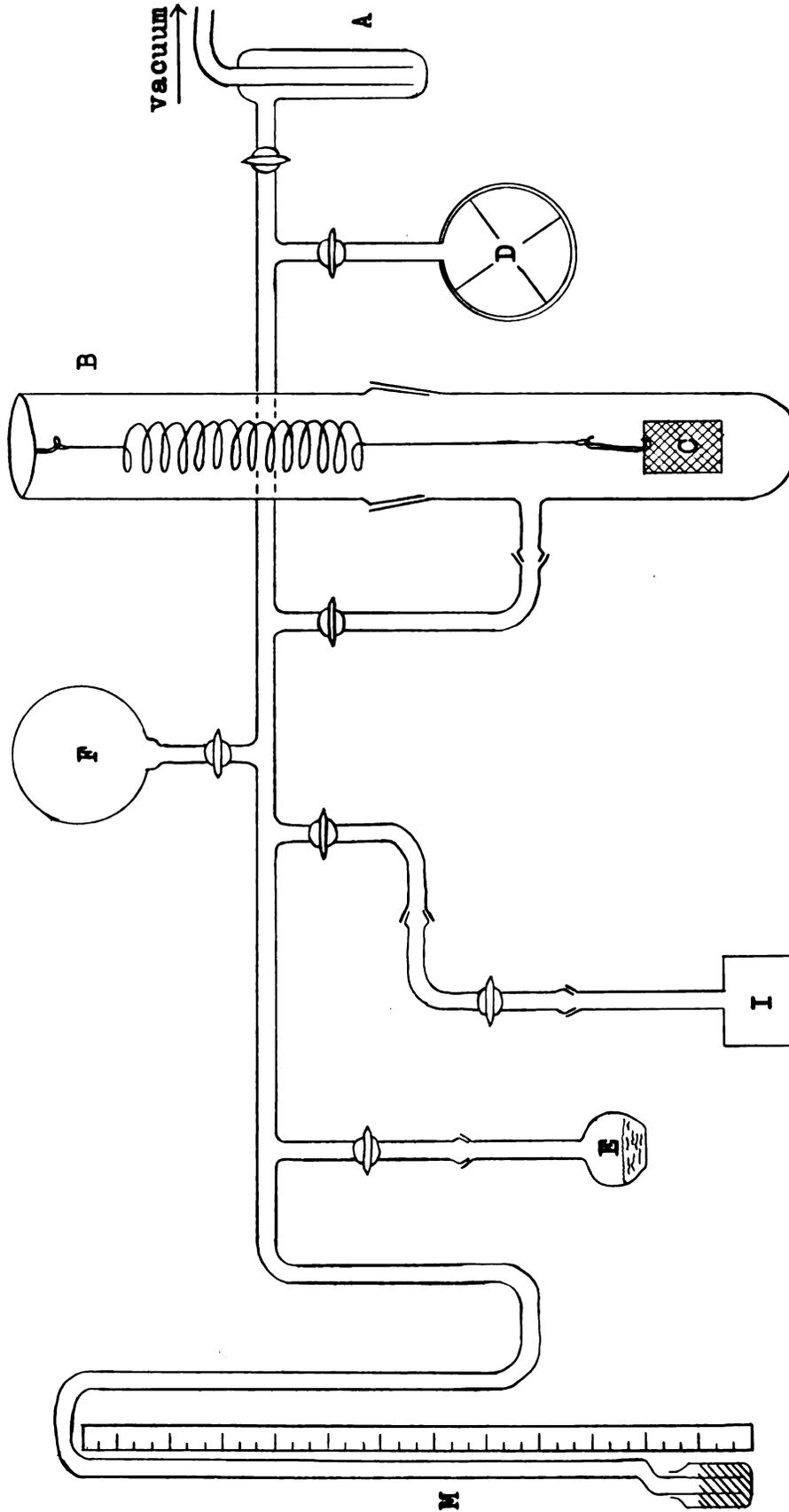


Figure 1. Schematic diagram of the system used for studying the adsorption of ethanol vapor on thin clay films. A, trap immersed in liquid nitrogen; B, quartz helix balance; C, clay film; D, x-ray chamber; F, ballast flask; I, infrared cell; E, ethanol source; M, mercury manometer.

well as displacement measurements of the quartz helix were taken with a cathetometer.

Infrared spectroscopy.

An evacuable brass cell fitted with sodium chloride windows was used in the work reported. A calibrated thermistor and a 80/20 nickel-chromel resistance wire, capable of heating the cell to 100°C , were components of the brass cell. Infrared spectra (4000 to 600 cm^{-1}) were recorded by a Beckman IR7 spectrophotometer fitted with a sodium chloride prism and grating. The clay films were positioned normal to the beam during scanning operations.

X-ray diffraction.

X-ray data were obtained with a Norelco diffractometer equipped with an evacuable chamber constructed by the R. L. Stone Co. This chamber had a sample holder which could be heated to temperatures up to 1100°C and was equipped with a thermocouple. Values for temperature were obtained from potentiometer readings. The chamber was fitted with an opening which allowed it to be connected directly to the system.

Procedures

Ethanol adsorption - desorption.

Portions of identical clay films were placed in the IR and x-ray sample holders and suspended from the quartz helix. A moisture determination was made on a fourth portion. After degassing by rotary pump against a liquid N_2 cold trap,

the system
vapor pressure
at approximately
used at each
when four
of the quantities
during the
and after
appropriate measurements
scans.

After
subjected to
hours. Periods
necessary
films. Additional
were further
then heated
once more
to rehydrate
humidity.
appropriate
replaced by
Glycol added
Clay
them in a
After evaluation

the system was exposed to successively increasing ethanol vapor pressures up to a relative pressure (P/P_0) of unity at approximately 20°C . A two hour equilibration period was used at each level of ethanol, except at saturation pressure when four hours were allowed for equilibration. Distension of the quartz helix indicated that equilibrium was reached during the first thirty minutes. Initially, after degassing, and after equilibration at each ethanol pressure, the appropriate measurements were taken, including x-ray and IR scans.

After these treatments, the same samples were subjected to degassing against a liquid N_2 cold trap for ten hours. Periodically, the evacuation was interrupted to take necessary readings and make appropriate scans of the clay films. At this point, the films in the x-ray and IR cells were further evacuated while being heated to $\sim 80^{\circ}\text{C}$, scanned, then heated to $\sim 100^{\circ}\text{C}$ for 20 minutes during evacuation, and once more scanned. After degassing, the films were allowed to rehydrate in the atmosphere of approximately 40% relative humidity. Again, the films were weighed and scanned at appropriate time intervals until all the ethanol had been replaced by water, as indicated by IR data.

Glycol adsorption - desorption.

Clay films were saturated with glycol by suspending them in a vacuum desiccator over a free glycol surface. After evacuation for ten minutes, the desiccator was placed

in a 115
ment, th
cooling,
atmosphe
and IR a
periodic
rehydrat

Determin

The
obtained
helix, a
adsorbed
tion of
weights o
net value

material
In order
organic m
to estima
rection t

This
and divid
placed in
helix, an
portion.
periodica

in a 115°C oven for 24 hours. Following the heat treatment, the desiccator was allowed to cool to 20°C. After cooling, the glycol saturated films were exposed to the atmosphere (20°C and 40% relative humidity). Weight, x-ray, and IR analyses were made immediately upon exposure and periodically with time as the clay films were allowed to rehydrate.

Determination of state of hydration.

The values for the weight of ethanol adsorbed by clay, obtained from the distension data of the calibrated quartz helix, are actually net values representing the ethanol adsorbed minus the water displaced. In the case of rehydration of films saturated with either ethanol or glycol, the weights obtained by use of an analytical balance are also net values representing the weight of adsorbed organic material plus the weight of water present at any given time. In order to arrive at a value for the absolute quantity of organic material present at any given time, it was necessary to estimate the amount of water present and apply this correction to the experimentally obtained net value.

This was accomplished by taking identical clay films and dividing them into three portions. One portion was placed in the IR cell, another was suspended from the quartz helix, and a moisture determination made on the 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 reading from the quartz helix, it was possible to make a plot of peak intensity versus amount of water present. The plots for Cu-, Al-, Ca-, Na-, and NH₄- montmorillonite are presented in figure 2. Since water retained by montmorillonite in the air-dried state is known to exist in two phases (Russell and Farmer, 1964), it was necessary to plot peak area rather than optical density of the water deformation band. The areas were determined by tracing them on tracing paper and then cutting out the areas and weighing them on an analytical balance. It should also be pointed out that the origin is considered a theoretical point and is based upon the assumption that dehydration of montmorillonite is complete at 300°C. To a first approximation, this appears to be a reasonable assumption since most differential thermal analysis data (Greene-Kelly, 1957) indicate that the water of hydration is lost at temperatures less than 300°C. In the case of NH₄-montmorillonite, the moisture determinations were based on 110°C and graphical extrapolation techniques used to determine the water loss between 110° and 300°C, since NH₄-clays decompose in this temperature region.

A Lambert-Beer's type plot using the origin and the peak optical density of the air-dried film was found to be unreliable. This was expected since Folman and Yates (1959) had observed an exponential decrease in the apparent extinction coefficient of the N-H stretching vibration of ammonia

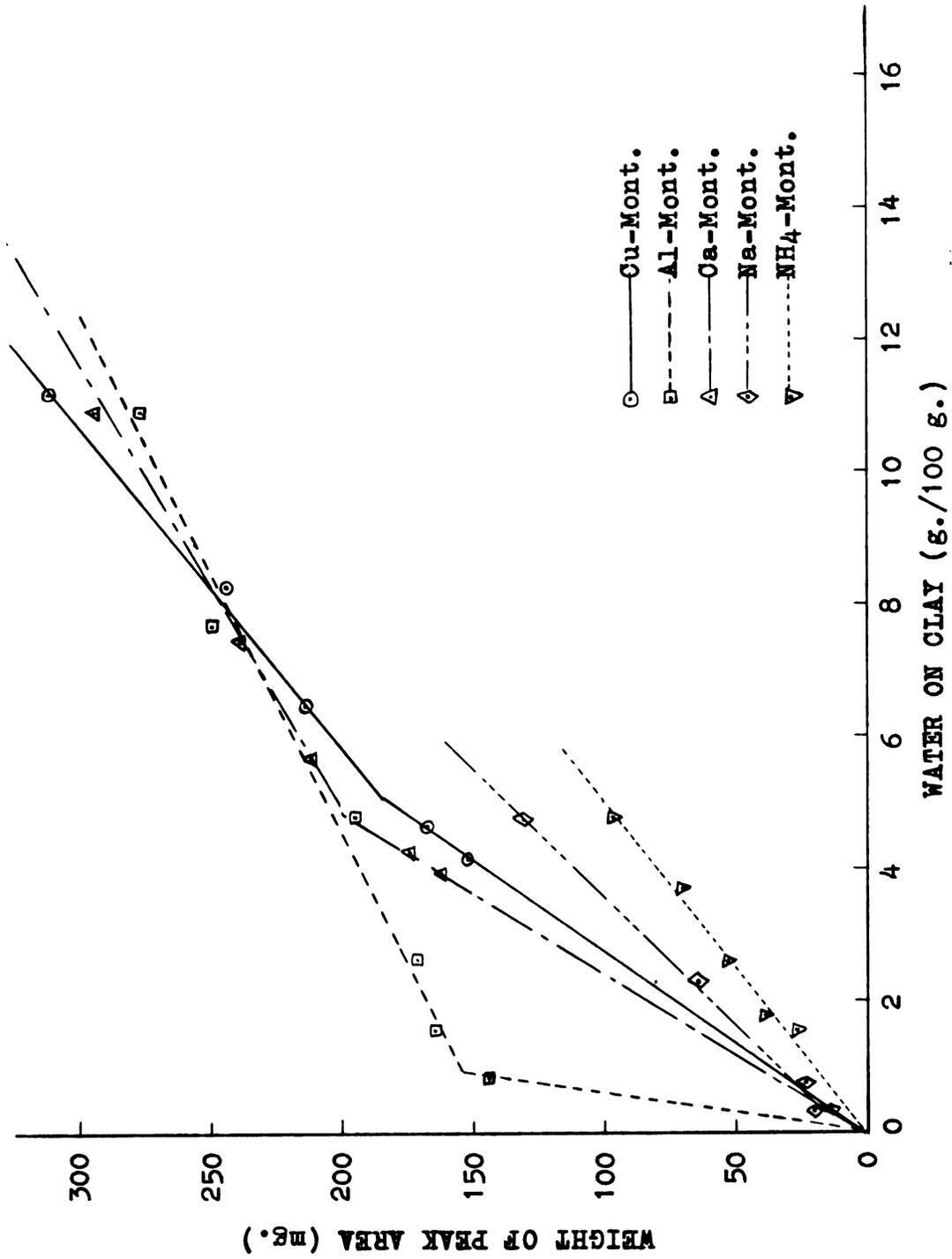


Figure 2. Relationship between the water adsorbed on homionic montmorillonite (300° basis) and the area of the 1650-1600 cm⁻¹ deformation band of water.

with increasing surface coverage of porous silica glass. They also reported an increase in the apparent extinction coefficient of the C-H stretching vibration of methyl chloride and acetone with increasing surface coverage. Likewise, Hoffmann and Brindley (1961b) noted an exponential decrease in the extinction coefficient as the surface coverage of Ca-montmorillonite by 2,5-hexandione and 2,5,8-nonanetrione increased. This simply says that with increased surface coverage, the molecules are less energetically held, resulting in less perturbation and a smaller extinction coefficient.

The curves presented in figure 2 clearly demonstrate two well documented phenomena: a) the two phase nature of the rather tightly bound water of hydration, and b) the differential effect of the saturating cation on this water, particularly that water retained at 110°C.

The weights of water, ethanol, and glycol presented in these studies are based on clays dried at 300°C.

RESULTS AND DISCUSSION

Ethanol adsorption - desorption studies

The infrared absorption frequencies of ethanol in both the pure and adsorbed states are given in table 1, as well as the band assignments for the various vibrational modes. It should be pointed out that the cited vibrational frequencies of pure ethanol are the same as those noted in this study. The vibrational bands shown for adsorbed ethanol represent an average value for the various homoionic clay systems studied. The broad O-H stretching band of adsorbed ethanol in the 3400-3310 cm^{-1} region of the spectrum is somewhat overlapped by the O-H stretching band of adsorbed water. Assignment of the O-H in-plane deformation vibration of ethanol was a point of uncertainty for a number of years. Plyler (1952) assigned this vibration to the observed 1391 cm^{-1} band. However, with the use of deuterioethyl alcohol (EtOD), 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 the C-H and O-H bending modes. Upon dilution, less interaction occurs and these bands separate into a 1384 cm^{-1} C-H bending and a 1250 cm^{-1} O-H deformation vibration. When deuterated, the 1250 cm^{-1} band is removed to 895 cm^{-1} (Stuart and Sutherland, 1956), while the 1384 cm^{-1} band

Table 1. Infrared frequencies of pure and adsorbed ethanol.

Infrared bands		Mode	References
Adsorbed (observed)	Pure		
-----cm ⁻¹ -----			
3310-3400	3680 (vapor)	OH stretch	Plyler (1952)
	3000-3500 (liquid)	OH stretch	Coburn & Grunwald (1956)
2984-2990	2984	asym.CH ₃ stretch	Drushel <u>et al.</u> (1963)
2915-2938	2936	asym.CH ₃ stretch	
	2898	sym. CH ₃ stretch	
---	1923 (vapor)	CO+CC stretch	Plyler (1952)
1478-1485	1467	CH ₂ scissoring	Drushel <u>et al.</u> (1963)
	1455	asym.CH ₃ bend	Plyler (1952)
	1400	sym. CH ₃ bend	Barrow (1952)
---	{ 1410 } { 1330 } doublet (liquid)	OH in-plane deformation	{ Stuart & Sutherland (1956) Tarte & Deponthiere (1957)
1265	1243 (vapor)		
---	1070	CO stretch	Krimm <u>et al.</u> (1956)
---	885	CC stretch	

remains unchanged. These results were confirmed the following year by Tarte and Deponthiere (1957). It should be noted that any band occurring in the 3700-3600 cm^{-1} and the 1200-600 cm^{-1} regions of the spectrum are masked by strong fundamental vibrations of the clay lattice.

Hydrated Cu-montmorillonite.

When air-dried Cu-montmorillonite is exposed to increasing pressures of ethanol, the water of hydration is displaced as shown by the decrease in absorbance of the 1632 cm^{-1} deformation vibration (curves A, B and C, figure 3). The replacement of water by ethanol is probably a mass action type reaction resulting in a moisture content of less than 0.7% at a relative pressure of unity.

The reduction of absorbance of the 1632 cm^{-1} band is accompanied by a splitting of the band with a maximum at 1598 cm^{-1} and the development of a shoulder near 1640 cm^{-1} . Such a splitting or separation is indicative of the presence of two phases of water in hydrated Cu-montmorillonite, similar to that proposed by Russell and Farmer (1964) for alkali and alkaline-earth metal-montmorillonite complexes. These two types 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. Upon dehydration, the more loosely held

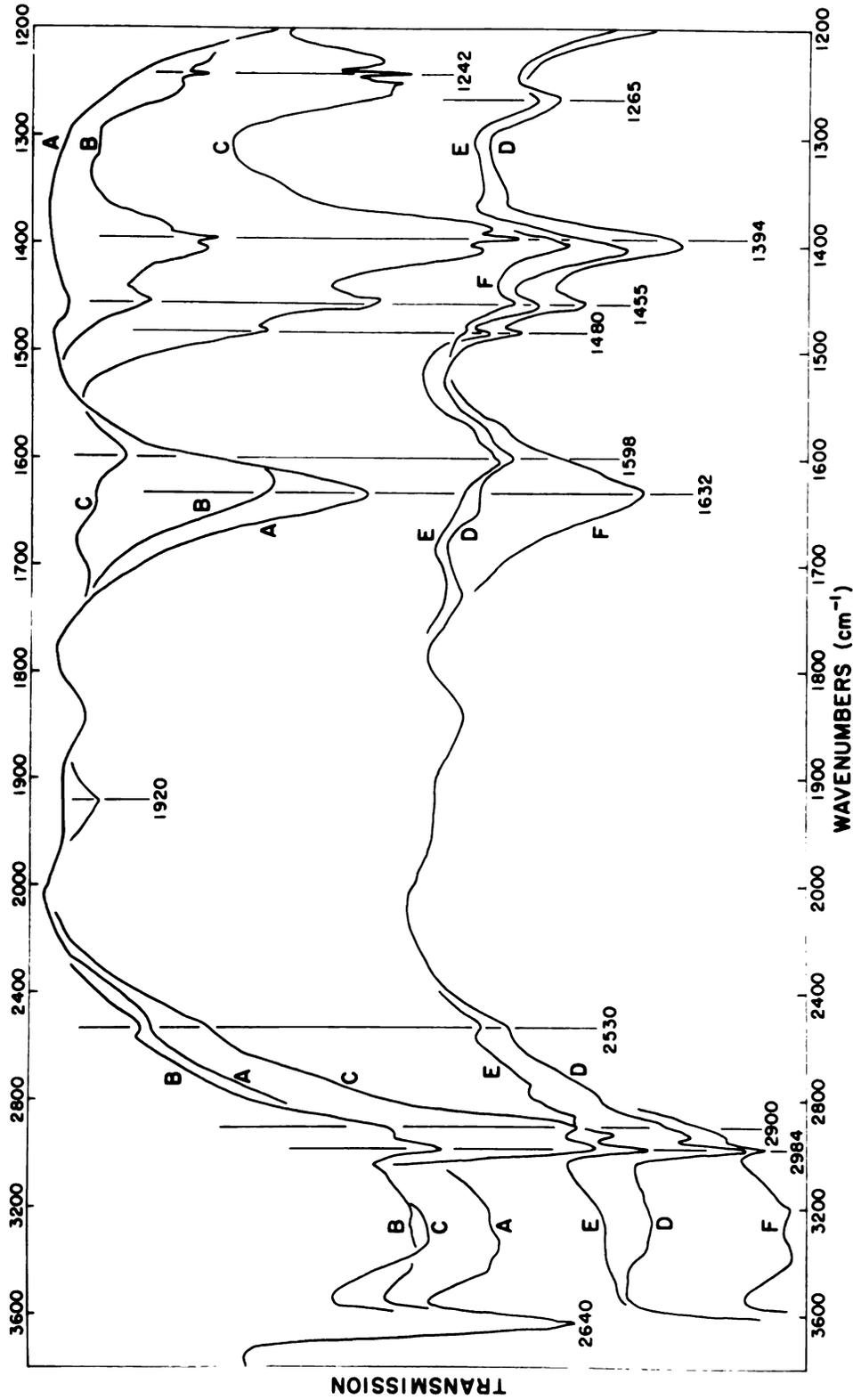


Figure 3. Infrared spectra of Cu-montmorillonite: A, air-dried; B, exposed to 0.15 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hour after EtOH saturation; E, degassed 10 hours after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 24 hours after EtOH saturation, degassing, and heating.

molecules are replaced by ethanol resulting in a weak shoulder at 1640 cm^{-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 (Redington and Milligan, 1962). Two other observations are noteworthy: 1) ordinary, hexagonal ice has been reported to have a deformation band near 1580 cm^{-1} (Ockman, 1958; Haas and Hornig, 1960), and 2) certain hydrated salts have been reported to have bending modes of water at frequencies as low as 1550 cm^{-1} . Some of those reported are $\text{LiOH}\cdot\text{H}_2\text{O}$ at $1586\pm 8\text{ cm}^{-1}$ (Jones, 1954); $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ at 1590 cm^{-1} (Gamo, 1961); and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ at 1550 cm^{-1} (Rundle et al. 1955). Therefore, it appears reasonable to conclude that this residual water is quite energetically bound to the copper 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.

Curves D and E, figure 3, show the retention of ethanol, against 10 hours of degassing and heating to 100°C under vacuum, by the persistency of C-H vibrations in the $3000\text{-}2900\text{ cm}^{-1}$ stretching and $1480\text{-}1400\text{ cm}^{-1}$ deformation regions. It should be noted at this point that the C-H vibration, as well as the alcoholic O-H deformation near 1250 cm^{-1} , in curves

B and C, are predominantly due to vapor phase vibrations of the vapor surrounding the clay film and consequently mask the vibrational character of the adsorbed phase. The asymmetrical CH_3 bending of adsorbed ethanol has shifted to 1403 cm^{-1} from its vapor phase position of 1394 cm^{-1} upon evacuation and heating to 100°C , while the EtO-H bending has shifted from 1242 to 1265 cm^{-1} . This is a shift in the direction and of the order of magnitude expected for ethanol molecules coordinated through the oxygen atom. The 1265 cm^{-1} EtO-H band is intermediate between that found in the pure liquid, which is actually a mixing of CH and OH modes, and that observed in the free vapor state. This suggests that in the adsorbed state there is little possibility of CH-OH interactions and that consequently the 1265 cm^{-1} band is purely EtO-H bending.

The C-H stretching vibrations of adsorbed ethanol are very similar to those found in the pure liquid or gaseous states. Detection of slight frequency shifts in this region is difficult for two reasons: 1) the wavenumber per centimeter of chart paper is one-fourth that used in the deformation region, and 2) the inability to resolve asymmetrical CH_2 , symmetrical CH_3 , and/or symmetrical CH_2 stretching vibrations. A slight shift from 2984 to 2990 cm^{-1} is indicated for the vapor to adsorbed phase transition of the symmetrical CH_3 stretch. In curve E, figure 3, the weak shoulder at 2864 cm^{-1} is a situation where it is possible

to resolve the symmetrical CH_2 stretching mode (Pozefsky and Coggeshall, 1951).

Very little information can be obtained from the O-H stretching region since water and ethanol occur simultaneously on the clay surface. Curve F, figure 3, shows the rehydration of the ethylated Cu-montmorillonite upon exposure to the atmosphere at 20°C and 40% relative humidity for 24 hours. The replacement of ethanol was essentially complete in 70 hours as indicated by the absence of the 1400 cm^{-1} CH_3 deformation band which proved to be the most sensitive vibration to the presence of ethanol in these studies. Thus it can be readily seen that the adsorption of ethanol on Cu-montmorillonite surfaces is a reversible process.

The adsorption isotherm for ethanol on Cu-montmorillonite is presented in figure 4B. The most striking feature of the isotherm (solid line) is the linear relationship existing between the amount of ethanol adsorbed and relative pressure. It should be noted that the solid line represents the absolute or total amount of ethanol adsorbed after being corrected for water loss, while the broken line shows the apparent sorption. This linear relationship indicates that the sum of the forces which must be overcome for adsorption to occur, must vary in a similar manner over the pressure range considered. The components of the total force do vary from one region of the isotherm to another and include such components as the cationic hydration energy, van der Waals

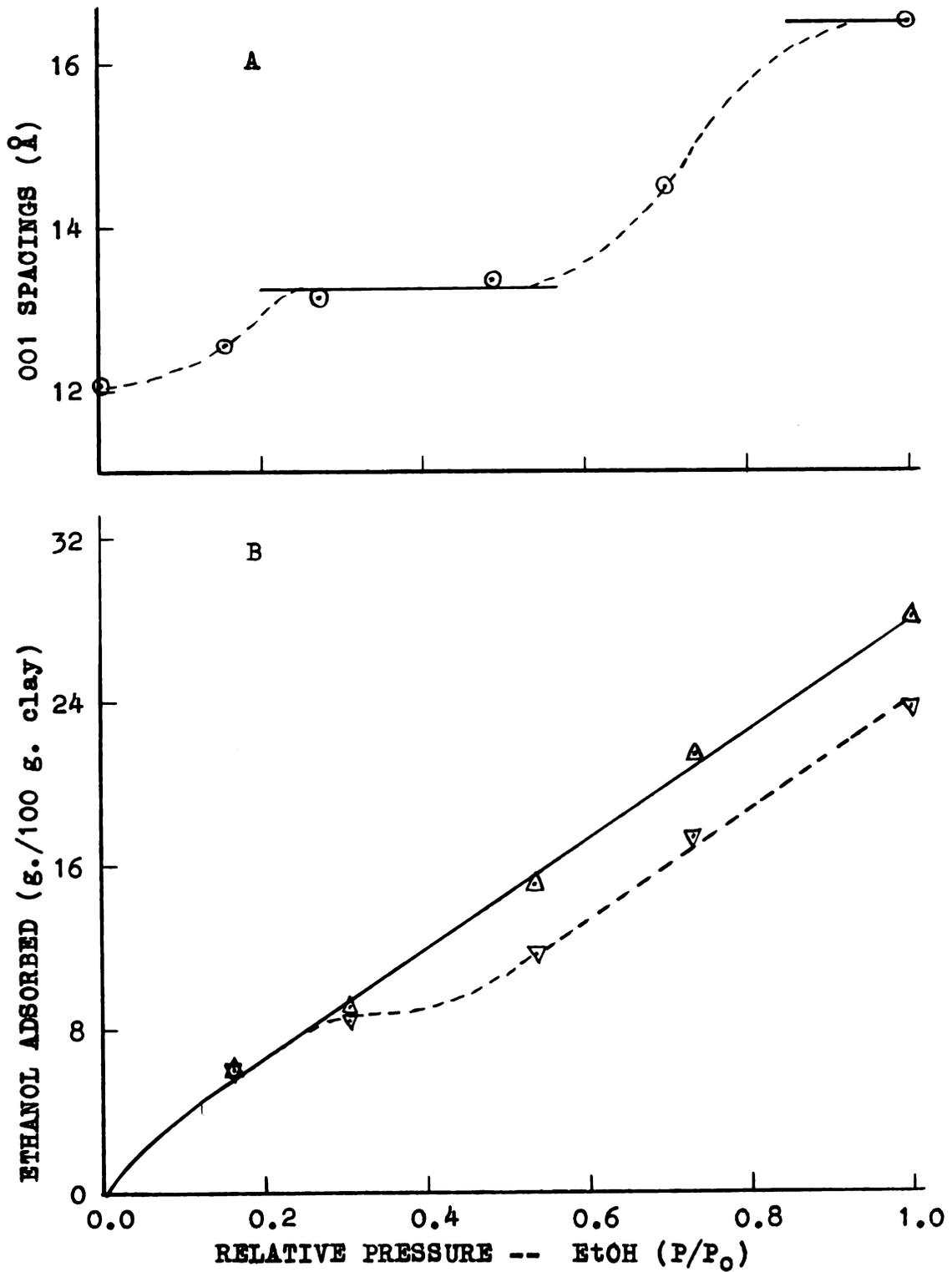


Figure 4. A: 001 spacing vs. relative pressure of EtOH for Cu-mont. solid line, sym. first order peaks; broken line, asym. first order peaks. B. EtOH adsorption isotherm for Cu-mont. Δ , absolute adsorption corrected for H_2O loss; ∇ , apparent adsorption.

type clay-water interactions and/or Coulombic type forces restricting expansion between individual clay platelets.

Vapor adsorption may be divided into three stages.

Initially, adsorption is physical in nature where ethanol is replacing loosely held water on external clay surfaces and in the outer coordination sphere of the copper ion.

Once the relative pressure reaches a critical point such that it can overcome the Cu-H₂O binding energy of the inner hydration sphere, there is an exchange of ethanol for this coordinated water. Evidence for this is the plateau in the apparent adsorption isotherm (broken line) between 0.25 and 0.5 relative pressure where the amount of water dispelled approaches that of alcohol adsorbed. Finally, as saturation pressure is approached, physical adsorption occurs by the filling of voids in interlamellar spaces which are created by expansion between the clay platelets as well as capillary condensation in the micropores between individual clay particles. The coincidence and parallel nature of the apparent adsorption isotherm with respect to the absolute isotherm in the first and final stages of adsorption suggests that the major portion of water was replaced between 0.25 and 0.5 relative pressure. This is simply one way of expressing the experimental observation that the major reduction in the absorbance of the water deformation band (1630 cm⁻¹ region) occurs over this relative pressure range.

A better insight into the restrictive forces imposed by the individual clay platelets can be obtained from a plot of lattice spacings versus relative pressure (figure 4A). Initial adsorption involves slight expansion from 12 to 13.25 Å. The second phase of adsorption is characterized by a rather stable 001 basal spacing where exchange of ethanol for water is occurring in the inner coordination sphere of the copper ion. The final stage of adsorption is characterized by a further weakening of electrostatic forces holding the clay platelet together with a resultant expansion from 13.25 to 16.5 Å.

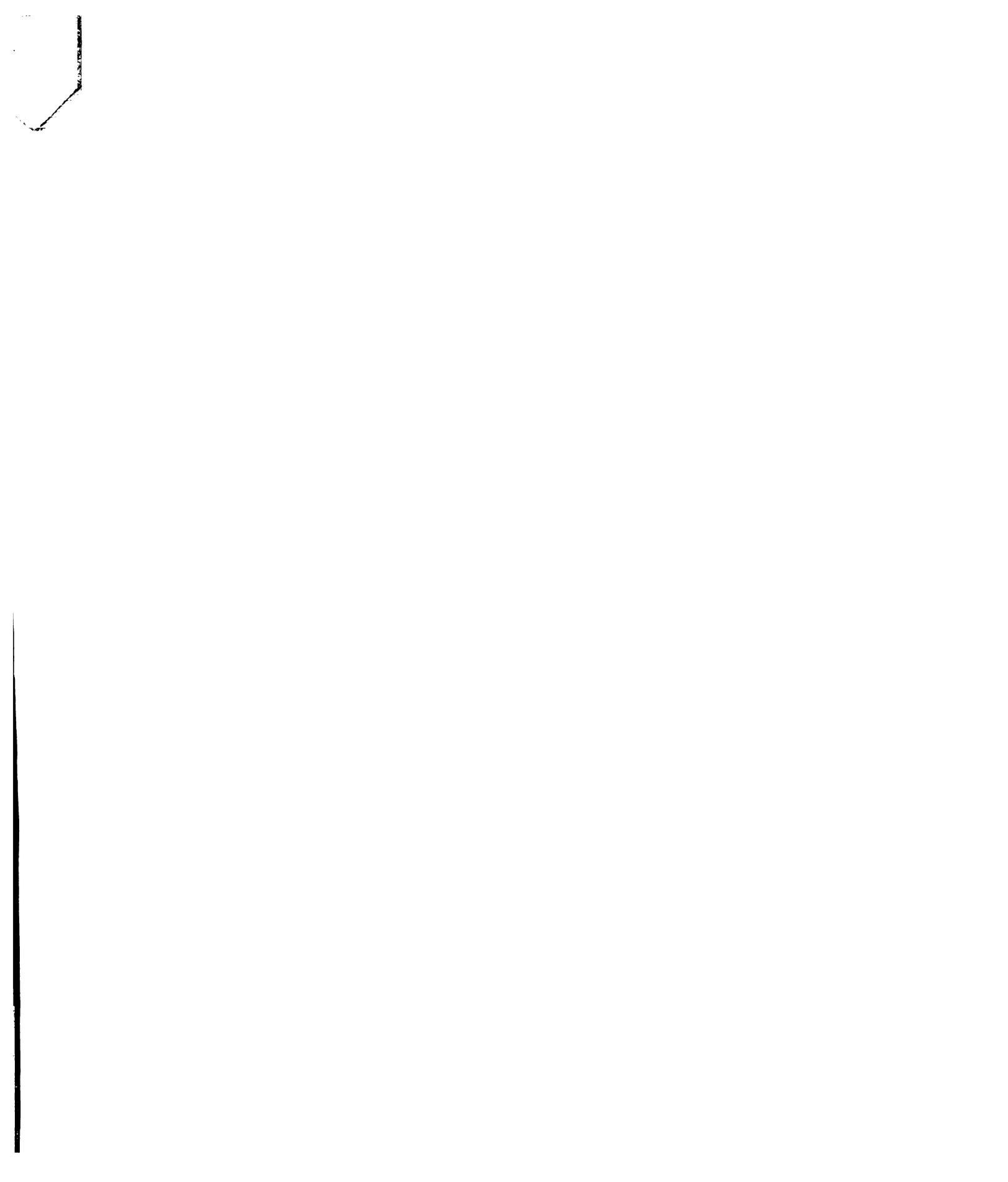
The solid lines in figure 4A represent the relative pressure regions where symmetrical first order x-ray diffraction peaks were observed. These x-ray tracings approach rationality, but as with clay-H₂O systems, strictly rational peaks are seldom observed. The 13.25 Å basal spacing is in very close agreement with results of Brindley and Ray (1964) for a single layer of ethanol between adjacent Ca-montmorillonite platelets. Since this basal spacing is characteristic of the pressure range where exchange of ethanol for water occurs in the inner coordination sphere, it is reasonable to conclude that the apparent stability of the basal spacing can be ascribed to a square planer Cu-ethanol complex. If the CCO plane of the ethanol molecule lies parallel to the oxygen surface of the clay lattice, the maximum layer spacing required for the molecule is theoretically 13.66 Å in the



-direction, using known bond distances and van der Waals radii (Brindley and Ray, 1964). However, by proper geometric-packing a shortening of 0.4 \AA can be achieved at each organic/silicate interface (Brindley and Hoffmann, 1962). Since a total contact shortening of 0.41 \AA at both interfaces is all that is required to fit the x-ray data, it is obvious that a Cu-EtOH coordination complex, with the CCO plane parallel to the lattice surface is geometrically feasible.

A Cu-EtOH coordination complex will explain the type of x-ray data which has been used by many investigators to propose the existence of a monomolecular layer of material between clay platelets. However, this is an entirely different approach than that used by Emerson (1957) and Brindley and Ray (1964) who proposed an alcohol-OH...O-clay type bond for alcohol adsorption on montmorillonite surfaces. It is, however, in agreement with the observation of these studies and those of Tensmeyer et al. (1960) which showed no change in the infrared C-H stretching vibrations upon adsorption. The lack of a shift in these vibrations tend to disprove an earlier theory that C-H...O-clay type interactions are important in the adsorption of polar aliphatic molecules on clay surfaces (Bradley, 1945; MacEwan, 1948).

The symmetrical 001 diffraction peak for a 16.5 \AA spacing is also in agreement with the 16.6 \AA spacing reported by Brindley and Ray (1964) for a double layer ethanol-Ca-montmorillonite complex. In light of the preceding discussion, the transition from a 13.25 to 16.5 \AA basal spacing can be



thought of as a transition of the square planer Cu-EtOH complex to an octahedral complex. This might be visualized as a rotation of the square planer complex from a position parallel to the lattice surface to one essentially perpendicular to the surface, which is followed by the approach of an ethanol molecule on each side to form a distorted octahedral Cu-EtOH coordination complex.

Hydrated Al-montmorillonite.

Curves A, B and C, figure 5, show the dehydration of Al-montmorillonite as the relative pressure of ethanol increases, as indicated by the decreased absorbance of the 1635 cm^{-1} deformation vibration. The frequency maximum shifts to 1650 cm^{-1} upon ethylation of the clay film. In contrast to Cu-montmorillonite, this is a shift to a higher frequency, which is in agreement with the principle that H-bonding of water molecules increases the frequency of its bending vibrations (Hass and Sutherland, 1956). The water deformation band is also characterized by a much broader and diffuse contour than was observed in the case of residual water on Cu-films. An explanation of these apparent anomalies in the behavior of residual water probably lies with the different type of coordination habit of the two species. All residual water molecules remaining on Cu-montmorillonite, having a square planer coordination complex, will be exposed to identical electrostatic forces, both those of the cation and the clay lattice. But, due to the octahedral coordination

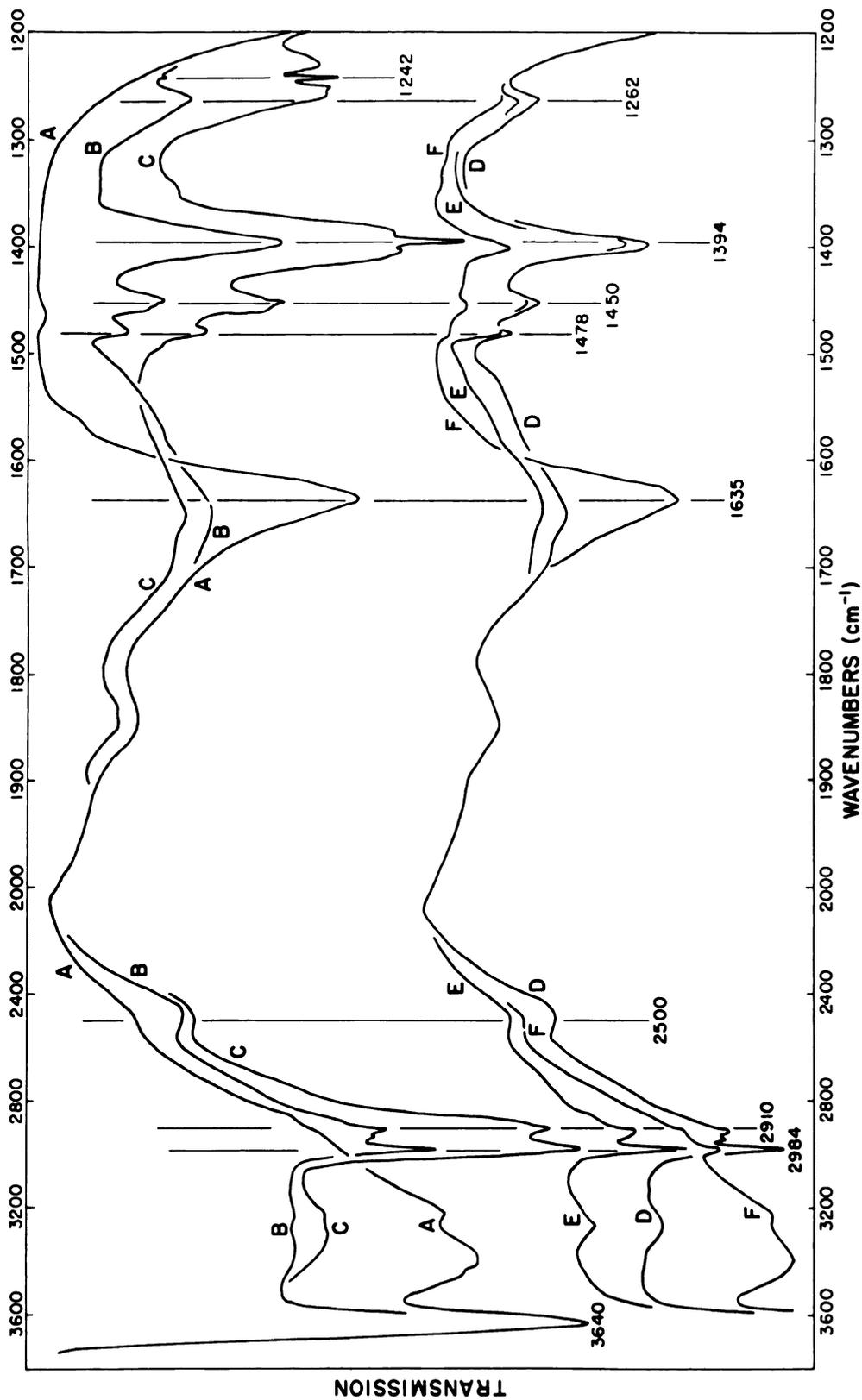


Figure 5. Infrared spectra of Al-montmorillonite: A, air-dried; B, exposed to 0.15 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hour after EtOH saturation; E, degassed 10 hours after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 1 hour after EtOH saturation, degassing, and heating.

habit of aluminum, the residual water molecules on an Al-film will be exposed to a varying clay lattice force field, because of their spatial arrangement.

The C-H and O-H bending and stretching modes of ethanol adsorbed on Al-montmorillonite (curves D and E, figure 5) show no differences from those of Cu-EtOH systems. The amount of ethanol retained against heating and evacuation was essentially the same as suggested by the absorbance of the CH_3 deformation vibration (curve E, figures 3 and 5). However, considerable difference in the time required for rehydration to occur does exist between the two systems. As shown in curve F, figure 5, Al-montmorillonite has lost more ethanol during the first hour of rehydration than Cu-montmorillonite had during 24 hours. Two possible explanations are given that might in part explain this faster exchange of water for ethanol: 1) since the hydration energy of aluminum is more than twice that of copper, a faster H_2O -EtOH exchange would be anticipated; and 2) as mentioned previously, the differential force fields exerted on the various ligands of the Al-complexes would be expected to distort the octahedral complex and thus allow a more rapid exchange.

The shoulder at $\sim 2500 \text{ cm}^{-1}$, which occurs on all curves in figure 5, is assigned to a vibrational mode of water, since it is present in the pure clay-water system. This band also occurs to a lesser extent in Cu- and Na-montmorillonite. Two possibilities arise for the increased intensity of this band

upon dehydration: 1) dehydration reduces the overlapping of other vibrational modes in this region, and 2) as dehydration occurs, the remaining water is more strongly H-bonded, which is accompanied by an enhanced absorbance. Farmer and Mortland (1966) have reported O-H stretching vibrations as low as 2780 cm^{-1} for strongly H-bonded water in Mg-pyridinium complexes of montmorillonite. On the other hand, this band could be assigned to a combination mode of the rocking and bending vibrations, ~ 865 and 1640 cm^{-1} , respectively, of water coordinated to metallic cations (Nakagawa and Skimanouchi, 1964).

A van der Waals type II adsorption isotherm was observed for the adsorption of ethanol on Al-montmorillonite (figure 6B). The plateau between 0.2 and 0.6 relative pressure in both the absolute and apparent isotherms can be easily explained by a combination of two factors. First, a ethanol pressure sufficient to overcome the hydration forces of aluminum has been attained which then allows exchange of ethanol for water in the inner coordination sphere of aluminum. This is shown by the steeper slope of the absolute isotherm with respect to the slope of the apparent isotherm. Secondly, the trivalent nature of aluminum prevents the expansion of clay platelets beyond 13.5 \AA (figure 6A) thus restricting the volume available for ethanol. The final portion of the isotherms between 0.6 and 1.0 relative pressure must then be characterized by multilayer adsorption on external surfaces as well as capillary condensation. Proof of this is also given by the parallel

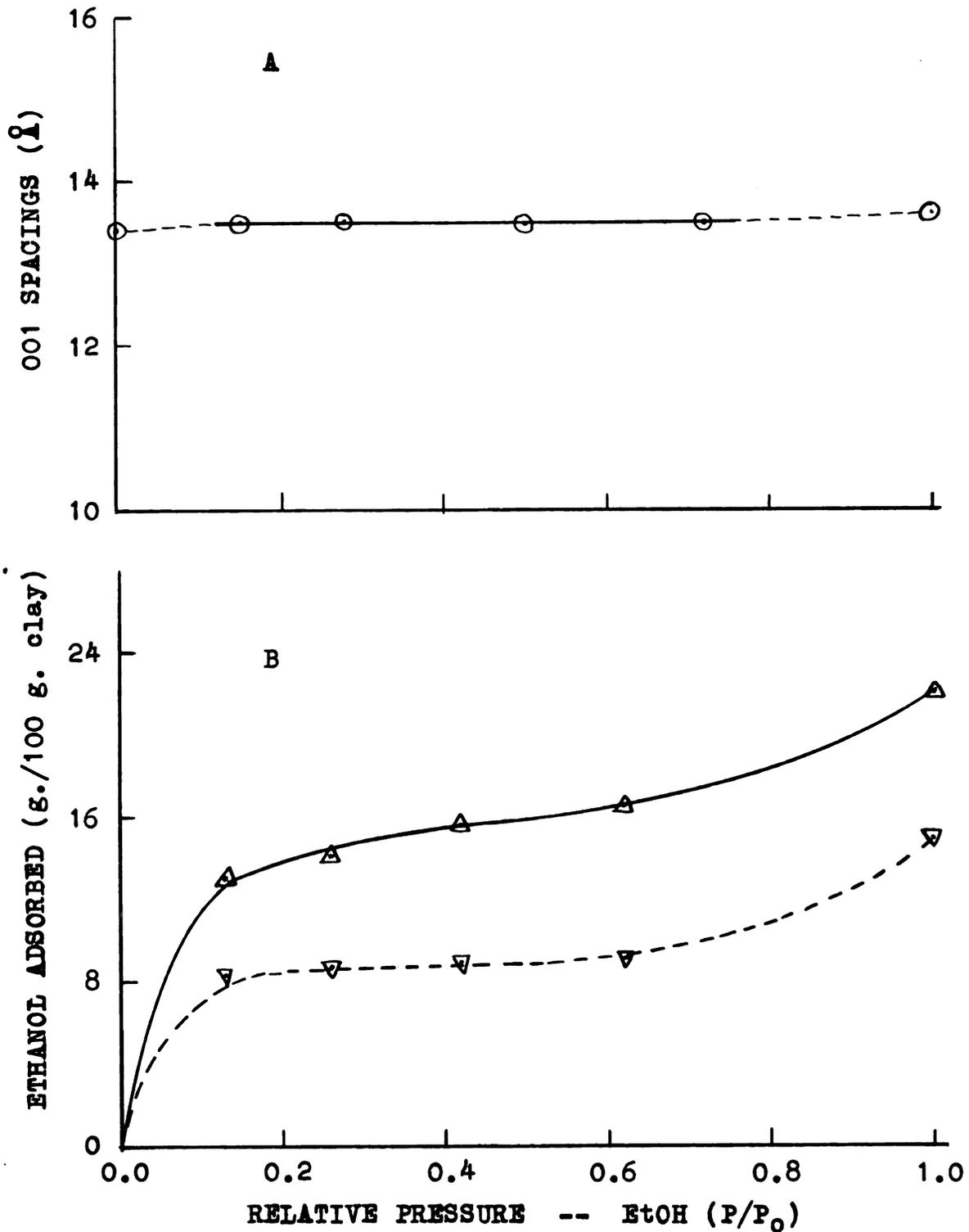


Figure 6. A: 001 spacing vs. relative pressure of EtOH for Al-mont. solid line, sym. first order peaks; broken line, asym. first order peaks. B: EtOH adsorption isotherm for Al-mont. Δ , absolute adsorption corrected for H₂O loss; ∇ , apparent adsorption.

nature of the two isotherms in this region, substantiating the experimental fact that little water is removed above 0.6 relative pressure of ethanol.

Hydrated Ca-montmorillonite.

The behavior of Ca-montmorillonite in the presence of ethanol is very similar to that of Al-montmorillonite. Such is expected since calcium prefers octahedral coordination as does aluminum. A relative ethanol pressure of unity brings about a more complete dehydration of Ca-montmorillonite (curve C, figure 7) than was true with either the Cu- or Al-systems. This is explained by the lower hydration energy of calcium which allows easier replacement of coordinated water. This also explains the fact that rehydration of the Ca-clay occurs somewhat faster than it does in Al-systems. It will be noted that all traces of ethanol are gone (curve F, figure 7) after exposure to the atmosphere for one hour. Like Cu- and Al-montmorillonite, Ca-clay does retain appreciable quantities of ethanol upon heating and evacuation (curve E).

The adsorption isotherms presented in figure 8B are of the same general type as those for the Al-system, with the exception that the plateau is much less pronounced and occurs as an inflection point near 0.5 relative pressure. There is also a greater total quantity of ethanol adsorbed because of the lower hydration energy of calcium accompanied by the fact that expansion of the clay lattice occurs more easily with divalent calcium as the saturating cation. A plot of the 001

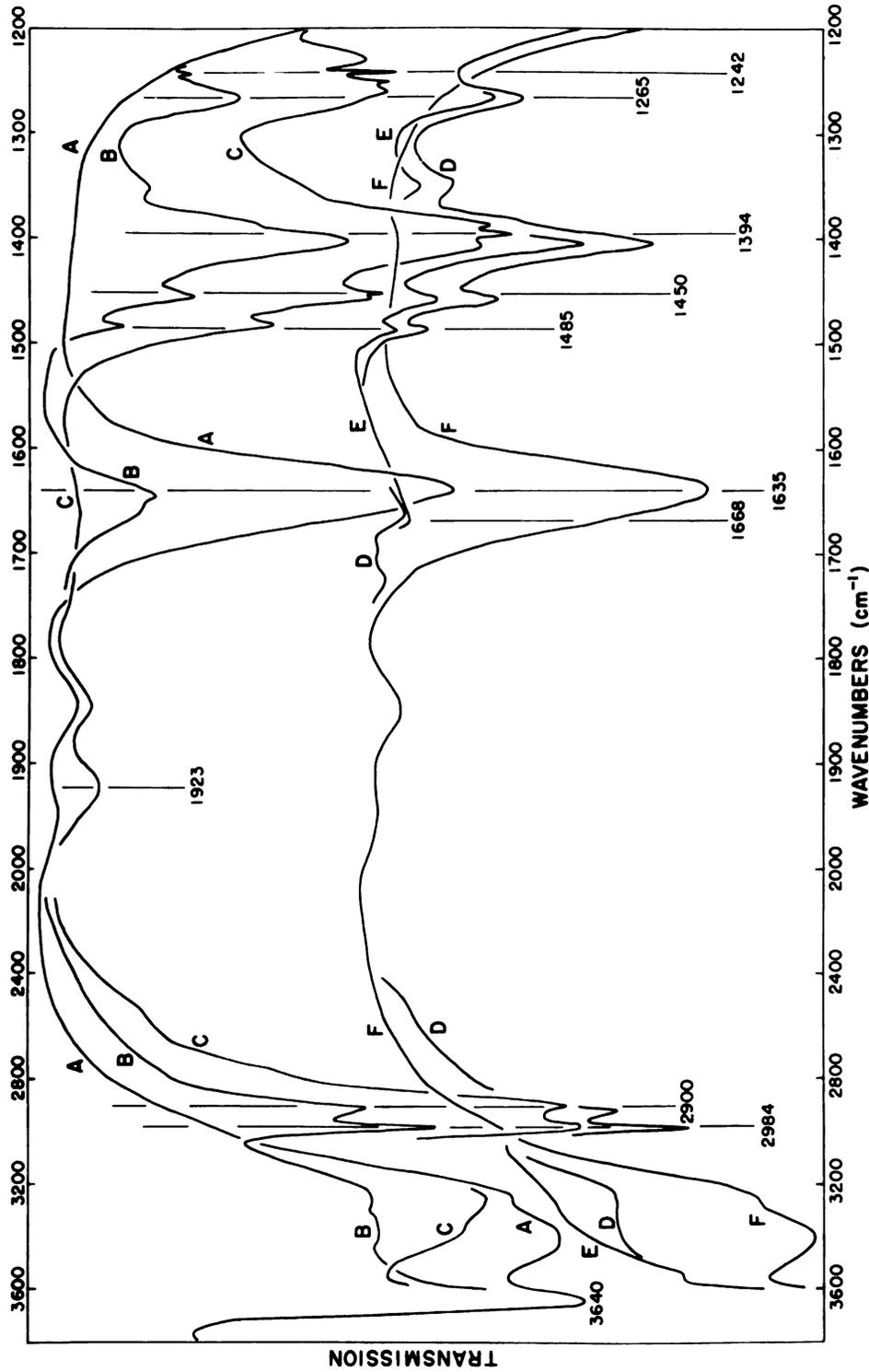


Figure 7. Infrared spectra of Ca-montmorillonite: A, air-dried; B, exposed to 0.14 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hour after EtOH saturation; E, degassed 10 hours after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 1 hour after EtOH saturation, degassing, and heating.

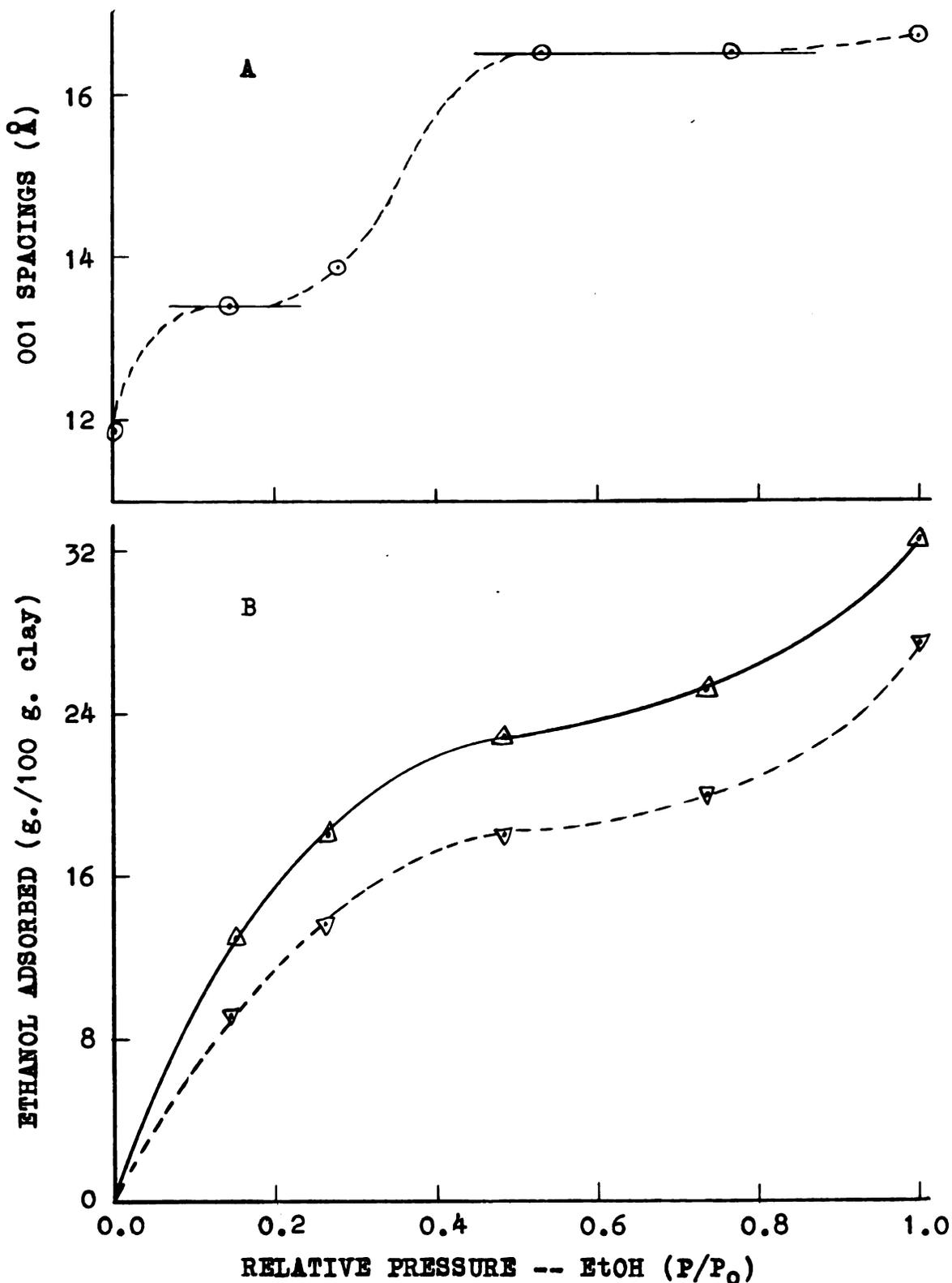
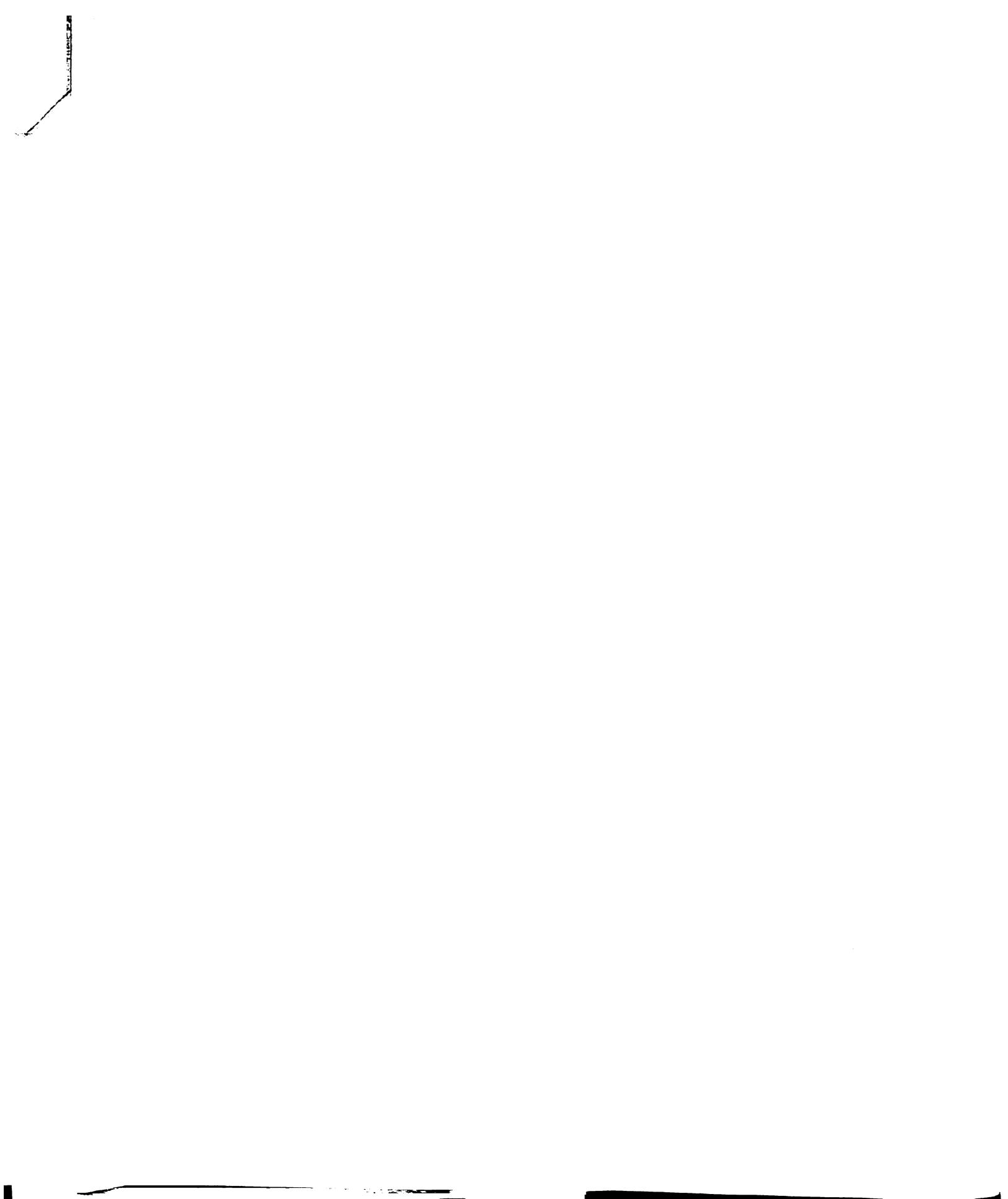


Figure 8. A: 001 spacing vs. relative pressure of EtOH for Ca-mont. solid line, sym. first order peaks; broken line, asym. first order peaks. B: EtOH adsorption isotherm for Ca-mont. Δ , absolute adsorption corrected for H₂O loss; ∇ , apparent adsorption.



basal spacing versus relative pressure in figure 8A shows a metastable inflection at 13.4 \AA and a more stable state at 16.5 \AA between 0.5 and 0.8 relative pressure. Between 0.8 relative pressure and saturation, further lattice expansion is indicated by the asymmetry of the diffraction peak toward higher spacings. A sharp upturn in the adsorption isotherms in the same region is added evidence of further lattice expansion.

Hydrated Na-montmorillonite.

The only significant difference between the infrared data of Ca- and Na-montmorillonite is that dehydration of Na-films is not accompanied by a shift in the water deformation band to a higher frequency (figure 9). This suggests that the residual water molecules are not necessarily associated with the sodium ion, a fact consistent with the low hydration energy of sodium. For the same reason, Na-clay retained less residual water at the saturation pressure of ethanol than clays saturated with polyvalent ions.

The adsorption isotherms presented in figure 10B are similar to those for Ca-montmorillonite, but are smoother with no sharp inflection point. The overall slope of the Na-montmorillonite isotherms is less than those for the Ca-system. A general restriction of lattice expansion will result in a decreased slope. As shown in figure 10A, expansion never exceeds a 001 spacing of 13.2 \AA . That Na-montmorillonite will not expand as much as Ca-montmorillonite at low vapor

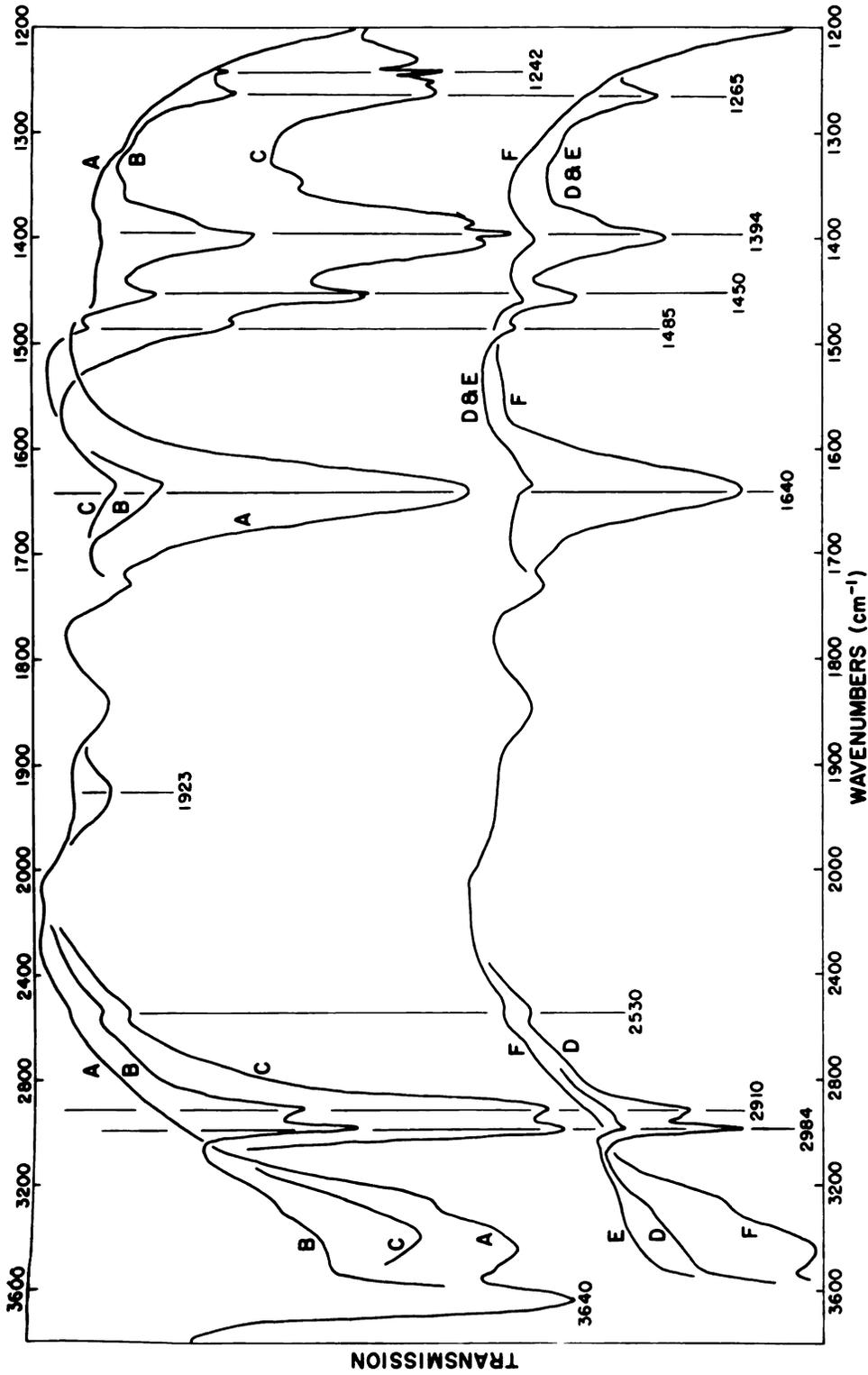


Figure 9. Infrared spectra of Na-montmorillonite: A, air-dried; B, exposed to 0.13 relative pressure EtOH; C, exposed to 1.0 relative pressure EtOH; D, degassed 1 hour after EtOH saturation; E, degassed 10 hours after EtOH saturation, then heated to 100°C while degassing; F, exposed to atmosphere for 1 hour after EtOH saturation, degassing, and heating.

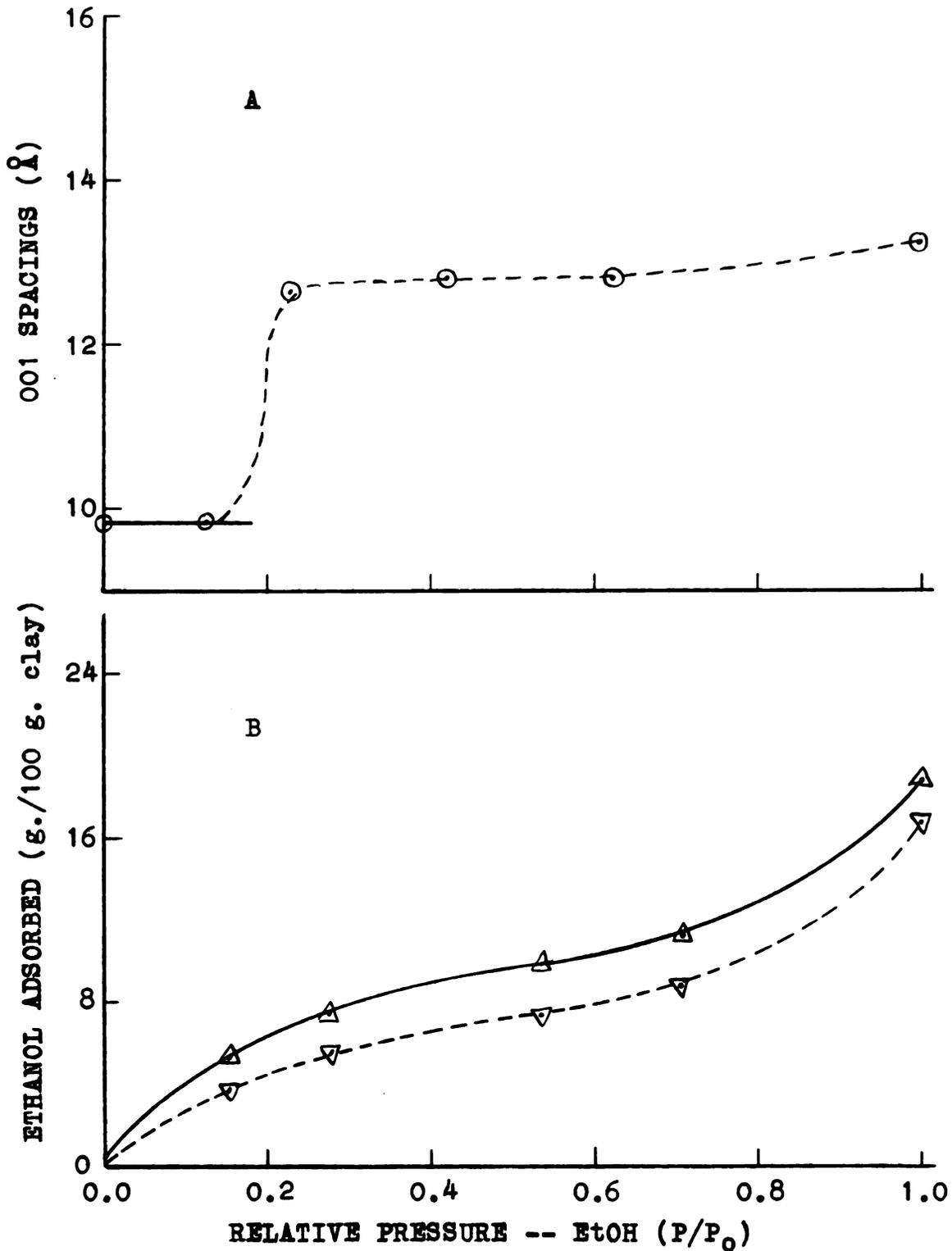


Figure 10. A: 001 spacing vs. relative pressure of EtOH for Na-mont. solid line, sym. first order peaks; broken line, asym. first order peaks. B: EtOH adsorption isotherm for Na-mont. Δ , absolute adsorption corrected for H₂O loss; ∇ , apparent adsorption.

pressures of water has been noted by many researchers including Mooney et al. (1952) and Gillery (1959). Barshad (1952) noted that Na-montmorillonite dehydrated at 170°C would only expand to 13.4 Å when immersed in ethanol, while similarly treated Ca-clay will expand to 17.0 Å. An explanation for the lack of expansion of Na-montmorillonite follows closely that offered by Brooks (1960) when studying the free energies of immersions of montmorillonite in water, ethanol, and n-heptane. Van der Waals forces between individual platelets are very important at distances of 3 Å or less and overcome the hydration energy of sodium, thus restricting the expansion of Na-montmorillonite.

Hydrated NH₄-montmorillonite.

Since infrared spectroscopic data has shown that NH₄-H₂O interactions do occur on montmorillonite surfaces (Mortland et al., 1963), 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 NH₄⁺ band centered at 1450 cm⁻¹ in curve A, figure 11, normally vibrates at 1427 cm⁻¹ in the unperturbed state. Upon degassing of the ethylated film, the 1427 cm⁻¹ band can be observed (curve F). The positioning of the NH₄⁺ band at 1427 cm⁻¹ when the clay film is saturated with ethanol suggests that little EtOH-NH₄ interaction occurs. Further evidence that ethanol is physically adsorbed on NH₄-montmorillonite is the linear plot presented in figure 12. In a linear form, this empirical equation

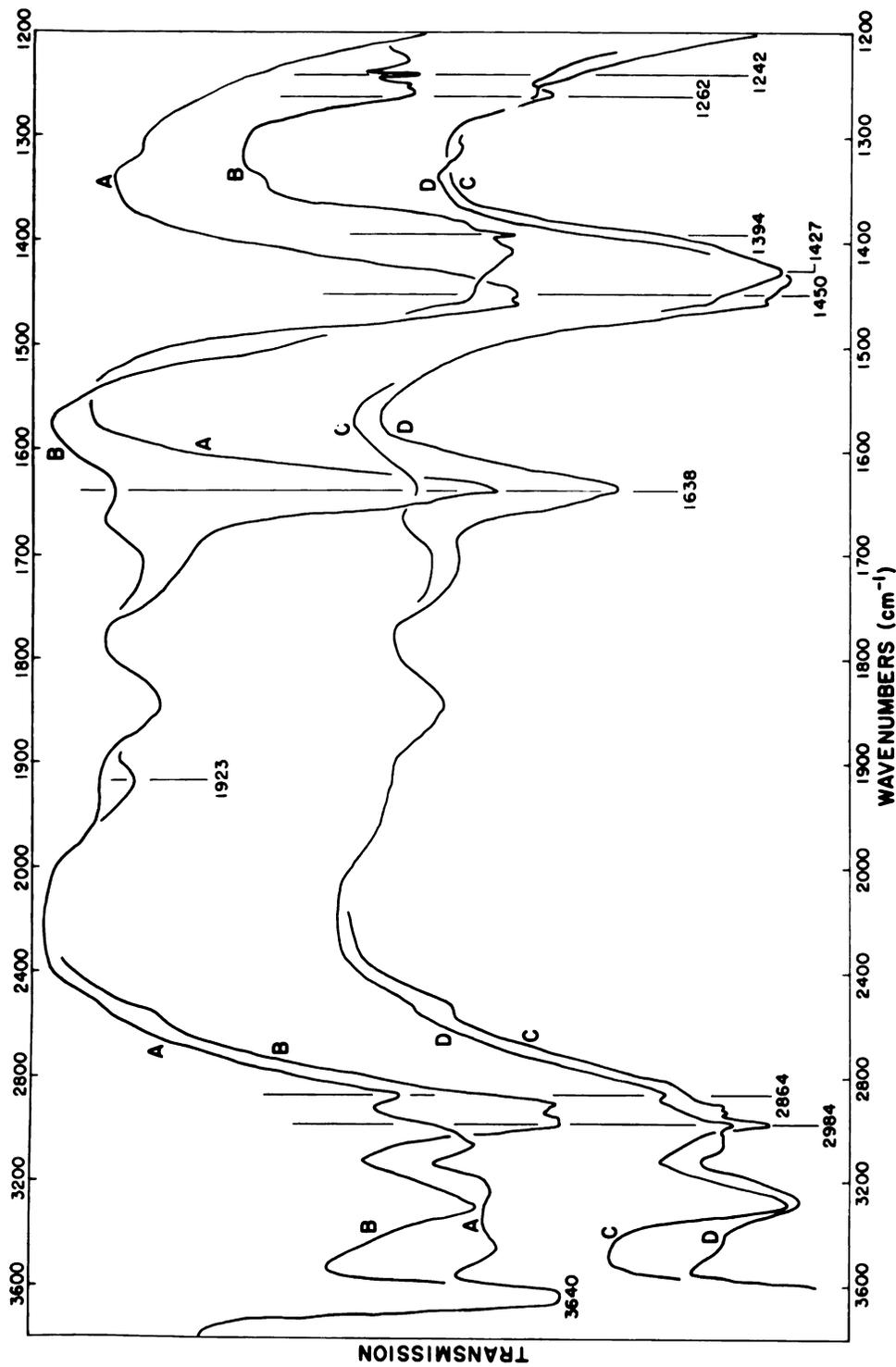


Figure 11. Infrared spectra of NH₄-montmorillonite: A, air-dried; B, exposed to 1.0 relative pressure EtOH; C, degassed 1 hour after EtOH saturation; D, exposed to atmosphere for 1 hour after EtOH saturation, degassing 10 hours, and heating to 100°C while degassing.



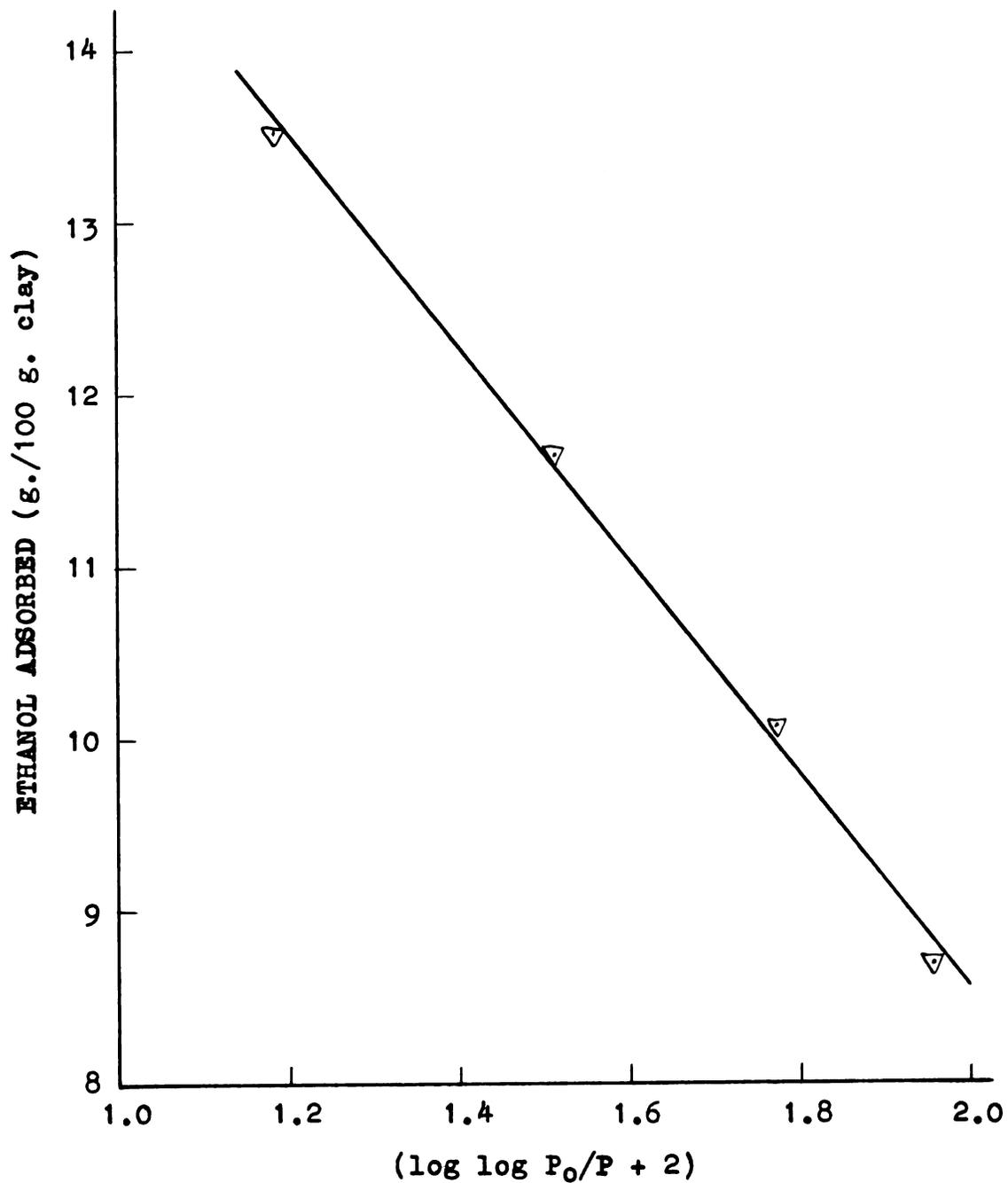
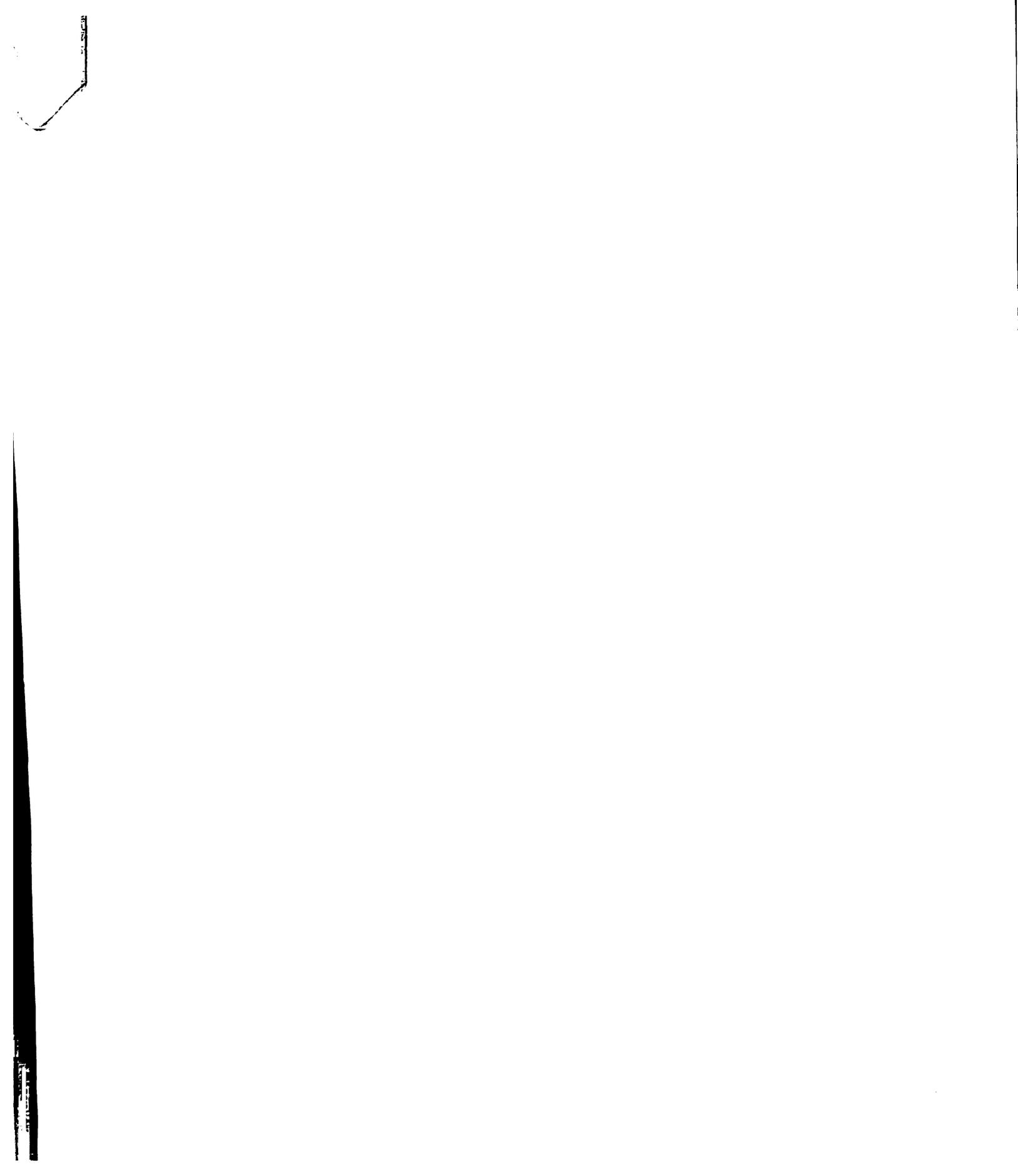


Figure 12. Adsorbed EtOH as a function of $(\log \log P_0/P + 2)$ for NH_4 -montmorillonite.



developed by Bradley (Orchiston, 1953) for the adsorption of molecules with large permanent dipoles onto ionic adsorbents, takes the form:

$$\log \log P_0/P = \log K_2 + x \log K_1 \quad (1)$$

where: P = pressure of adsorbate, P_0 = saturation vapor pressure at the temperature of experiment, x = mass of adsorbed gas, and K_1 and K_2 are constants depending upon the particular system. It will be noted that the plot is linear over the relative pressure range between 0.125 and 0.70. It should also be noted that none of the metallic cation-clay systems obeyed this relationship, which is indirect proof that forces other than cation-dipole interactions bring about the adsorption of ethanol vapor. Studying water vapor adsorption on soils, Orchiston (1953) observed that this equation was obeyed over the relative pressure range from 0.08 to 0.9.

The other infrared data in figure 11 and the isotherms and x-ray data in figure 13 are essentially the same as that presented for Na-montmorillonite.

Deuterated ethanol studies.

In order to separate the O-H vibrations of residual water from those of ethanol and take a closer look at these vibrations, films of Cu- and Al-montmorillonite were exposed to C_2H_5OD followed by outgassing. The same procedures were followed for like films being exposed to CH_3CD_2OH , in order that the vibrations of methyl and methylene groups might be

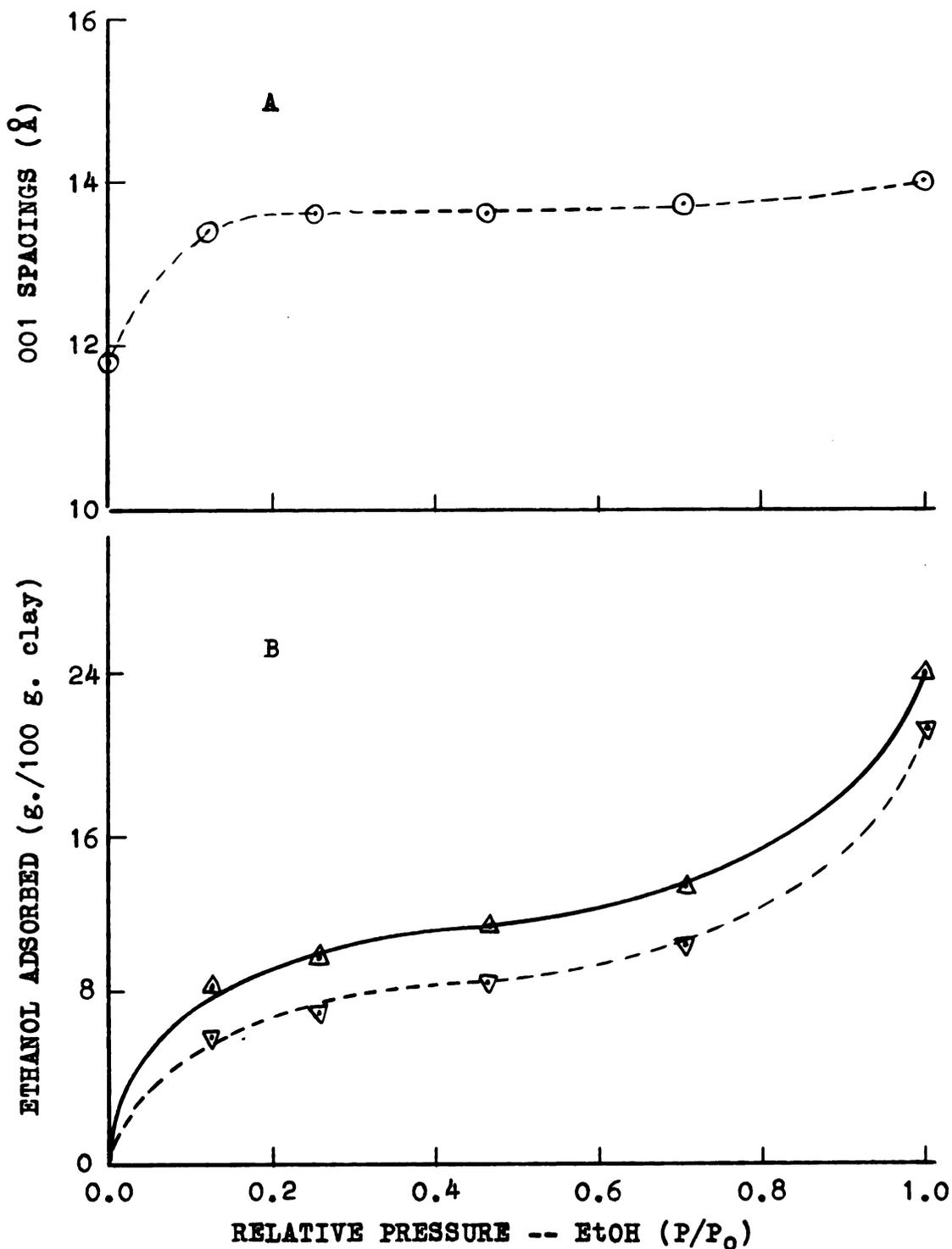


Figure 13. A: 001 spacing vs. relative pressure of EtOH for NH_4 -mont. solid line, sym. first order peaks; broken line, asym. first order peaks.
 B: EtOH adsorption isotherm for NH_4 -mont.
 Δ , absolute adsorption corrected for H_2O loss;
 ∇ , apparent adsorption.

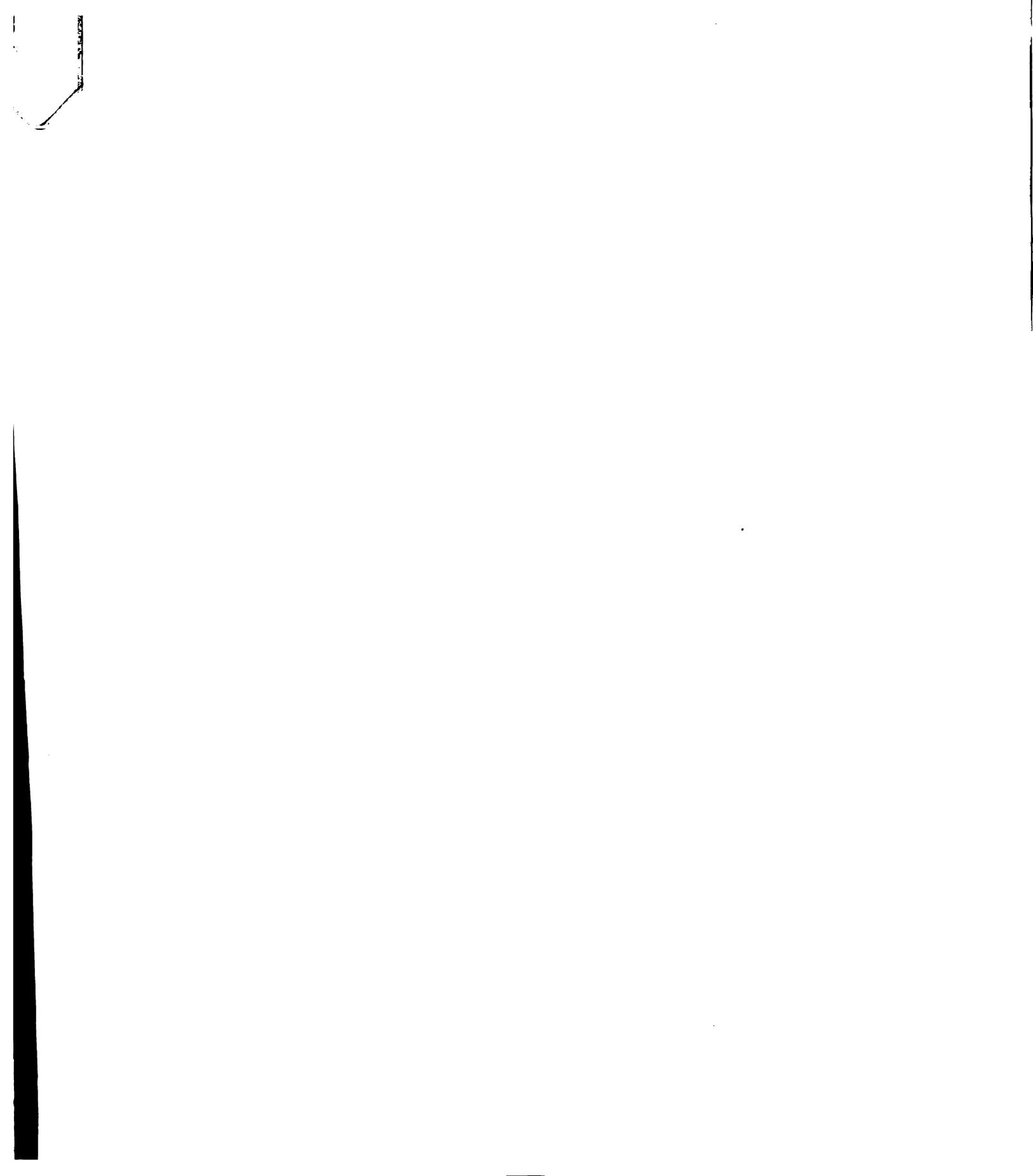
separated and studied more closely. The various vibrational modes of these two species in the 3400-1200 cm^{-1} region of the spectrum are listed in table 2. Unfortunately the sample of $\text{CH}_3\text{CD}_2\text{OH}$ contained both water and normal ethanol in detectable quantities as indicated by the appropriate OH and CH_2 vibrations.

Tracings A and B in figure 14 are those recorded after equilibration of Al- and Cu-montmorillonite films, respectively, with EtOD for two hours at a relative pressure of unity followed by evacuation for 30 minutes. By comparison with curve D in figures 3 and 5, it is immediately obvious that the absorbance of the 1650-1600 cm^{-1} band of HOH is less. This suggests an OH-OD exchange between HOH and EtOD. This is further supported by the appearance of the EtO-H deformation band at 1265 cm^{-1} . The band at 1575 cm^{-1} is thought to be that of water coordinated to copper ions as previously discussed. The 3440 cm^{-1} O-H stretching band is also thought to be that of coordinated water. In this respect, Gamo (1961) reported a strong 3420 cm^{-1} band for the O-H stretching of water in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. There exists the possibility that the 3440 cm^{-1} band may be due to the O-H stretch in $\text{Cu}_2(\text{OH})_3\text{Cl}$ as reported by Tarte (1958). However, two factors cast doubt upon the presence of such a species: 1) the Cu-clay was originally washed free of chlorides as indicated by negative AgNO_3 tests and 2) a species of this type would be expected to give a much sharper peak positioned at 3448 cm^{-1} .

Table 2. Infrared frequencies of liquid and adsorbed C_2H_5OD and CH_3CD_2OH .

Infrared bands		Mode ¹
Adsorbed (observed)	Liquid	
-----cm ⁻¹ -----		
<u>C₂H₅OD</u>		
2984	2984	asym. CH ₃ stretch
2915-2935	{ 2935 2890	asym. CH ₂ stretch
		sym. CH ₃ stretch
2460-2500	2460-2500	OD stretch
1480	1480	CH ₂ scissoring
1450	1450	asym. CH ₃ bend
1394	1386	sym. CH ₃ bend
<u>CH₃CD₂OH</u>		
3260-3360	3200-3500	OH stretch
2984	2984	asym. CH ₃ stretch
2935	2935	sym. CH ₃ stretch
--	2208	asym. CD ₂ stretch
2135	2105	sym. CD ₂ stretch
1448	1447	asym. CH ₃ bend
1384	1378	sym. CH ₃ bend
1315	1400	OH deformation

¹These tentative assignments are based on comparable bands of normal ethanol as well as work of Hadzi and Jeramic (1957), Hadzi et al. (1962), and Margottin-Maclou (1963).



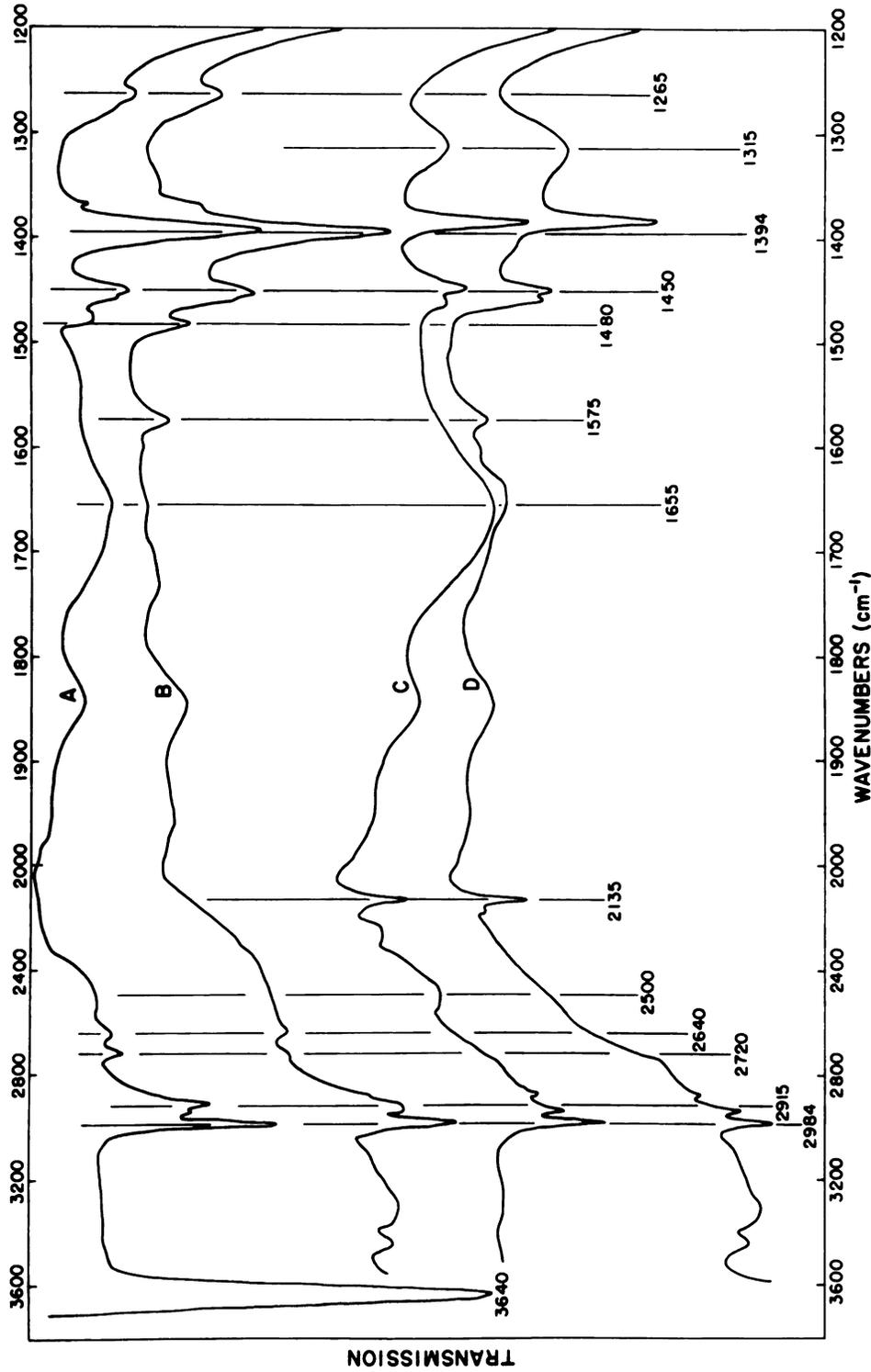


Figure 14. Infrared spectra of montmorillonite after exposure to 1.0 relative pressure of deuterated ethanol and then degassed 30 minutes.
 C_2H_5OD : A, Al-montmorillonite; B, Cu-montmorillonite.
 CH_3CD_2OH : C, Al-montmorillonite; D, Cu-montmorillonite.

The broad O-D stretching band of adsorbed EtOD at 2500 cm^{-1} does not differ significantly from that observed in the liquid phase. It should be noted that this band coincides with a band in pure Al- and Cu-clays which has been assigned to a highly perturbed O-H stretching mode of coordinated water (see curve A in figures 3 and 5). The band at 2640 cm^{-1} is assigned to the O-D stretching of the clay lattice. This would yield a $\nu_{\text{OD}}/\nu_{\text{OH}}$ ratio of 0.725 which is very close to that reported by Mortland et al. (1963). Since the 2720 cm^{-1} band persists upon exposure to the clay film to the atmosphere for seven days, it is also assigned to a lattice O-D vibration. These two bands are probably the deuterated counter-parts of the 3640 and 3700 cm^{-1} O-H lattice vibrations, respectively (Russell and Farmer, 1964). However, the intensities of these OD bands are very slight compared to the OH bands, suggesting that deuteration is not extensive and is probably confined to exposed surface groups.

Curves C and D, figure 14, show the spectra of Al- and Cu-montmorillonite after adsorption of $\text{CH}_3\text{CD}_2\text{OH}$ following the same procedure as given above. From these spectra, confirmation of the assignment of the 1480 cm^{-1} band to the methylene scissoring vibration is obtained. Shifts in the position of the OH in-plane deformation were the same as observed for EtOH ($\Delta\nu = 25 \text{ cm}^{-1}$), while no significant shifts were noted for either the CH_3 bending or stretching vibration.

Acetaldehyde adsorption.

Heating Cu-montmorillonite in the presence of ethanol vapor resulted in the appearance of a band in the 1750 cm^{-1} region of the spectrum. Comparison of band position and contour with that of acetaldehyde (Depireux, 1957) suggested that ethanol was oxidized to acetaldehyde. Further investigation showed that this reaction was catalyzed by the brass cell in the absence of clay. Degassing the system showed that the acetaldehyde was present in the vapor phase and was not adsorbed on the ethylated clay. However, exposure of an air-dried Cu-film to acetaldehyde vapor for two hours followed by two hours of evacuation, showed that adsorption did occur (curve B, figure 15). Tracing A is the spectrum for a similarly treated Cu-EtOH clay film and is included for comparison. A shift of the C-O stretching to lower frequencies suggests that acetaldehyde is coordinated to the copper ion through the carbonyl group similar to the Cu-amide complexes observed by Tahoun and Mortland (1966). Carbonyl bands at 1675 and 1715 cm^{-1} suggests two types of adsorbed acetaldehyde: the first band that of acetaldehyde coordinated directly to the copper ion, and the second that of acetaldehyde present in an outer coordination sphere or coordinated through a HOH bridge similar to that proposed by Farmer and Mortland (1966) for Cu-H₂O-pyridine complexes. The disappearance of the 1715 cm^{-1} band upon heating and its reoccurrence upon exposure to the atmosphere is evidence to support a Cu-H₂O acetaldehyde type

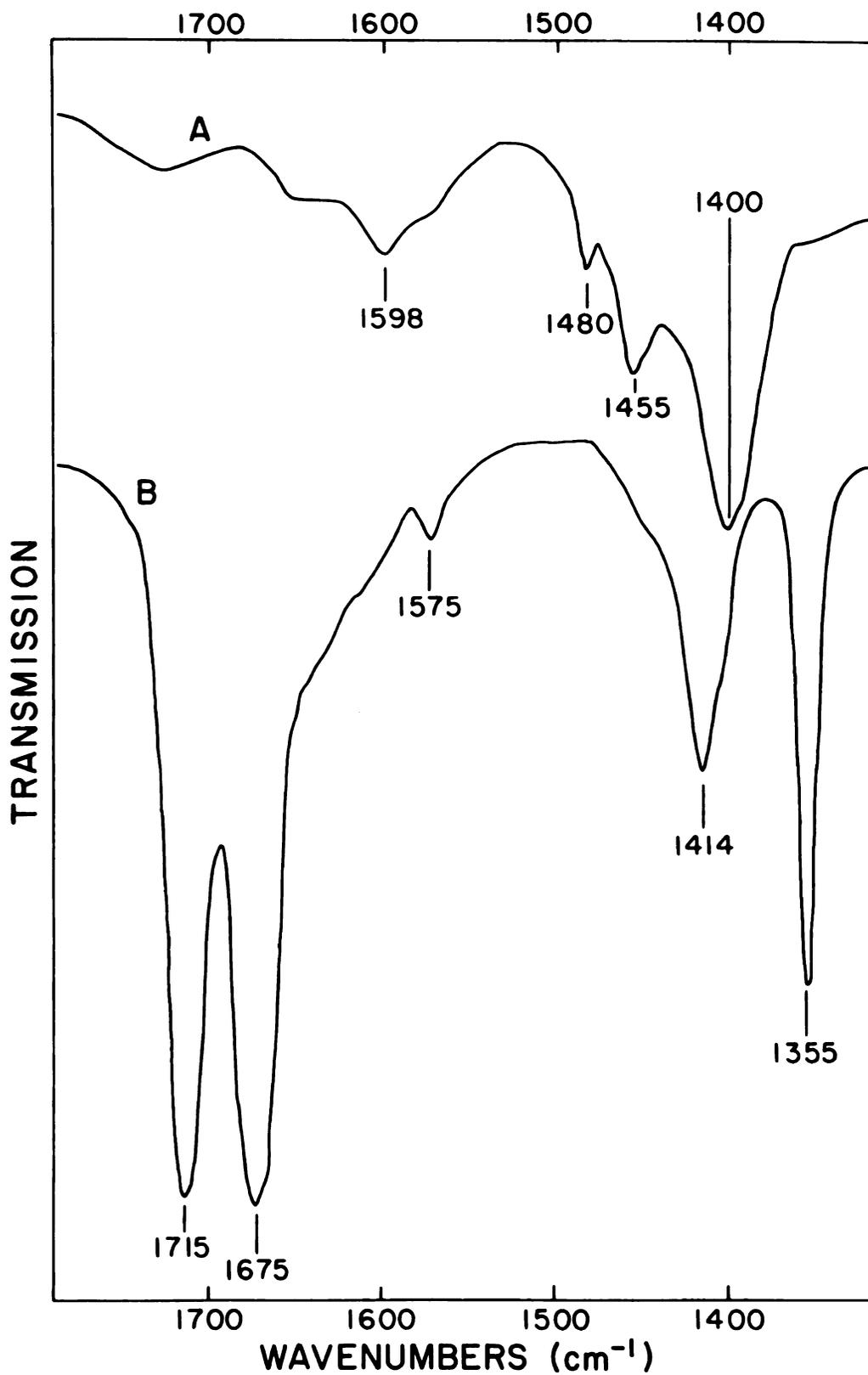


Figure 15. Infrared spectra of Cu-montmorillonite: A, degassed 1 hour after exposure to 4.8 cm. EtOH; B, degassed 2 hours after exposure to 4.3 cm. CH₃CHO.

complex. As was true with ethanol, no changes were observed in the CH bands upon adsorption.

General considerations.

The infrared data presented have shown that the bulk of the water retained on air-dried homoionic clays is replaced by equilibrating the clay with ethanol vapor at its saturation pressure. By using the absorbance of the 1650-1600 cm^{-1} deformation band of water and the procedures outlined previously, it is possible to follow the dehydration of the clay films with increased pressure of ethanol. The data given in figure 16 are a result of these calculations and show the water loss as a function of the relative pressure of ethanol. First, it is obvious that the water content in all of the systems has been reduced to less than 0.7% (based on 300°C). Na-clay, because of its weak hydration energy, has lost essentially all of the adsorbed water.

It will be noted that the Cu- and Al-montmorillonite curves break near 0.5 relative pressure, while Ca-, NH_4 - and Na-systems break at somewhat lower values, 0.4 to 0.3 relative pressure. This can also be explained by energies of hydration. By this argument, the aluminum should break at a somewhat higher value than copper since the hydration energy of the former is 609 kcal.mole^{-1} greater (Hunt, 1963). However, this apparent anomalous behavior can be, in part, explained by closer consideration of the two cations and their properties. As mentioned previously, due to its square

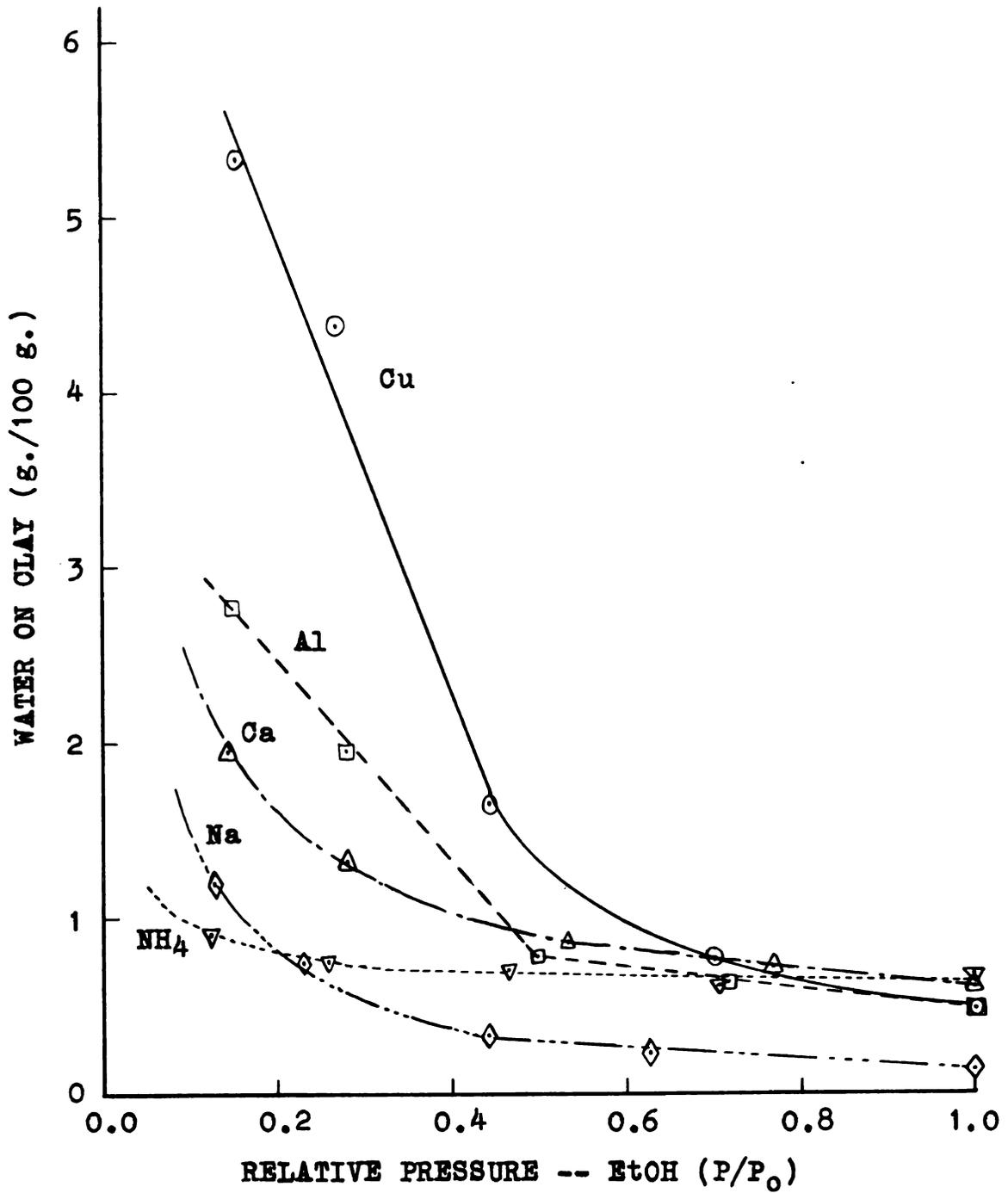


Figure 16. Variation in H₂O content as a function of the relative pressure of EtOH for homoionic montmorillonite.

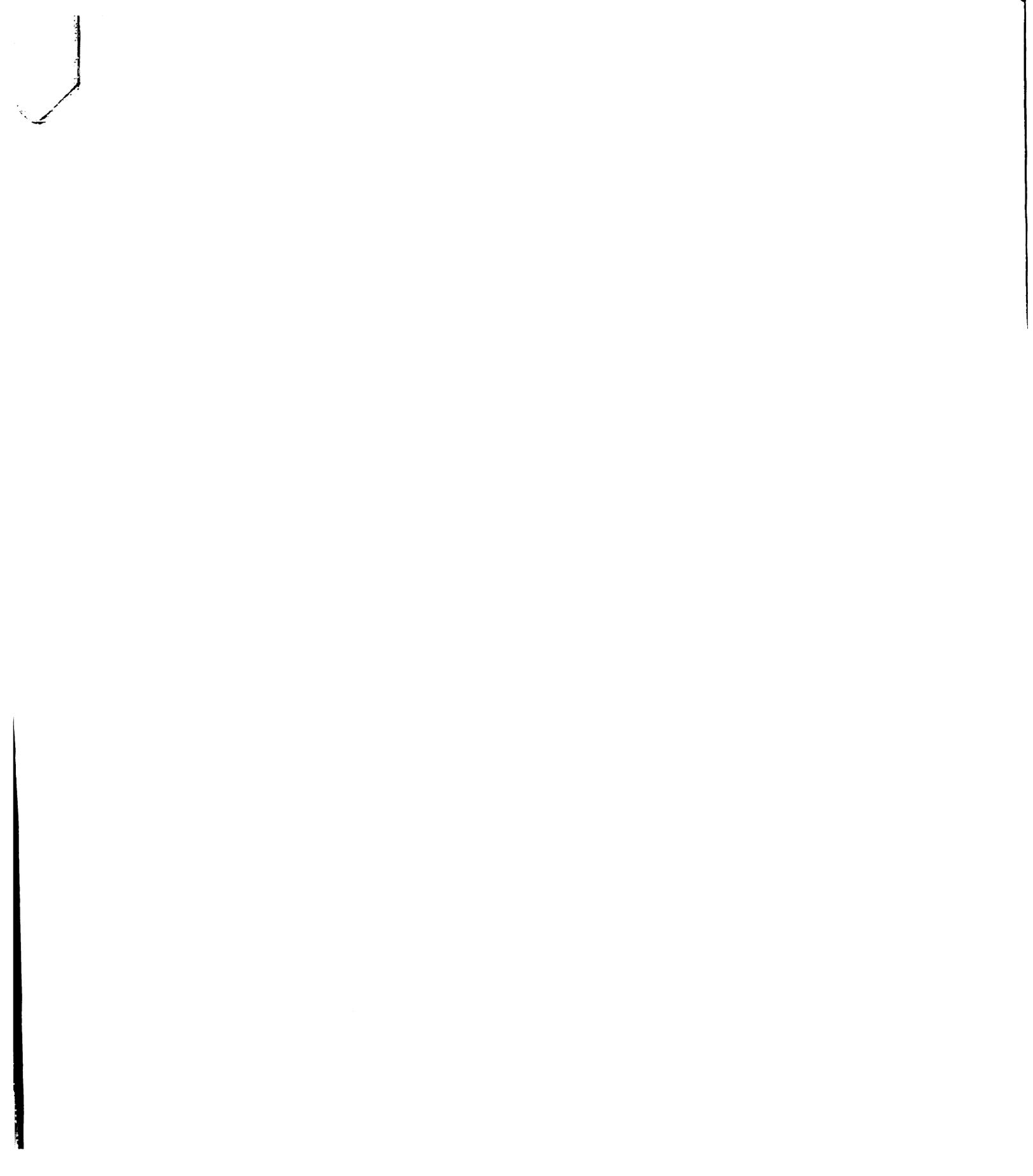
planer coordination habit, copper ligands will be subjected to the same intensity level of the force field in the inter-lamellar space, which will tend to stabilize the complex. On the other hand, because aluminum prefers octahedral coordination, this will place different ligands at different intensity levels in the force field and in turn cause distortion of the complex. Also, trivalent aluminum will bind the clay platelets together more energetically than will divalent copper which causes distortion of the coordination complex and partially negates its hydration or coordination energy. The break in the calcium curve occurs at a point intermediate between those of Cu- and Al- and those of NH_4 - and Na-clays, which is in accord with its intermediate hydration energy.

In the preceding discussions, the simultaneous occurrence of both water and ethanol in coordination complexes has been indicated. Such is undoubtedly true. However, it is very unlikely that both water and ethanol molecules simultaneously serve as ligands about the same cation since this is a thermodynamically less stable configuration. Therefore, even though statistically speaking, the number of water molecules per copper ion is less than 0.7 at a relative pressure of unity, the water present is distributed as four molecules per cation. Along this same line of argument, the asymmetry of the first order (001) x-ray diffraction peak and the irrationality of higher orders at any particular relative pressure, can be explained by the random interstratification of

layers containing only water or ethanol, a corollary of ideas suggested by Mortland and Barake (1966) in their metal ion-organic ion work.

The plot of ethanol retained versus length of time of evacuation in figure 17 shows the relative stability of the cation-ethanol systems. All curves fall rapidly at first with the removal of loosely held molecules and then level out after about five hours of evacuation. The contour of the copper curve indicates that a somewhat longer time is required to reach a state of apparent equilibrium. It is noted that polyvalent cationic systems retain appreciably more ethanol than monovalent cationic systems. Cu- and Al-clays retain 4.5 and 6.8 molecules per ion, respectively, after ten hours of evacuation, which is very close to their preferred coordination numbers. Ca-montmorillonite also retains approximately 4.5 molecules per cation, while Na- and NH_4 -systems, which do not show strong inner sphere coordinating behavior, retain less than 1.0 molecule per cation.

The curves in figure 18 show the influence of saturating cations upon the behavior of clay systems. These curves show the desorption of ethanol by replacement with atmospheric water after evacuation and heating. The same reasoning presented earlier in this section for the desorption of water upon ethylation, applies here for the differential behavior of the various cationic-clay systems. As shown, Na-montmorillonite has very little ethanol present at the start of rehydration, which is slowly replaced. This slow replacement



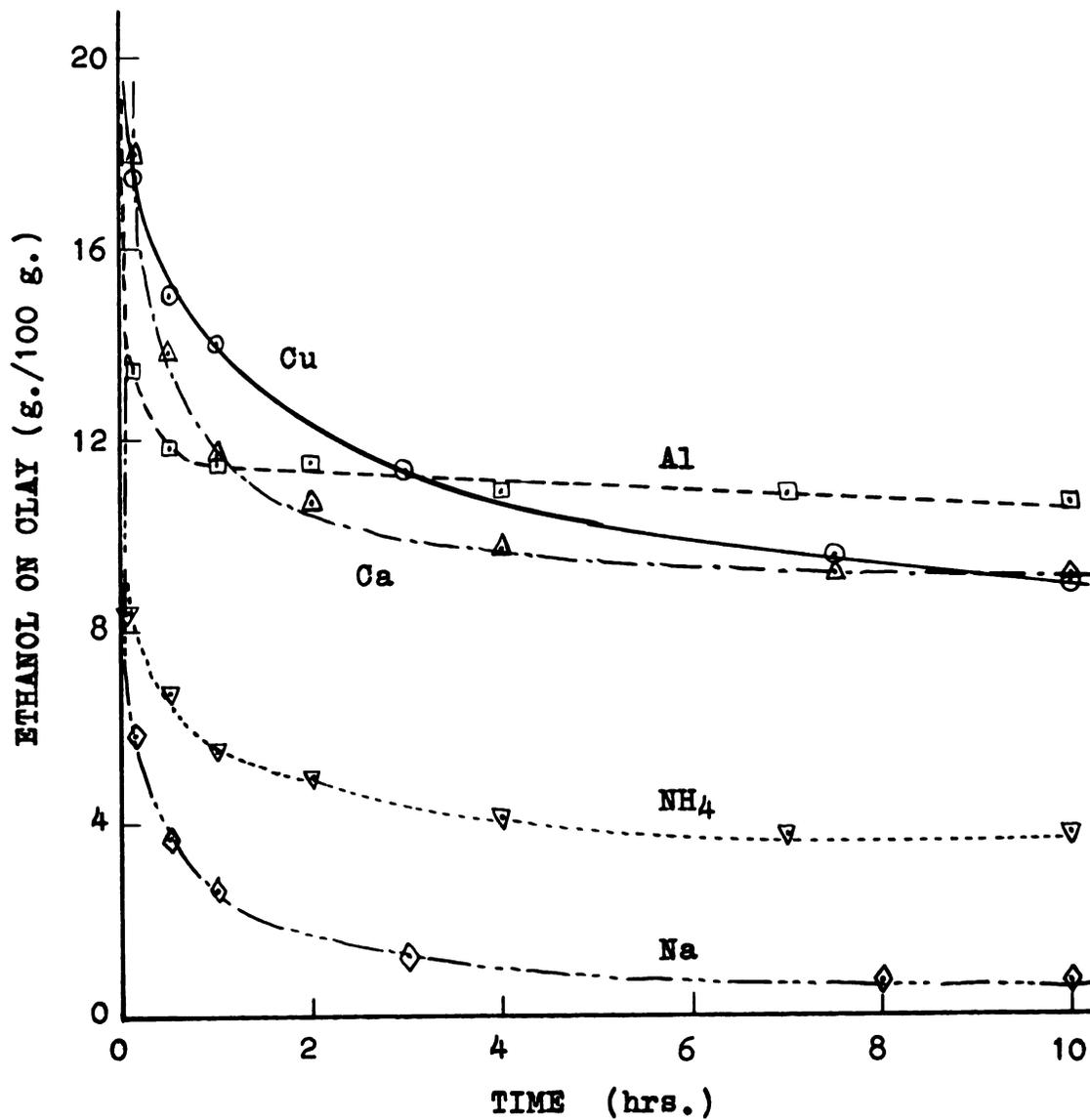


Figure 17. Adsorbed EtOH as a function of the evacuation time for homoionic montmorillonite.

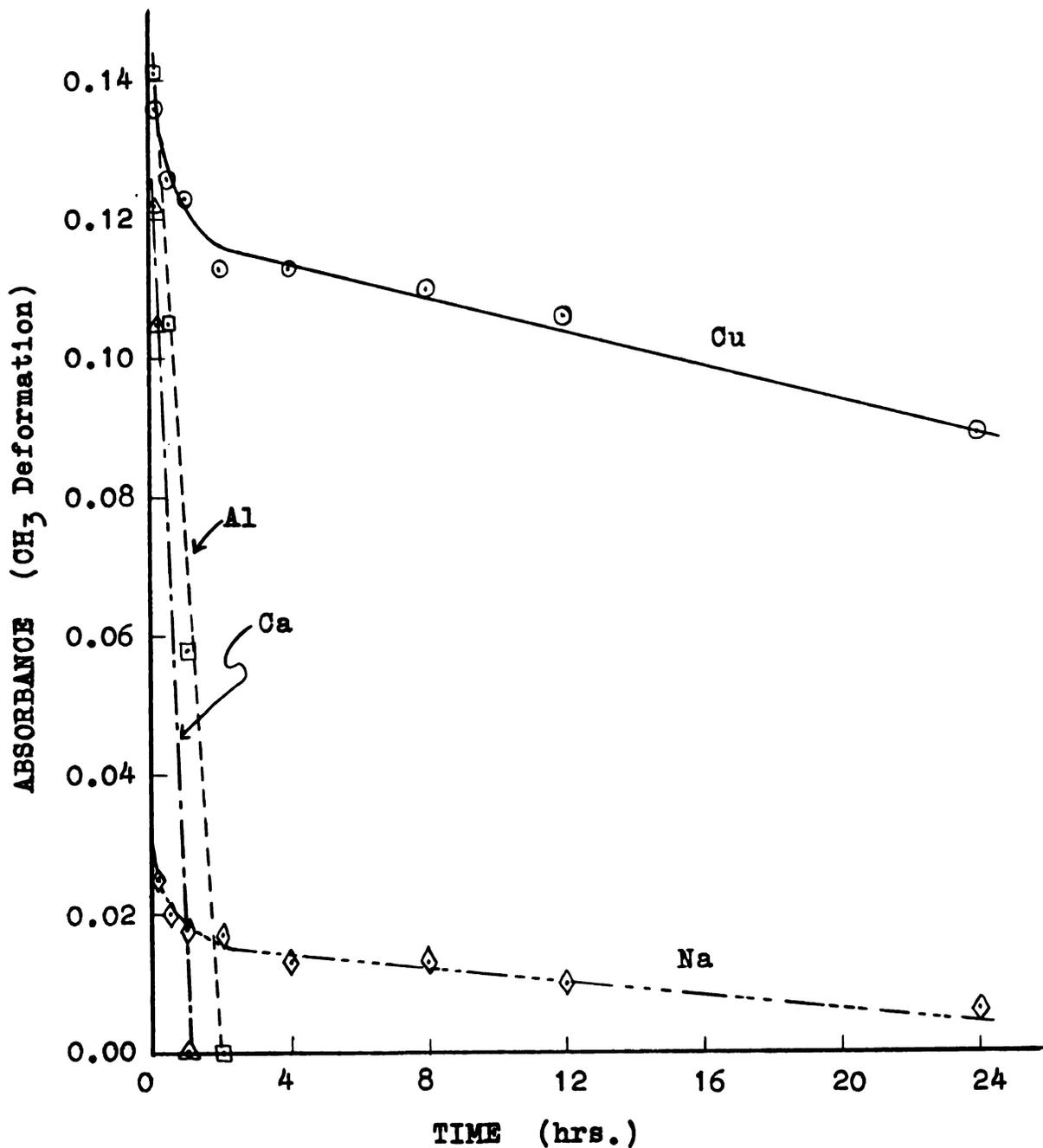


Figure 18. Absorbance of the CH₃ deformation band of EtOH as a function of rehydration time for ethylated, homoionic montmorillonite.

can be explained by the fact that the 001 basal spacing is only 11.8 Å compared to spacings of greater than 13.3 Å for Cu-, Al-, and Ca-clays. Hence, the tortuosity factor is much greater for a molecule escaping the interlamellar space of a Na-clay. With the additional information that all of the ethanol was removed from Cu-montmorillonite in approximately 70 hours, it can be observed that the adsorption-desorption of ethanol from these homoionic montmorillonite surfaces is a reversible process.

Since the rate of loss of ethanol from Cu-montmorillonite was slow enough to be measured by the techniques and design of these studies, the data were plotted according to the equation:

$$\log (1 - A/A_0) = -0.16 - 2.515 \frac{D}{r_0^2} t \quad (2)$$

where: t = time, A_0 = absorbance of the CH_3 deformation band at $t = 0$, A = absorbance of CH_3 deformation vibration at any given time, D = diffusion coefficient, and r_0 = radius of montmorillonite particles assuming disk shaped platelets. This is a derivation used by Fripiat and Helsen (1966) for the diffusion of "free" ammonia between clay sheets. They noted a diffusion coefficient of $6.6 \times 10^{-19} \text{ cm}^2 \text{ sec}^{-1}$ at 55°C for the diffusion of NH_3 , which resulted from the decomposition of $\text{Co}(\text{NH}_3)_6^{3+}$ -montmorillonite complexes. It can be seen by plotting of $\log (1 - A/A_0)$ against time (figure 19) that the data fit reasonably well a straight line between 4 and 56 hours. Using a value of 120 Å for r_0 (Eeckman and Loudelout,

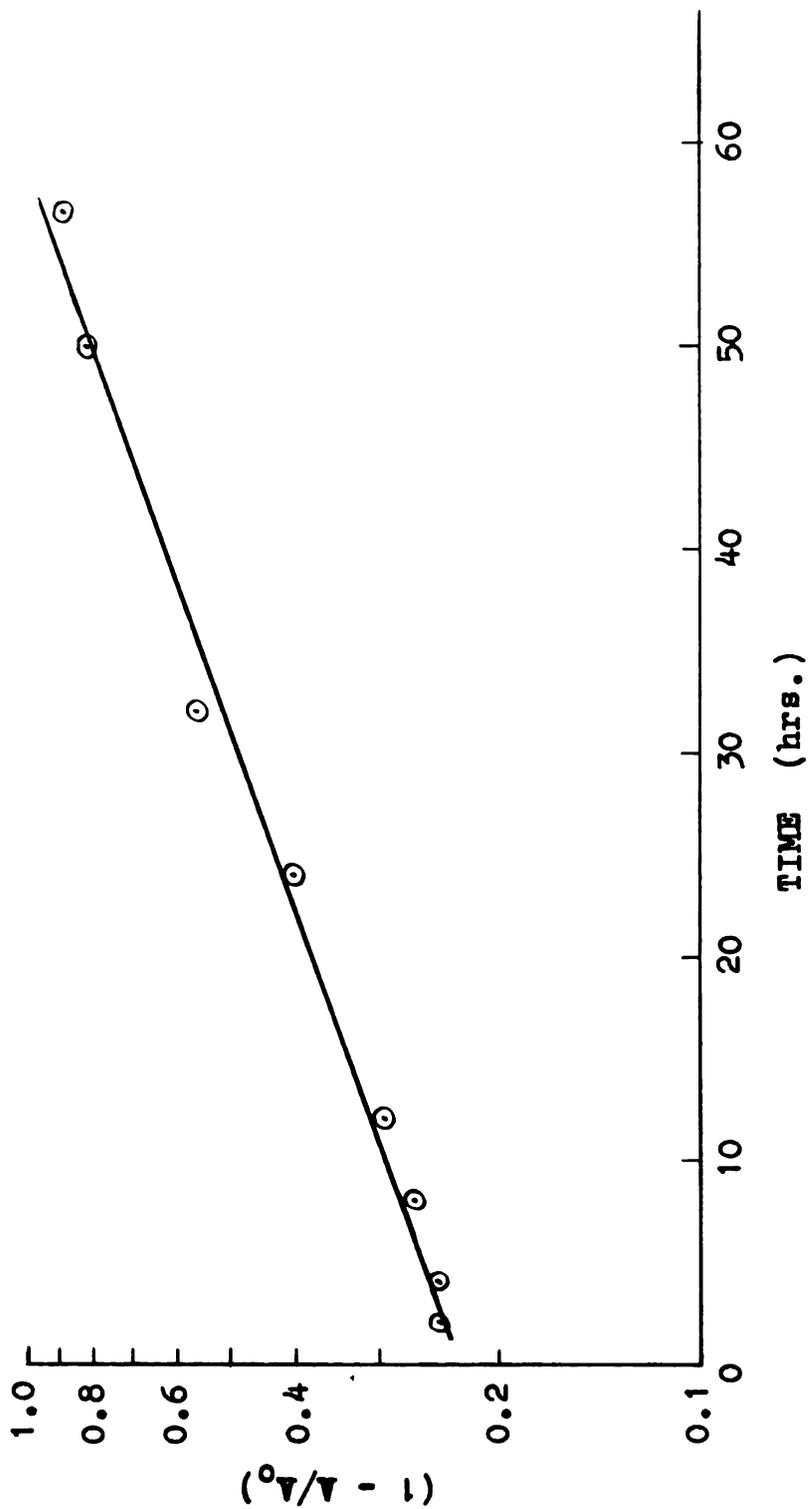


Figure 19. $\log(1 - A/A_0)$ as a function of time for Cu-montmorillonite.

1961), the diffusion coefficient, calculated from the slope of the line, is $1.71 \times 10^{-18} \text{ cm}^2 \text{ sec}^{-1}$ at 20°C . Hence, after the rapid initial loss, the desorption of ethanol on Cu-montmorillonite follows a stationary diffusion process until the exchange with water is essentially complete.

Glycol adsorption - desorption studies

Infrared absorption frequencies for both liquid and adsorbed glycol are given in table 3 for the $3400\text{-}1200 \text{ cm}^{-1}$ region of the spectrum. When compared with ethanol, very little work has been done with the vibrational assignments of ethylene glycol. Although no assignments are made, Kanbayashi and Nukada (1963) have published an identical spectrum of glycol, in the $1500 \text{ to } 600 \text{ cm}^{-1}$ region, to that observed in the present studies. Using polarized infrared techniques, Miyazawa et al. (1962) have concluded that the CH bands in the $1400\text{-}1200 \text{ cm}^{-1}$ region are combinations of wagging and twisting vibrations and are not simply one or the other. As with ethanol, the OH deformation of glycol appears to interact with the CH bending bands in the liquid state, giving rise to a doublet with maxima at 1410 and 1330 cm^{-1} (Krimm et al. 1956).

Cu-montmorillonite.

Infrared spectra of glycol-water-Cu-montmorillonite complexes are presented in figure 20. It should be noted again that the complex was formed initially by suspending

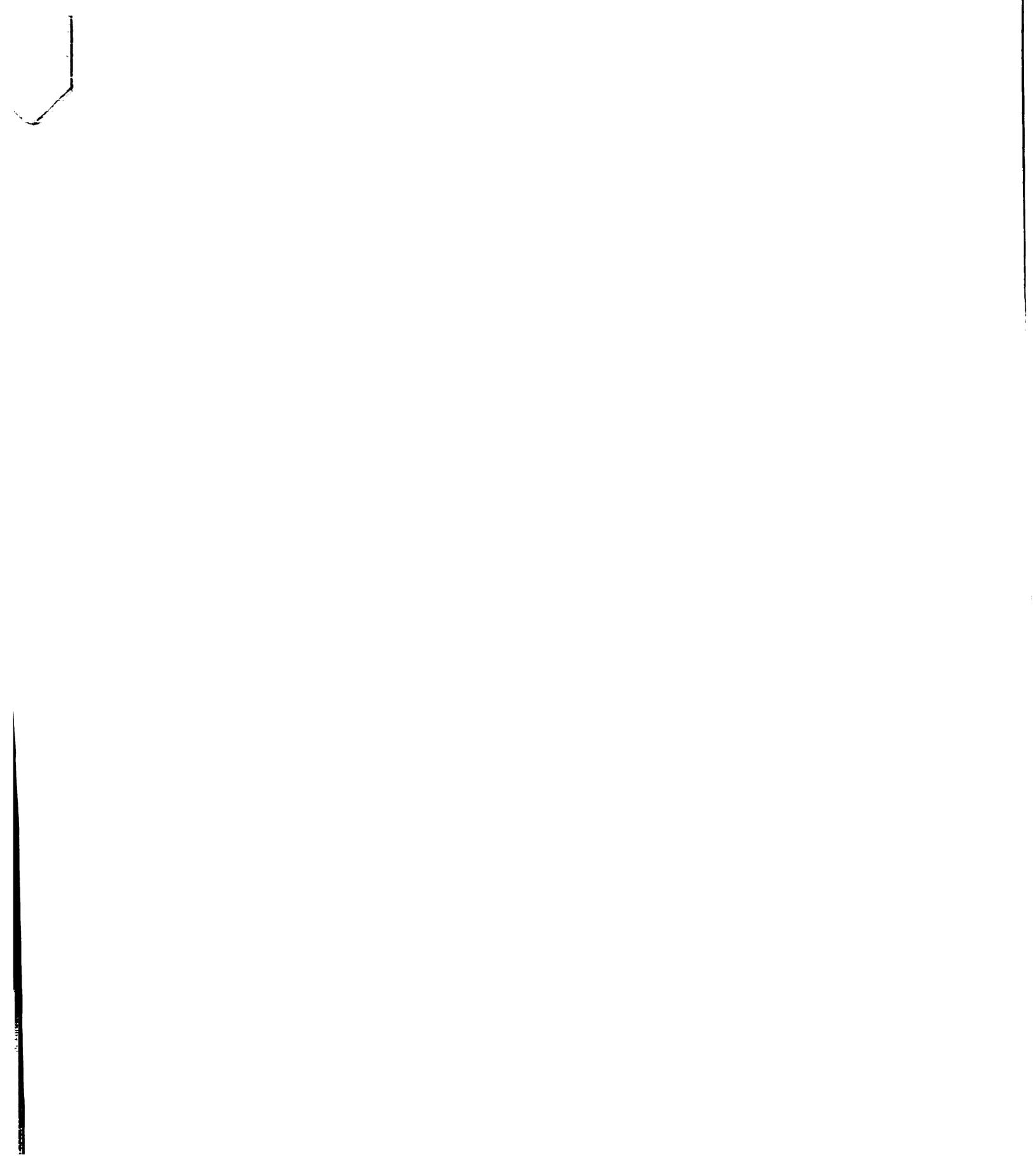


Table 3. Infrared frequencies of liquid and adsorbed ethylene glycol.

Infrared bands		Mode ¹
Adsorbed	Liquid	
-----cm ⁻¹ -----		
3300	3360	OH stretch
2960	2950	asym. CH ₂ stretch
2890	2884	sym. CH ₂ stretch
1463	1457	CH ₂ scissoring
1370	1370	CH ₂ ; 70% wag, 25% twist
--	1253	CH ₂ ; 40% wag, 60% twist
--	1205	CH ₂ ; 25% wag, 70% twist
1400 } 1350 }	{ 1410 1330 }	combination: (CH + OH bend.) ²

¹For assignment of the absorption frequencies see: Davison (1955), Kuhn et al. (1959), and Miyazawa (1962).

²After Krimm et al. (1956).

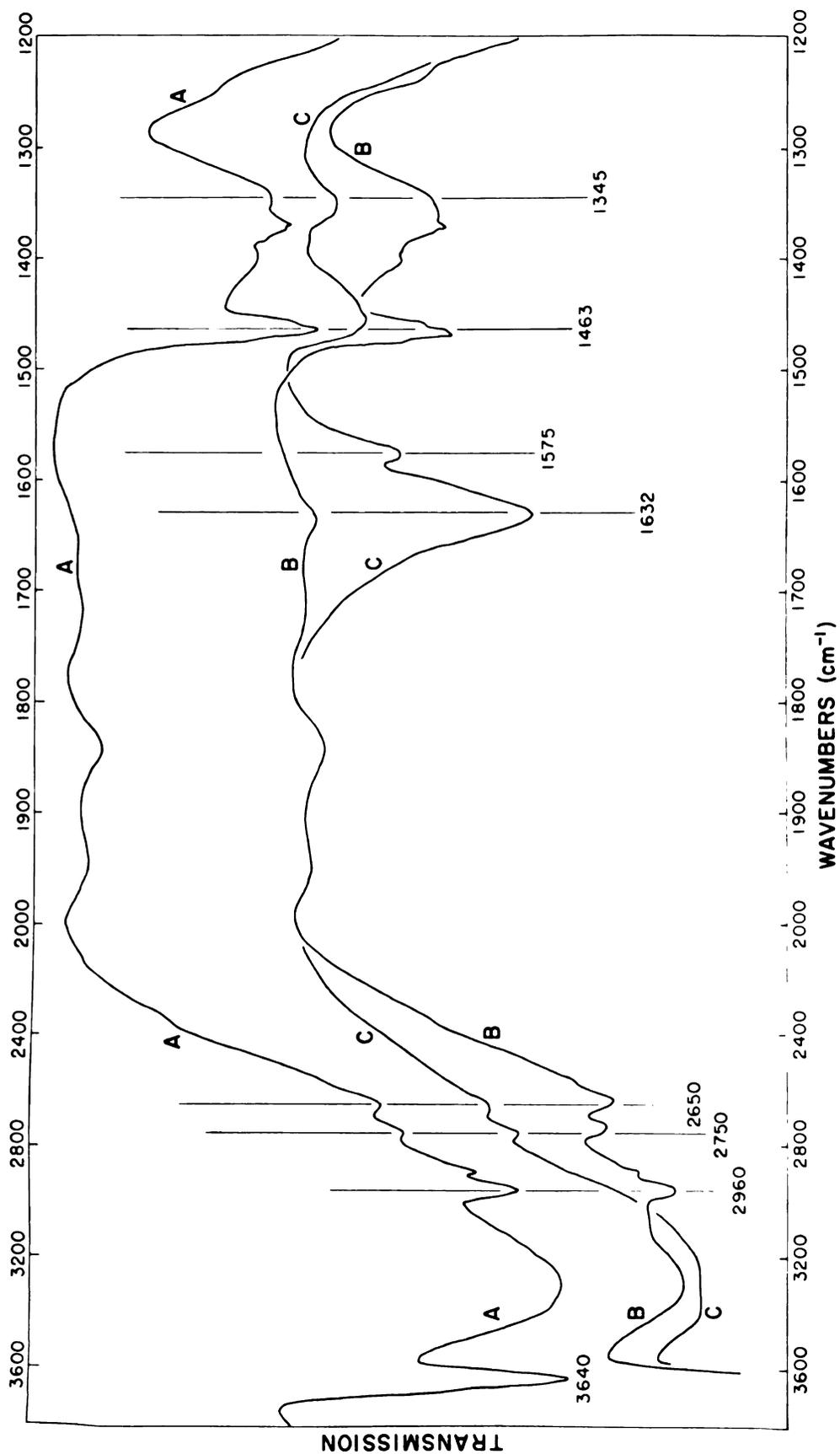
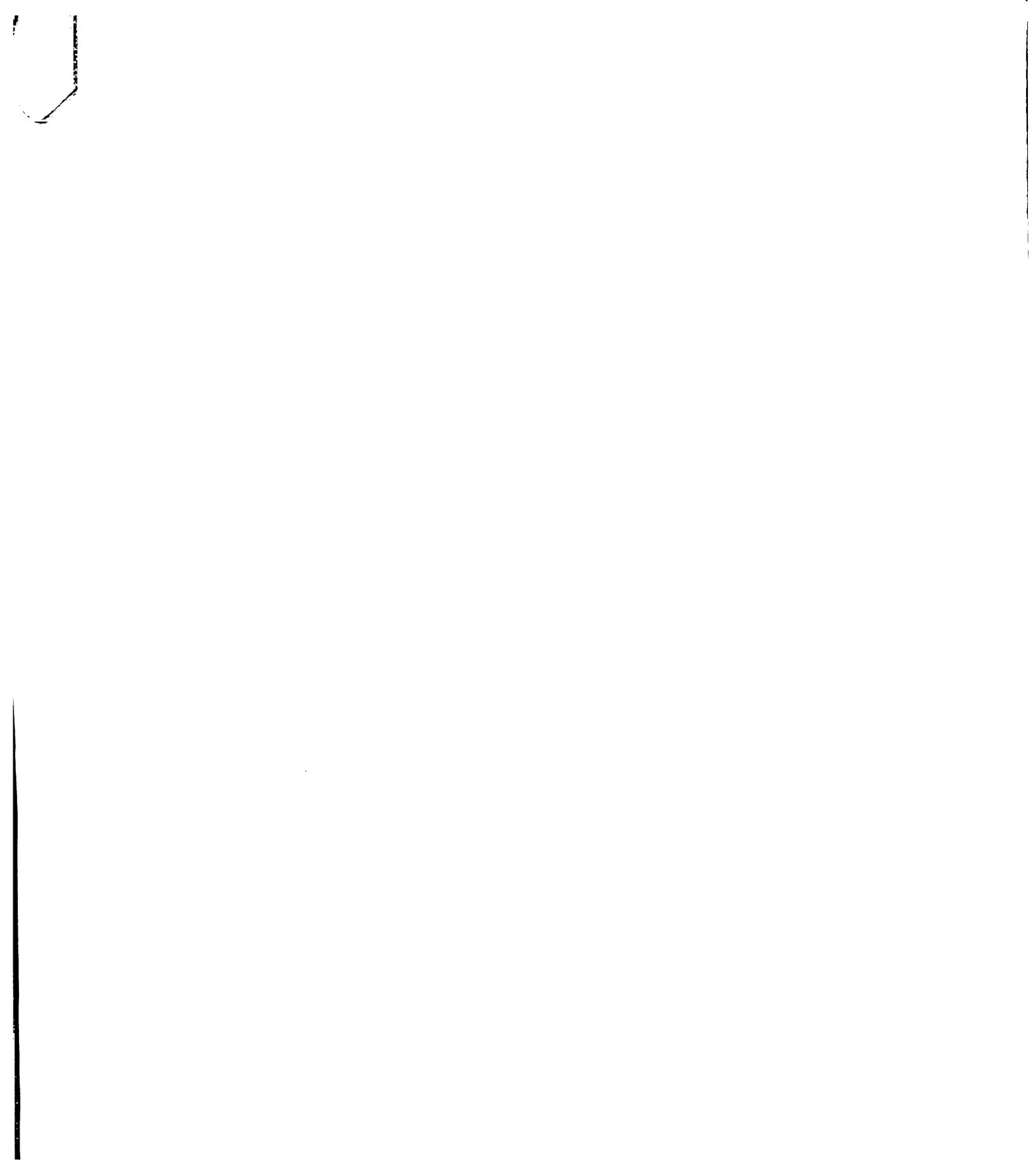


Figure 20. Infrared spectra of glycol-Cu-montmorillonite: A, after adsorbing glycol at 115°C for 24 hrs.; B, same after exposure to the atmosphere for 4 hrs.; C, same after exposure to the atmosphere for 163 hrs.

the clay film over a free glycol surface at 115°C for 24 hours in a evacuated desiccator. Tracing A was recorded immediately upon exposure of the cooled clay to the atmosphere. Therefore, the bands arising from various glycol vibrations are essentially those of liquid glycol, since this is the predominant form at the time of exposure to the atmosphere. However, it will be noted that the Cu-clay is completely dehydrated as indicated by the absence of the 1632 cm^{-1} deformation band. After four hours exposure to the atmosphere, most of the glycol in the micropores and on the external surfaces of the clay has evaporated and a trace of water has been adsorbed (curve B). Further exposure to the atmosphere results in the replacement of glycol by water accompanied by a strong 1632 cm^{-1} band.

Probably the most significant observation with regard to the glycol-Cu-clay complex is the development of new bands at 2750 and 2650 cm^{-1} . These bands are thought to arise from the glycolic O-H stretching vibration of molecules coordinated directly to the copper ion. Since two bands appear, it is likely that coordination occurs through one of the OH groups, while the other group is involved in either intra- or intermolecular H-bonding. This is the type of metal-glycol coordination complex suggested by Miyake (1959) for cobalt (II) and nickel (II) when the chloride salts are added to liquid glycol. A slight shift of 20 cm^{-1} to a lower frequency after four hours exposure to the atmosphere (curve B, figure 20) is expected, due to stronger bonding as a result of loss



of the excess glycol. Since these bands do not occur to any great extent in other cation-glycol or ethanol-clay systems, they are not considered to arise from perturbed C-H stretching vibrations as alluded to by Tettenhorst et al. (1962).

There is complete agreement with Tettenhorst et al. (1962) that no significant band shifts were observed for any of the C-H vibrations of adsorbed glycol. A slight shift of 10 and 6 cm^{-1} toward a higher frequency was indicated for the CH_2 asymmetrical and symmetrical stretching vibrations, respectively. If such a shift does indeed occur, it would: a) fit well into the argument for coordination through the oxygen atoms, and b) exclude the hypothesis of C-H...O-clay interactions. Also, a slight shift does occur in the 1330 cm^{-1} band of liquid glycol to 1350 cm^{-1} in the adsorbed state. Although this band is predominantly O-H in character, discretion must be exercised in making interpretations, since some CH interaction is present.

The 1575 cm^{-1} band (curve C, figure 20) is thought to arise from perturbed water, while the broad band in the 1454 cm^{-1} region is thought to arise from a carbonate vibration. Both of these bands will be discussed later.

The time course of glycol desorption from Cu-montmorillonite is given in figure 21. It should be pointed out that the solid line represents an estimate of the absolute amount of glycol present while the broken line represents the sum of glycol plus water on the clay at any given time. If it

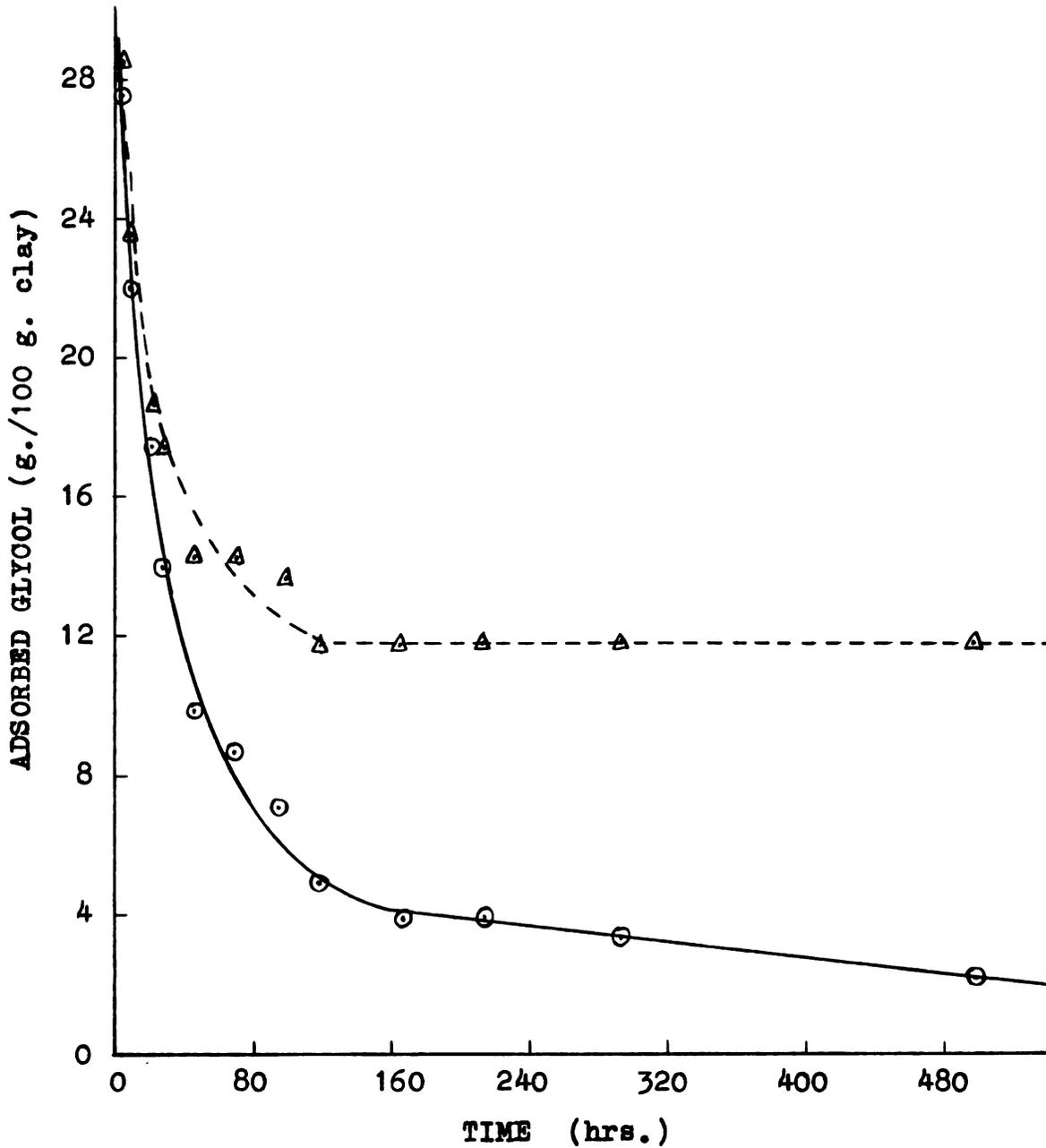


Figure 21. Adsorbed glycol as a function of time of atmospheric exposure for Cu-montmorillonite: \circ , glycol; Δ , glycol + H₂O.



is assumed that 25 g. glycol per 100 g. montmorillonite is required for monomolecular coverage of the total surface (Dyal and Hendricks, 1950), then all the glycol contributing to multilayer and capillary adsorption has been dissipated in approximately four hours at which time water has begun to enter the complex. The desorption curve (solid line) is then characterized by a rather rapid loss up to 160 hours of exposure to the atmosphere at which time the rate of loss becomes a constant until all of the glycol has been replaced by water (\sim 800 hours). It will be noted also that the apparent desorption curve (broken line) levels off, suggesting that at this time glycol lost is equal to water gained.

Al-montmorillonite.

The infrared data for Al-montmorillonite (figure 22) does not differ greatly from that for Cu-montmorillonite. The principle difference that occurs is the greatly reduced absorbance in the $2750-2650\text{ cm}^{-1}$ region of the spectrum. Although a distinct peak does occur at 2660 cm^{-1} , the reduced intensity suggests much less perturbation of directly coordinated glycol. This difference might be explained by the different coordinating habits of the two cations. As explained in the section on ethanol adsorption, the spatial arrangement of ligands and the restrictive nature of the clay platelets impose greater distortion upon the octahedral complexes of aluminum than it does on the square planer complexes of copper. Further indirect proof of this argument arises

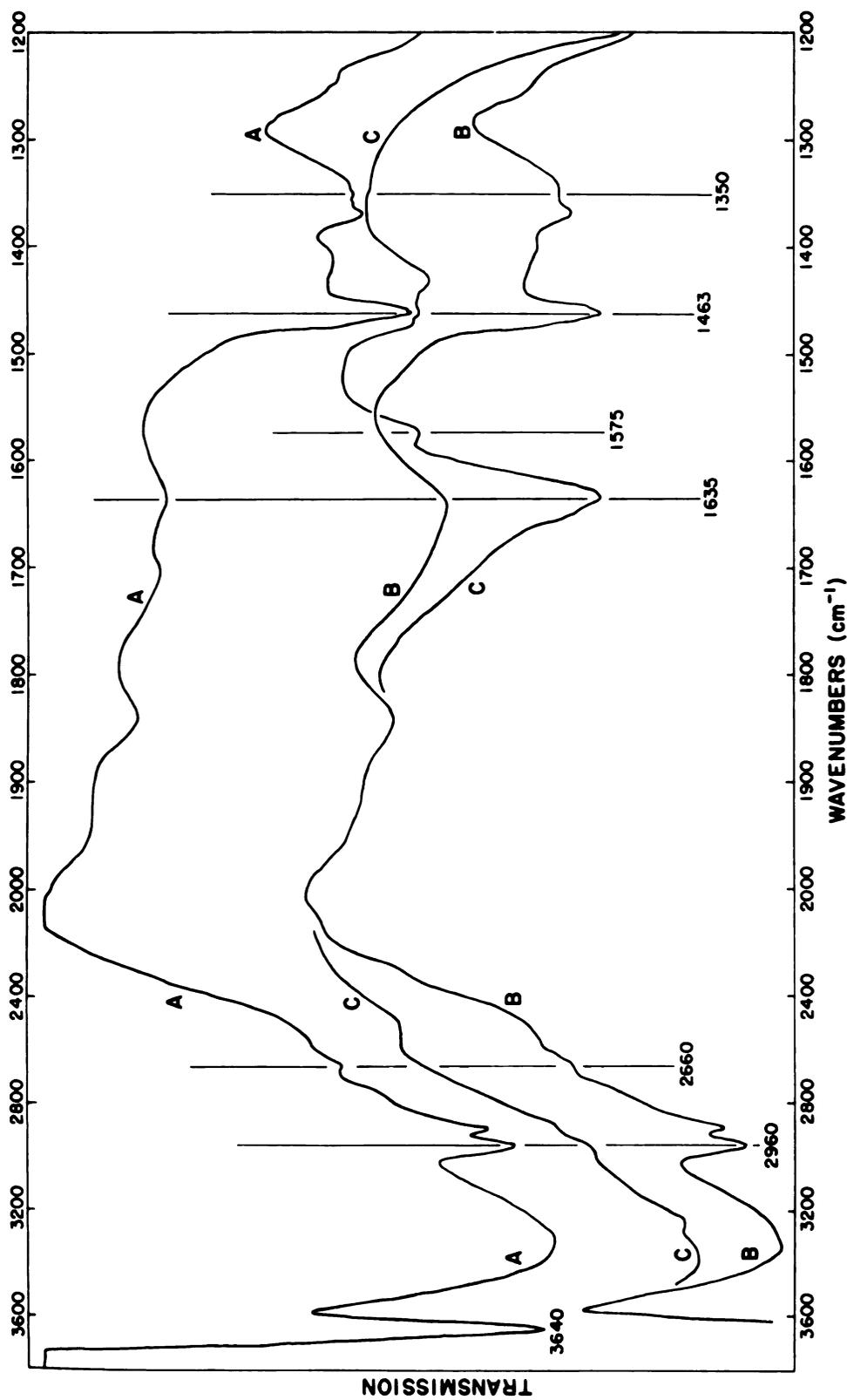


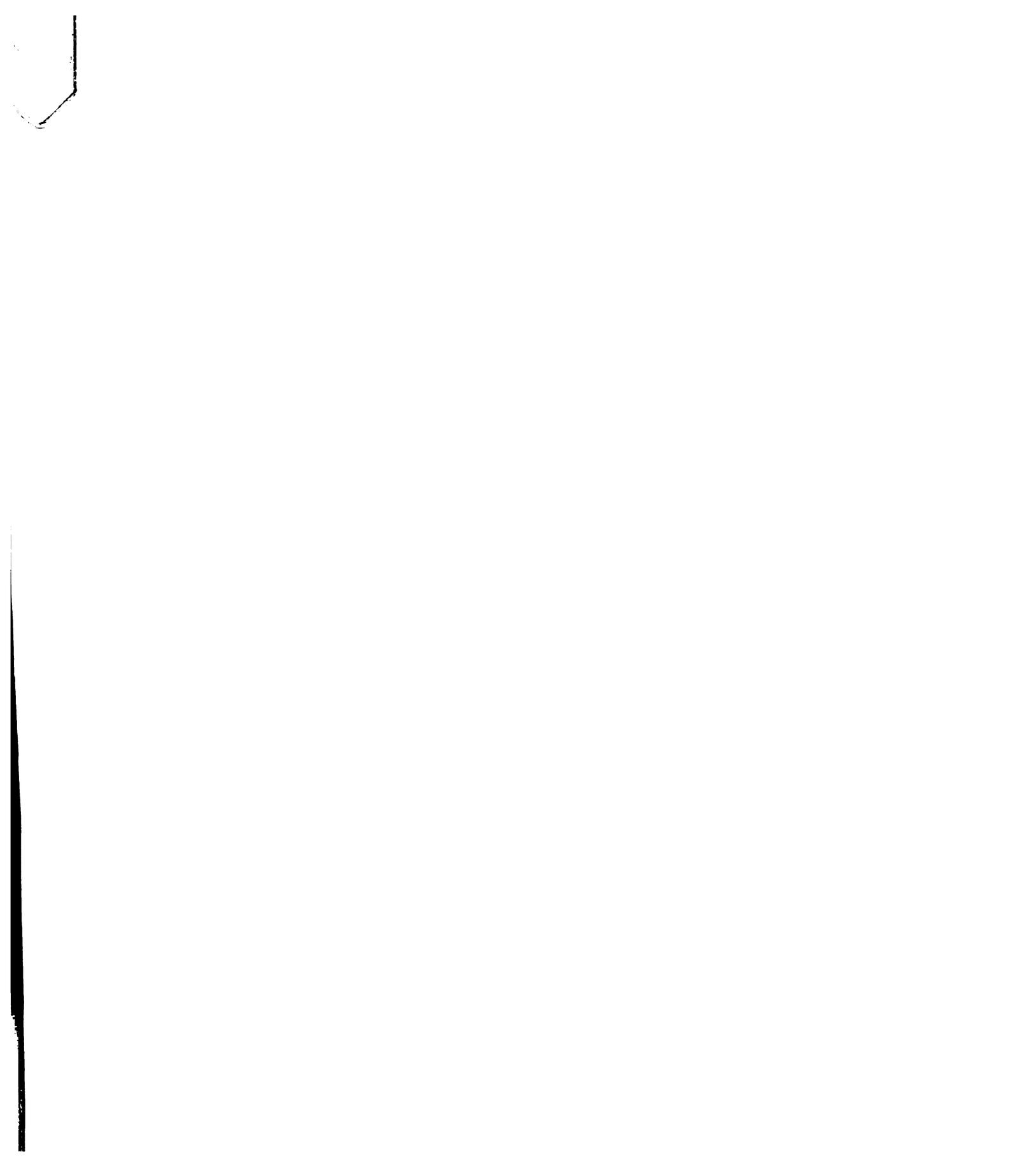
Figure 22. Infrared spectra of glycol-Al-montmorillonite: A, after adsorbing glycol at 115°C for 24 hrs.; B, same after exposure to the atmosphere for 4 hrs.; C, same after exposure to the atmosphere for 280 hrs.

from the initial speed of hydration. As can be noted in curve B, figure 22, more water has been adsorbed by the Al-clay after four hours of exposure to the atmosphere, as indicated by the 1635 cm^{-1} deformation vibration of water, than was adsorbed by the Cu-clay in the same length of time.

Desorption curves presented in figure 23 are very similar in character to those for Cu-montmorillonite. The curves level off after approximately 160 hours exposure to the atmosphere as did those for Cu-clay. Whether a true glycol-water equilibrium has been attained or not, cannot be stated with certainty, since the infrared vibrations for glycol have been masked after exposure to the atmosphere for 280 hours (tracing C, figure 22).

Ca-montmorillonite.

The infrared spectra for glycol solvated Ca-montmorillonite presented in figure 24 are essentially the same as those presented for Al-clay. Slight adsorption of water has occurred by four hours of exposure to the atmosphere (curve B). The main difference between the Ca- and Al-complexes is the position of the predominantly O-H deformation band of glycol. In Ca-montmorillonite the band is positioned at 1335 cm^{-1} , which is very close to that of the pure liquid, and is 15 cm^{-1} lower than in the Cu- and Al-complexes (compare curve B in figures 20, 22 and 24). This suggests that ion-dipole interactions are not as great in the Ca-glycol complex as they are in the Cu- and Al-clay systems, which is in complete



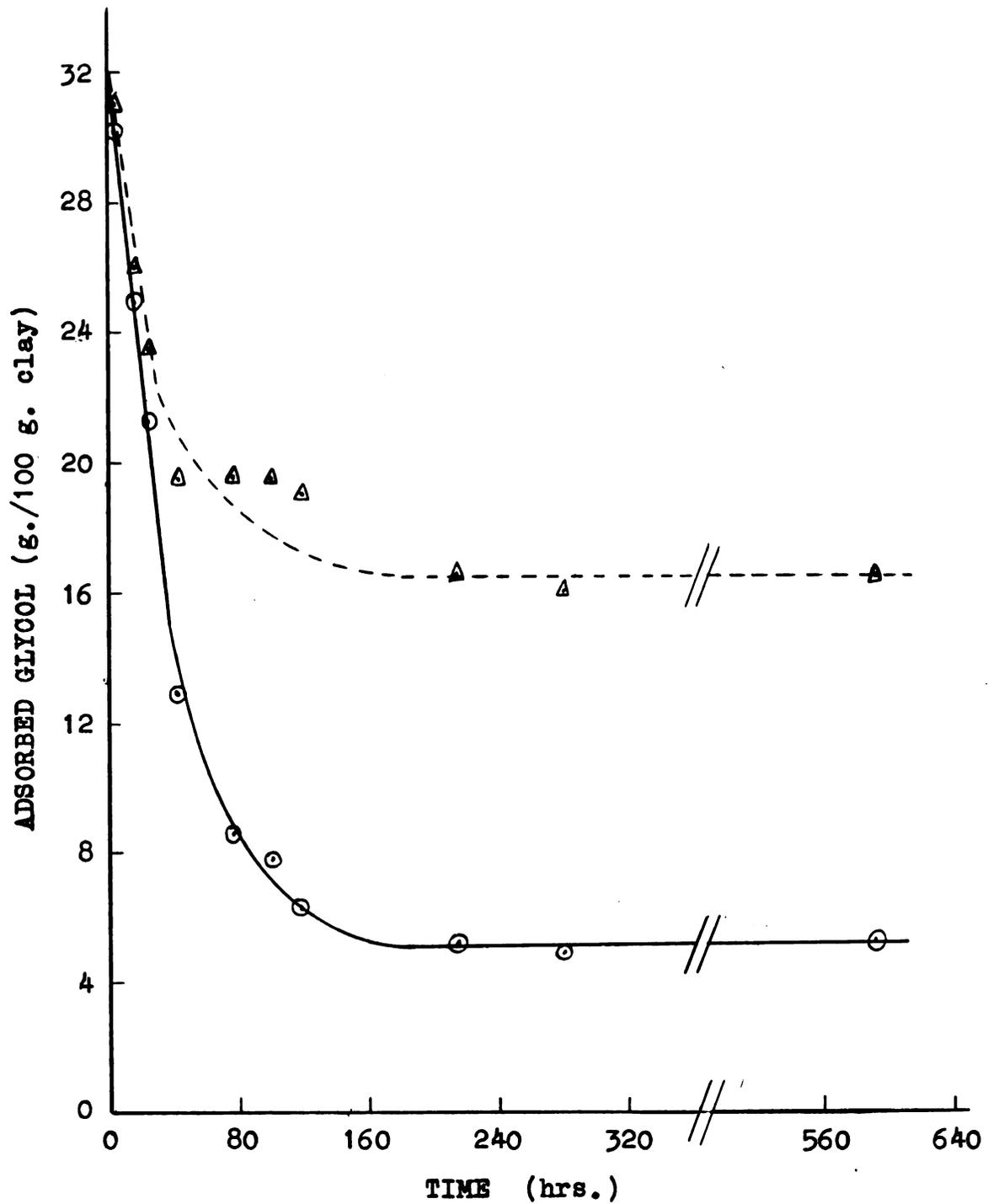
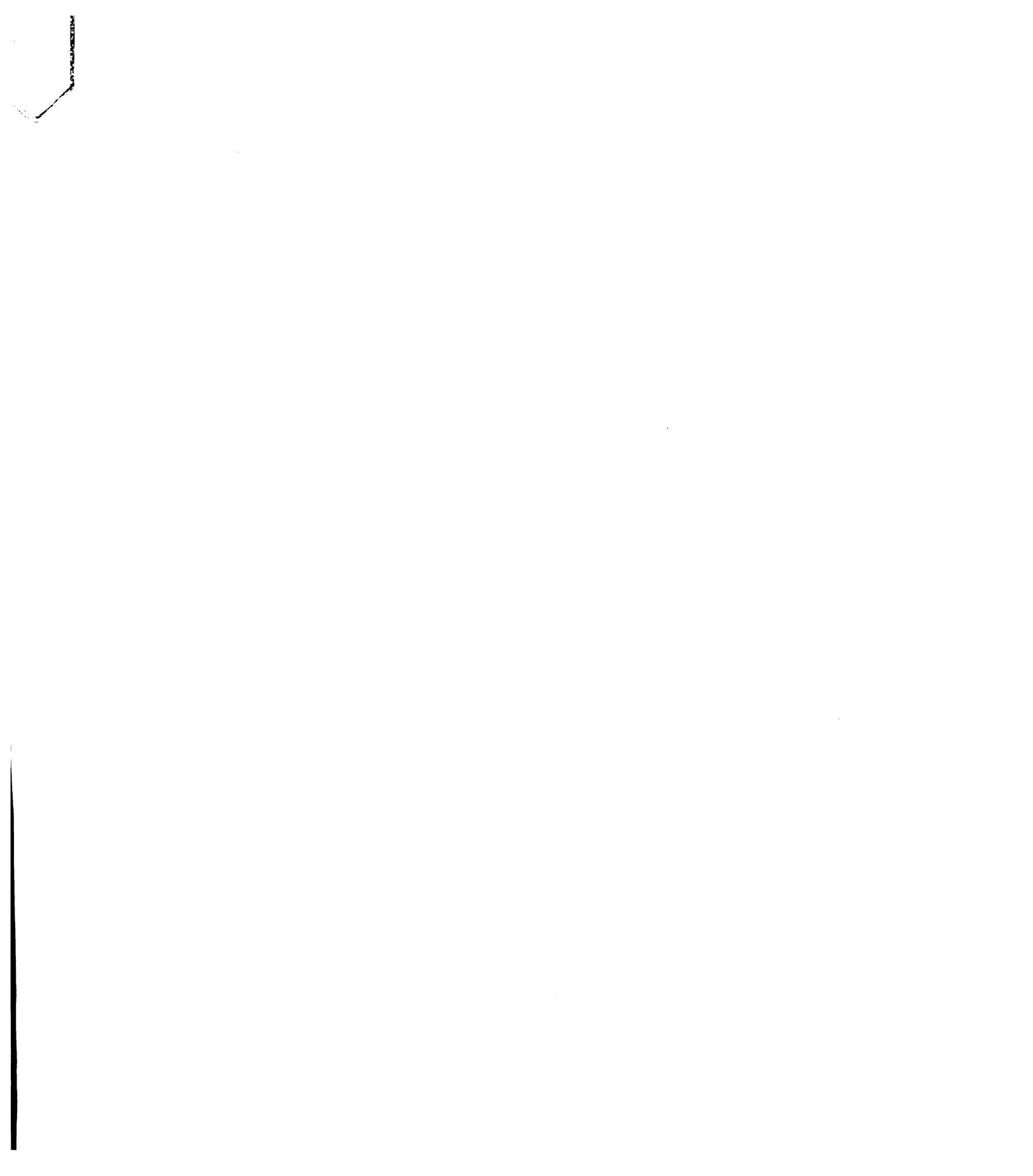


Figure 23. Adsorbed glycol as a function of time of atmospheric exposure for Al-montmorillonite: \odot , glycol; Δ , glycol + H₂O.



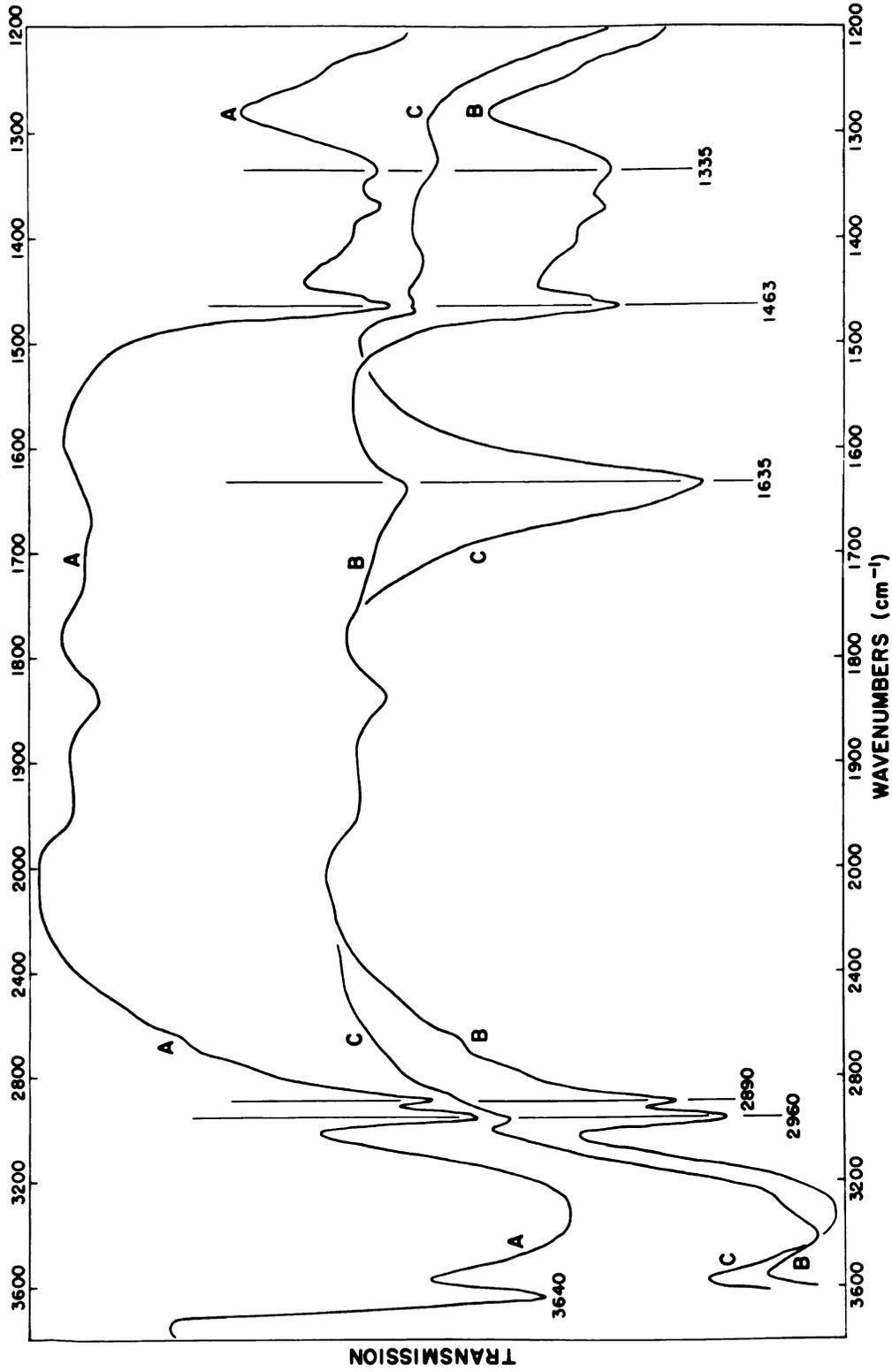


Figure 24. Infrared spectra of glycol-Ca-montmorillonite: A, after adsorbing glycol at 115°C for 24 hrs.; B, same after exposure to the atmosphere for 4 hrs.; C, same after exposure to the atmosphere for 215 hrs.

agreement with the lower solvation energy of calcium.

The desorption of glycol from Ca-montmorillonite as a function of rehydration time is presented in figure 25. The curves are of the same general character as those observed for Cu- and Al-montmorillonite, but replacement of glycol by water is achieved at a somewhat slower rate in the Ca-clay. Consequently, the break in the curves occurs after longer exposure to the atmosphere (~ 280 hours). It is also of interest to note that the break in the desorption curves occur at a glycol level between 4 and 5 g. per 100 g. clay for the three homoionic montmorillonite systems studied.

General considerations.

The x-ray data for the three homoionic glycol montmorillonite complexes are presented in figure 26. It should be noted that these data are for desorption-rehydration studies. The shaded symbols represent rational diffraction peaks for which an integral series of Bragg reflections were obtained, while the open symbols are irrational and represent random interstratified and transitional states.

In the glycol solvated state, the diffraction peaks are very rational with basal spacings ranging from 16.6 Å for Ca-montmorillonite to 17.1 Å for the most highly solvated Al-clay. Since glycol solvation has been used quite extensively in clay mineral identification studies employing x-ray techniques, numerous characteristic basal spacings for montmorillonite have been published covering the range observed

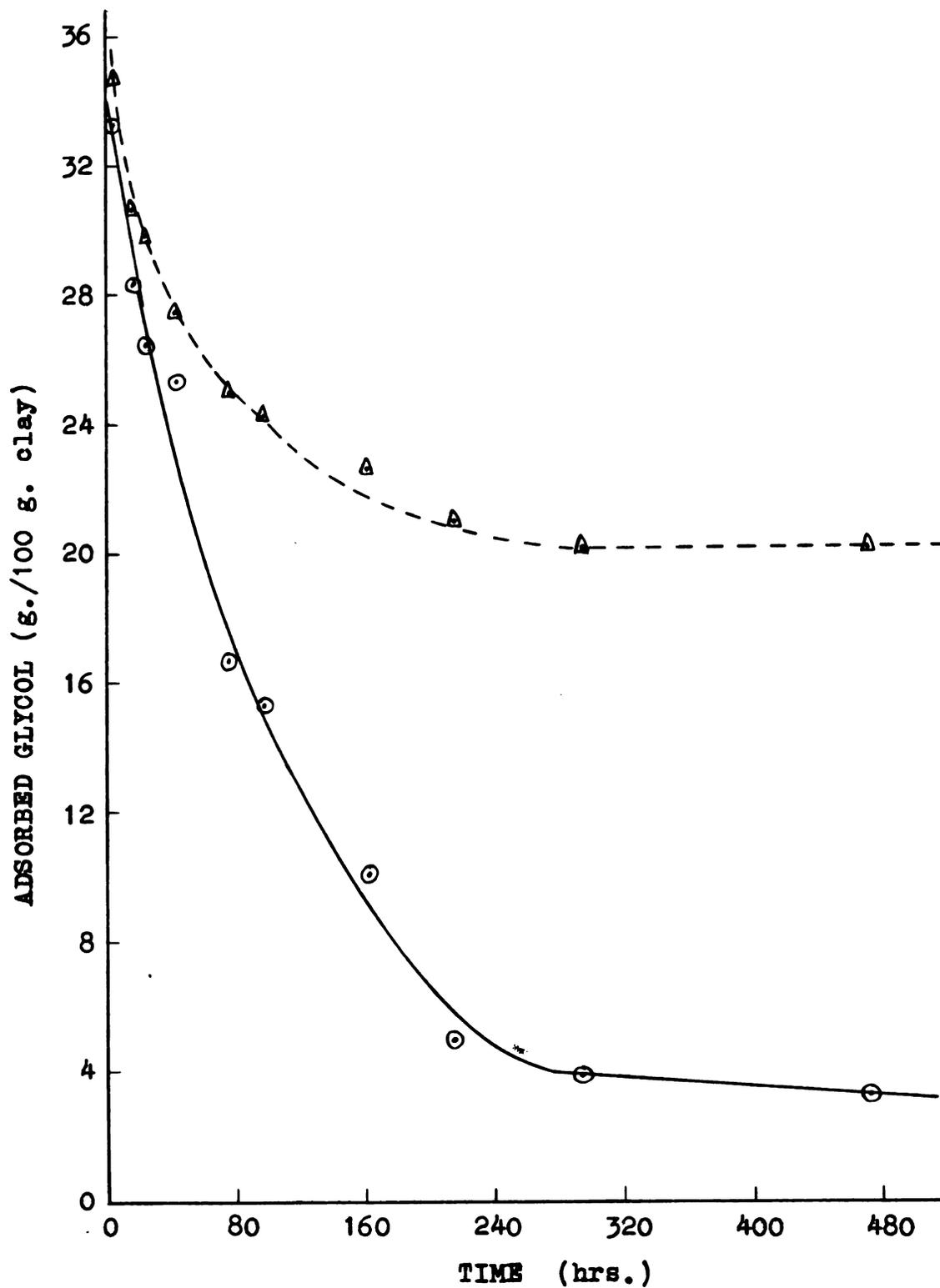


Figure 25. Adsorbed glycol as a function of time of atmospheric exposure for Ca-montmorillonite: \odot , glycol; Δ , glycol + H₂O.

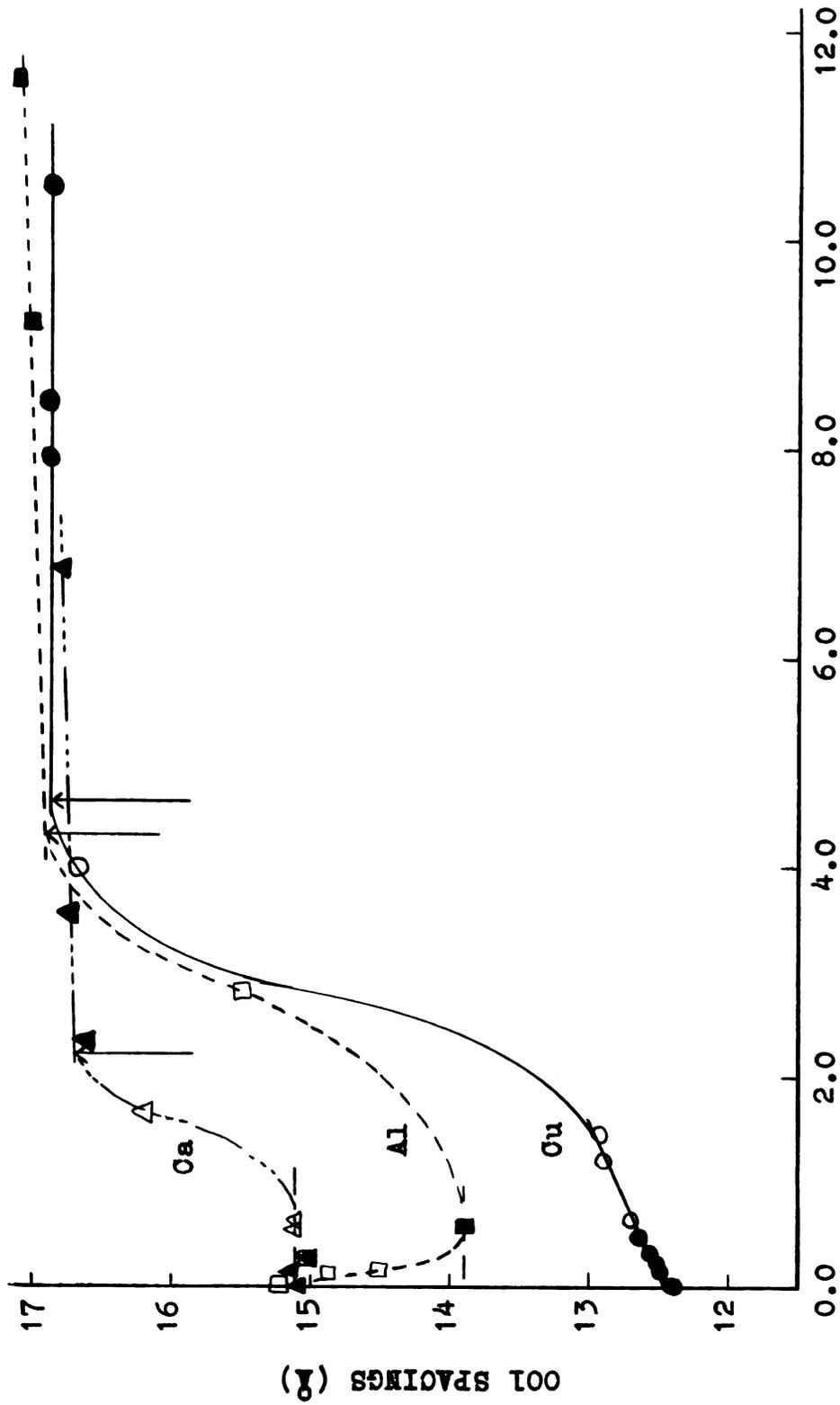


Figure 26. Curves showing variation of (001) spacing as a function of the mole ratio of glycol:water for homiontic montmorillonite. Shaded symbols represent rational non-interstratified systems, and open symbols indicate presence of random interstratification. (\uparrow) represents the point where 25 g. glycol/100 g. clay exists on the respective clays.



in this study. Such variations can be easily explained by the different types of coordination complexes in the interlamellar spaces. Rearrangement in the complexes with varying degrees of packing around the cation can explain the decrease in basal spacings of octahedral Al- and Ca-complexes while still maintaining rational diffraction peaks. However, in spite of these differences, it was noted that all systems begin to show random interstratification once the glycol content drops below 25 g. per 100 g. clay which is the value calculated by Dyal and Hendricks (1950) for monomolecular coverage of the total montmorillonite surface. This break occurs when the mole ratio (glycol:water) has decreased to approximately six for Cu- and Al-montmorillonite and 2.3 for the Ca-clay. Kunze (1955) also noted that some glycol-montmorillonite complexes were not stable in the atmosphere, while Mackenzie (1948) noted that Ca-montmorillonite would maintain a constant 17.1 \AA basal spacing over a wide range of water contents as long as six water molecules were adsorbed for each glycol displaced.

With the advance of rehydration, the basal spacings of all three homoionic montmorillonites decrease and approach their respective air-dried spacings as glycol is replaced. The values given on the ordinate of figure 26 represent the basal spacings for clay films equilibrated at 20°C and 40% relative humidity. It is interesting to note that the plot of (001) spacings versus glycol content for Al-montmorillonite

passes through a minimum at 13.9 \AA , which has rational diffraction peaks and agrees with a stable 13.9 \AA "one layer" glycol-Mg-montmorillonite complex observed by Hoffmann and Brindley (1961a). This 13.9 \AA spacing occurs at a mole ratio (glycol:water) of 0.57 and is characterized by 7.2 molecules of glycol per aluminum ion, which is a value somewhat greater than the preferred coordination number of six for aluminum. Hence it is suggested that the random interstratification occurring in Al-montmorillonite at mole ratios greater than 0.6 is characterized by a vaporization of glycol and reorientation of coordination complexes. This reorientation might be thought of as a repositioning of the CCO plane from a parallel position to one that is more nearly perpendicular between the clay platelets. Such orientation would allow a reduction in the basal spacing leaving "glycol columns" between the clay platelets and allow water to fill in around these columns. Below a mole ratio of 0.6, the glycol complexes begin to break up and the randomly interstratified systems might well be characterized by complete layers of water as well as 13.9 \AA "glycol layers" (Mortland and Barake, 1966). The glycol-Ca-montmorillonite system might behave in a similar manner, except that the Coulombic type attractions between the cation and the clay platelets are not great enough to result in a minimum.

Similarly, the Cu-glycol system is initially characterized by a transition from octahedral to square planer

coordination, accompanied by a loss of glycol and a reduction in the basal spacing. This transition would result in a randomly interstratified system containing complete layers of either octahedrally or square planer coordinated glycol. Before this transition is complete, water begins to replace the glycol ligands which results in further interstratification. Once the mole ratio (glycol:water) reaches 0.5, the basal spacing of Cu-montmorillonite is characterized by the hydrated state.

Turning attention to the process of desorption of glycol from montmorillonite surfaces (see figures 21, 23 and 25), it will be noted that the loss of glycol can be divided into three steps. First, glycol that is contributing to capillary condensation and multilayer adsorption is rapidly lost by vaporization within the first four hours of exposure to the atmosphere. The next step is a curvilinear loss of glycol with respect to time which extends over the time interval from 4 to 160-200 hours. Finally, the remaining glycol is slowly lost at a constant rate with the possible exception of the Al-glycol system where an apparent equilibrium is reached. Hence, the adsorption-desorption of glycol is a reversible process in the systems studied.

The intermediate phase of glycol loss appears to obey the conditions of second order chemical kinetics (figure 27):

$$\frac{-d [C_2H_6O_2]}{dt} = k [C_2H_6O_2] [H_2O] \quad (3)$$

where: k = rate constant. Over the time interval where

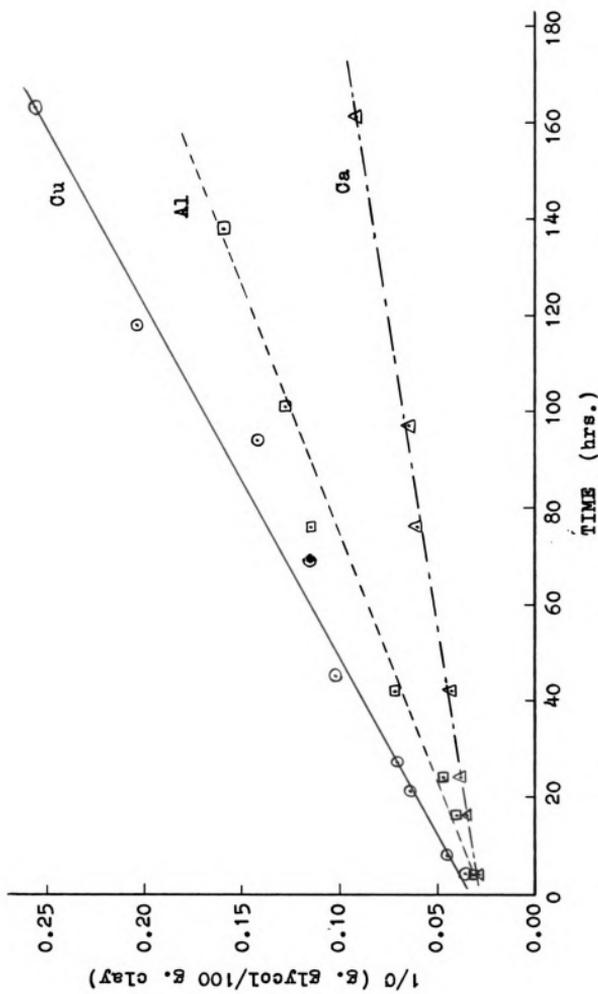


Figure 27. Reciprocal concentration of adsorbed glycol as a function of time of atmospheric exposure for homiohonic montmorillonite.

equation (3) is obeyed, the values for the rate constant (k) are: 13.6, 9.7, and 4.0×10^{-4} (100 g. clay) $\text{g}^{-1} \text{hrs}^{-1}$ for Cu-, Al-, and Ca-montmorillonite systems, respectively. It is to be noted that the kinetic order of a reaction is not necessarily related to the form of the stoichiometric equation for the reaction. However, it appears that neither glycol nor water are in excess over the time interval being considered. Therefore, it would intuitively appear that this second order reaction was bimolecular in nature as indicated by equation (3).

The 1575 cm^{-1} band

The development of a band at 1575 cm^{-1} has been noted when Cu- and Al-montmorillonite-glycol systems are exposed to the atmosphere (tracing C, figures 20 and 22). It was suggested that this band belonged to the deformation vibration of a particular species of water. It was then observed that this band occurred in clay films of Cu- and Al-montmorillonite treated in the same manner as was used in the glycol adsorption studies, with the exception that glycol was not present in the system. Tracing B, figure 28, shows the development of this band after heating to 115°C for 24 hours and followed by exposure to the atmosphere for 44 days. This 1575 cm^{-1} band was not present in a freshly prepared Cu-film (curve A, figure 28) and was only slightly developed immediately following the heat treatment.

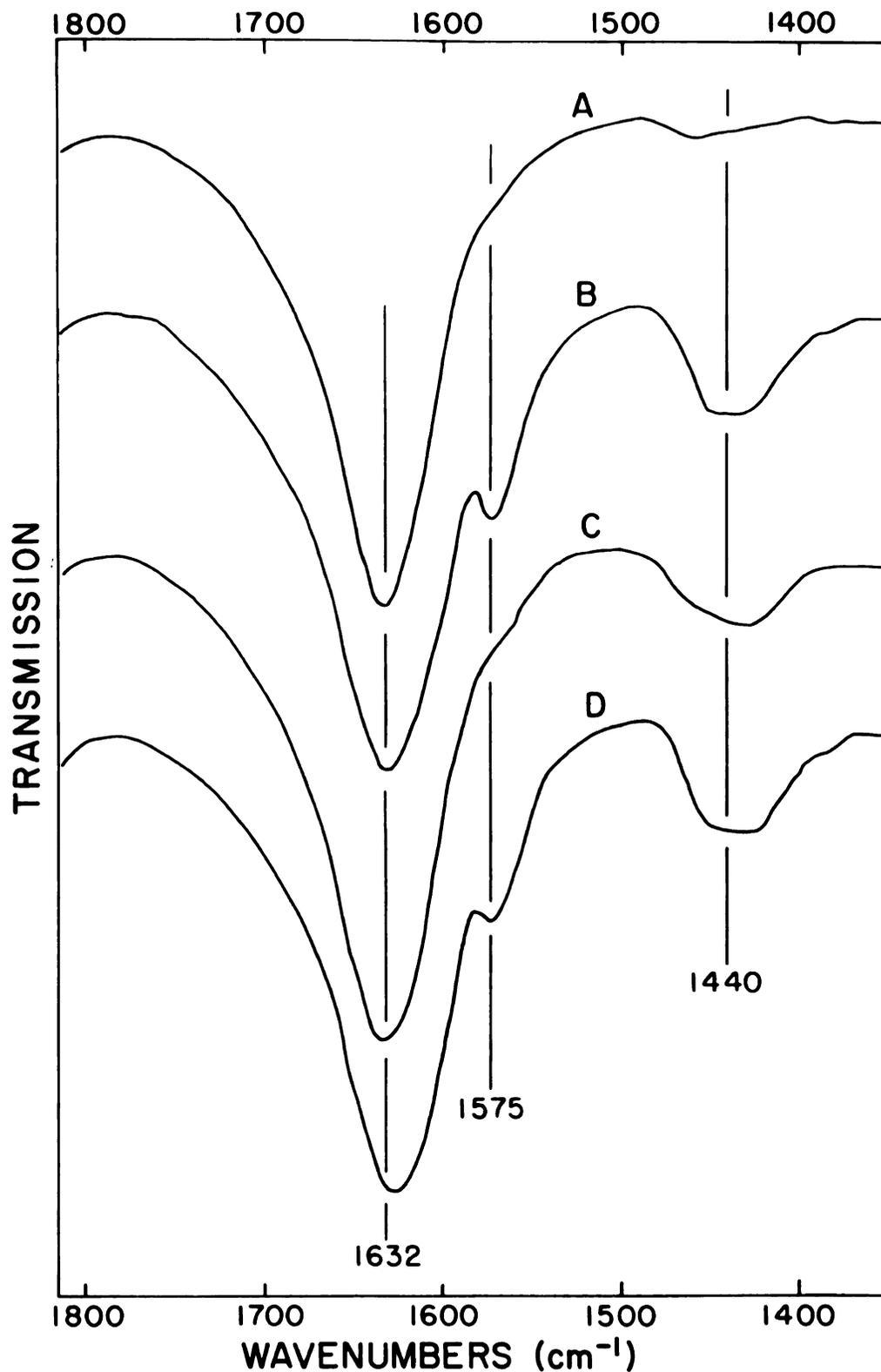


Figure 28. Infrared spectra of Cu-montmorillonite: A, air-dried; B, 44 days after heating at 115°C for 24 hrs.; C, after exposure to D₂O vapor for 3 hours on 65°C hotplate; D, same as C after exposure to atmosphere for 7 days.

A deuteration study was made to provide evidence that the 1575 cm^{-1} band was indeed arising from water. Cu- and Al-films that had been heated and exposed to the atmosphere for 44 days were suspended over a D_2O source for three hours on a 65°C hotplate at atmospheric pressure. The results of this deuteration for Cu-montmorillonite are presented in tracing C, figure 28. Tracing D is for the same film after exposure to the atmosphere for seven days following deuteration. This reversible deuteration of the 1575 cm^{-1} absorbing species is taken as strong evidence supporting its assignment to the deformation mode of water. The Al-montmorillonite as well as glycol analogs behaved in the same way. It is also of interest to note that the interlamellar H_2O absorbing at 1632 cm^{-1} was not replaced by D_2O under the conditions of this experiment, which suggests that the H_2O absorbing at 1575 cm^{-1} is associated with the external clay surfaces.

The $1480\text{-}1400\text{ cm}^{-1}$ band

It was noted that a broad band in the $1480\text{-}1400\text{ cm}^{-1}$ region of the spectrum emerged as glycol was lost from Cu-, Al-, and Ca-montmorillonite (tracing C, figures 20, 22, and 24). Like the 1575 cm^{-1} band, this band also developed in the absence of the glycol treatment (tracing B, figure 28). Since carbonates are known to have very strong absorption bands in this region of the spectrum (Lyon, 1964), it is suggested that the $1480\text{-}1400\text{ cm}^{-1}$ absorbing band arises from a carbonate species. Qualitative justification for a carbonate

assignment is the similarity in position and contour of the observed bands with those of known carbonates (Huang and Kerr, 1960; Hunt et al., 1950; Miller and Wilkins, 1952; Ross and Goldsmith, 1964). These similarities and the lack of any other known absorbing species in these systems are the bases for a carbonate assignment.

The particular carbonate species that may spontaneously occur is rather uncertain and somewhat speculative, and may vary from one system to another. Of course, the atmosphere is a ready source of carbon dioxide. It is known that clay minerals are subject to degradation at low pH values which will release magnesium from the structural lattice. It is also known experimentally that the residual water on an air-dried or drier clay is very dissociable when compared to the dissociation of pure water (Fripiat and Helsen, 1966; Mortland et al., 1963). Therefore, it appears reasonable that hydrolysis could occur with the protons then satisfying the negative charge of the clay lattice and releasing the saturating cations to form carbonates and basic salts such as $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. Degradation of the clay lattice would release magnesium for the formation of MgCO_3 . In the Ca-montmorillonite systems, there is the possibility of CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$ formation. Hence, it appears that carbonates could slowly form with time and that the particular species may vary from system to system. However, the available information precludes a more definitive statement.

Since the 1575 and 1480-1400 cm^{-1} absorption bands develop with time, it might be suggested that both bands are associated with a hydrated carbonate complex. An apparent relationship can be observed in figure 29 where the absorbance of the 1575 cm^{-1} band is plotted against the absorbance of the 1480-1400 cm^{-1} band for Cu- and Al-montmorillonite. The only explanation as to why a 1575 cm^{-1} water band does not arise in the Ca-system is that a different type of carbonate complex exists in the Ca-clay.

Irrespective of possible band assignments, the above observations tend to suggest the difficulty in maintaining clean clay surfaces and support the ideas of Martin (1962). It further suggests that storage of clays in an air-dried or drier state may alter the surfaces to such an extent that resulting data may not be representative of the true surface reactivity.

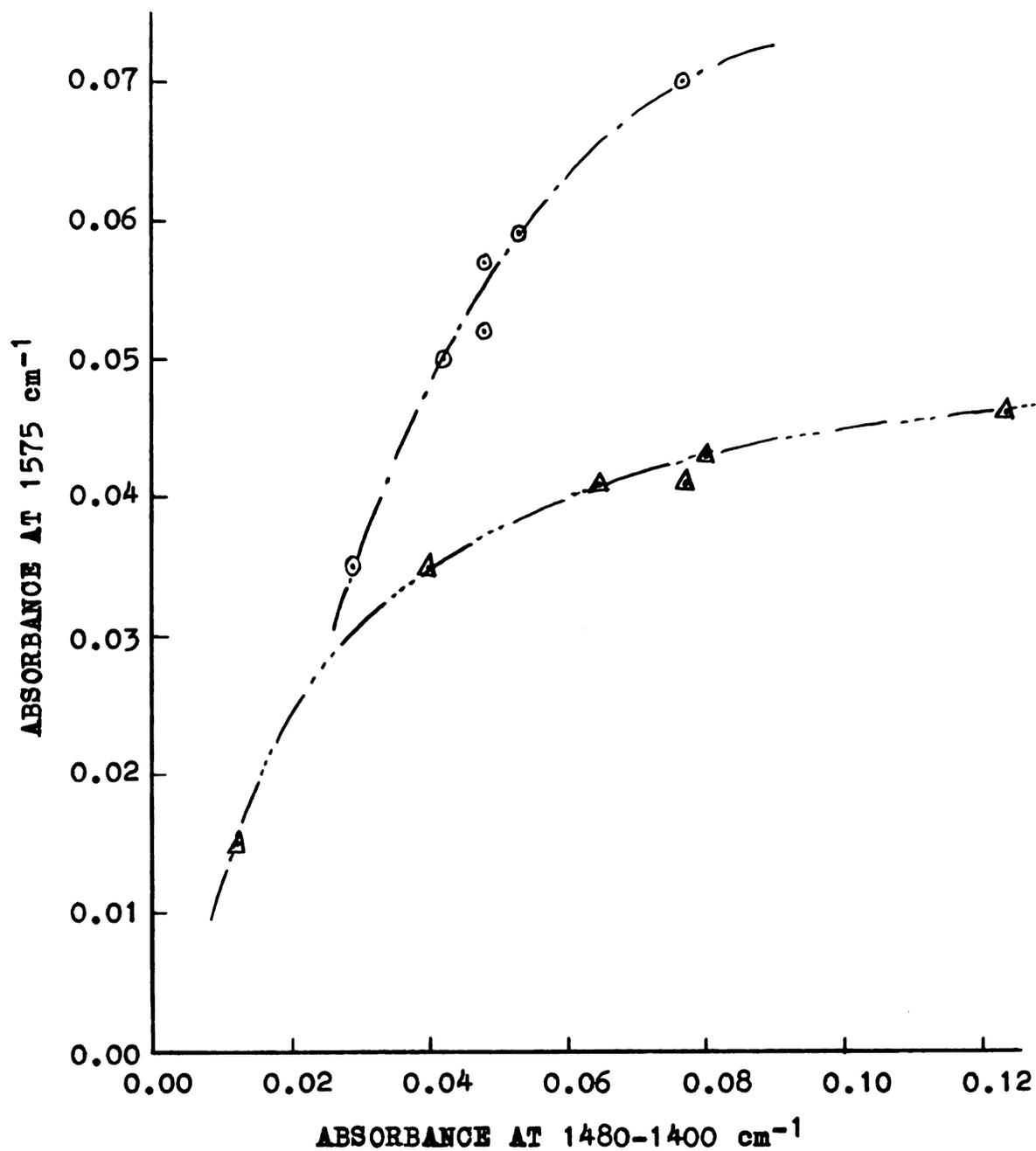


Figure 29. Absorbance of 1575 cm⁻¹ H₂O deformation band as a function of the absorbance of the 1480-1400 cm⁻¹ carbonate absorption band for Cu-montmorillonite (⊙) and Al-montmorillonite (△).

GENERAL DISCUSSION AND SUMMARY

Infrared data obtained from the ethanol studies showed that adsorbed water is replaced by ethanol on montmorillonite surfaces. Ethanol at relative pressures of less than 0.5 removed the major portion of the water retained by air-dried clay films, while a relative pressure of unity reduced the water content to less than 0.7%. In the case of Na-montmorillonite, essentially all of the water was removed. As dehydration occurred, 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 the two phase nature of adsorbed water as suggested by Russell and Farmer (1964). The 1598 cm^{-1} absorbing species is the more strongly adsorbed and is thought to be directly coordinated to the copper ion. On the other hand, the deformation band of water was displaced to a higher frequency as Al- and Ca-montmorillonite were dehydrated. Such shifts are in agreement with the principle that H-bonding and perturbation increases the frequency of bending modes (Hass and Sutherland, 1956). These apparent anomalies are reconciled by a consideration of the different types of coordination habits of the cations. Octahedrally coordinated complexes of aluminum and calcium are subjected to greater distortion in the interlamellar

spaces than the square planer complexes of Cu-montmorillonite. In contrast to the polyvalent cation systems, the position of the water deformation band was unchanged in Na- and NH_4 -montmorillonites, which suggested that forces other than ion-dipole interactions are predominant during dehydration-ethanol adsorption in these systems. This reduced ion-dipole interaction is easily explained when it is remembered that the solvation energies are much less for sodium and ammonium.

The adsorption isotherms for ethanol on the different homoionic montmorillonites further substantiate the interpretations of the infrared data. X-ray diffraction results for Cu- and Ca-EtOH complexes showed two stable regions at basal spacings of 13.3 and 16.5 Å. This is in agreement with the observations of Brindley and Ray (1964) for Ca-montmorillonite. Al-, Na-, and NH_4 -complexes never expand beyond 13.3 Å. The trivalent nature of aluminum restricted further expansion between the clay platelets, while the low solvation energies of sodium and ammonium were not great enough to overcome the ion-clay and van der Waals binding forces holding the clay platelets together.

Evacuation against a liquid nitrogen cold trap did not remove all of the adsorbed ethanol. Apparent equilibrium was reached within five hours. Cu- and Al-montmorillonite retained 4.5 and 6.8 molecules per ion, respectively, which is very close to their preferred coordination number, while Na- and NH_4 -clays, which do not exhibit strong coordination,

retained less than one molecule per cation. Rehydration accompanied by ethanol loss occurs very rapidly except in the Cu-montmorillonite system where approximately 70 hours were required. In the case of Cu-montmorillonite, the loss of ethanol followed a diffusion controlled process, of the type noted by Fripiat and Helsen (1966) for diffusion of "free" ammonia between clay sheets.

Deuterated ethanol studies confirmed that water does exist after equilibration of clay films with EtOH at a relative pressure of unity through OD-OH exchange between EtOD and HOH. Two lines of proof were noted: 1) the decreased absorbance of the 1630 cm^{-1} H_2O deformation band on the clay equilibrated with EtOD, and 2) the appearance of a EtO-H deformation band at 1265 cm^{-1} on the deuterated clay.

All the water on air-dried Cu-, Al-, and Ca-montmorillonite was replaced by glycol when the clay films were equilibrated with glycol at 115°C for 24 hours. Infrared spectra of glycol-Cu-montmorillonite complexes showed two new bands at 2750 and 2650 cm^{-1} . These bands were assigned to the O-H stretching modes of glycol coordinated directly to the copper ion for two reasons: 1) this would represent the most perturbed environment to lower the vibrations to such a low frequency, and 2) these bands do not appear with as much intensity in Al- and Ca-clays, which would exclude any type of bonding to the clay surface. Since two bands occur, it was suggested that one of the OH groups was coordinated directly

to the cation, while the other was involved in either intra- or intermolecular H-bonding. Similar complexes have been suggested by Miyake (1959) for cobalt (II) and nickel (II) complexes in liquid glycol. The infrared spectra also showed that the predominantly OH deformation band of glycol at 1330 cm^{-1} was shifted to 1335 cm^{-1} when adsorbed on Ca-montmorillonite and to 1350 cm^{-1} when adsorbed on Cu- and Al-montmorillonite. This suggested that ion-dipole interactions were not as great in the glycol-Ca-clay systems as they were in the Cu- and Al-systems.

The glycol desorption curves were similar for Cu-, Al-, and Ca-montmorillonite. They were easily divided into three sections: 1) the rapid vaporization of the glycol contributing to multilayer and capillary adsorption, which was dissipated in approximately four hours; 2) the curvilinear loss of glycol with respect to time, which extended over the time interval from 4 to 160-200 hours and obeyed the conditions of second order chemical kinetics; 3) the constant rate loss of the remaining glycol. When the glycol content was greater than 25 g. per 100 g. clay, rational x-ray diffraction peaks were observed which ranged from 16.6 \AA for Ca-montmorillonite to 17.1 \AA for the highly solvated Al-montmorillonite. As water begins to enter the interlamellar spaces, rearrangements within the coordination spheres and glycol loss resulted in randomly interstratified systems. These results are in contrast to those of Mackenzie (1948) who noted a constant

17.1 Å basal spacing over a wide range of glycol:water ratios for Ca-montmorillonite.

Absorption bands at 1575 cm^{-1} and $1480\text{-}1400\text{ cm}^{-1}$ were observed to develop on clay films that were exposed to the atmosphere following 24 hours of heating at 115°C in an evacuated system. By deuteration with D_2O , it was concluded that the 1575 cm^{-1} band arises from water external to the interlamellar space. By the process of elimination and comparisons with spectra of known substances, the $1480\text{-}1400\text{ cm}^{-1}$ band was assigned to a carbonate vibration. Since the absorbance of both of these bands increased with time of atmospheric exposure, it was suggested that both may arise from a rather undefined hydrated carbonate material. This type of spontaneous contamination of the clay surfaces emphasizes the importance of using freshly prepared clay films, which supports the ideas of Martin (1962).

The results of these studies clearly demonstrate the influential nature of the exchangeable cation in the adsorption-desorption of ethanol and ethylene glycol on homoionic montmorillonite surfaces. This is in agreement with the well established fact that the water content of clay under a given set of conditions is directly related to properties of the saturating cation. However, there have been considerable differences of opinion as to the influential nature of the exchangeable cation upon the adsorption of non-ionic polar organic molecules on clay surfaces. Hoffmann and Brindley

(1961a) noted that "... 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 MeOH and EtOH than did Na-montmorillonite. Numerous workers have shown that the adsorption of glycol varies with the type of saturating cation (Dyal and Hendricks, 1952). This led Quirk (1955) to conclude that glycol molecules may "... be adsorbed around the cations on clay surfaces."

No evidence was found to support the hypothesis put forth by Bradley (1945) that C-H...O-clay type interactions are important in the adsorption of non-ionic polar organic materials on clay surfaces. The C-H stretching vibrations of ethanol and glycol were not observed to shift to a lower frequency upon adsorption, which should occur if C-H...O-clay bonds occur. In fact, upon adsorption, the CH vibrations of both ethanol and glycol appeared to shift to a slightly higher frequency, which would suggest bonding through the oxygen atom of the molecule (Bellamy, 1958). More direct evidence of oxygen-metal interaction was obtained in the Cu-montmorillonite system where infrared bands attributable to the O-H stretching modes of coordinated glycol were observed. To a lesser extent, similar bands were observed for Al-glycol complexes and were absent in the Ca-system. The O-H deformation vibrations of both ethanol and glycol were noted to shift to a slightly higher frequency upon adsorption, which is in agreement with the above considerations.

The adsorption of both ethanol and glycol is reversible to exchange with water at 40% relative humidity with the possible exception of Al-glycol complexes where a low level of glycol appears to remain in equilibrium with atmospheric moisture. Both ethanol and glycol are effective in dehydrating the various homoionic clays, leaving only a highly dissociable species of water, which can contribute to the spontaneous degradation of the clay lattice. Since ethanol vapor can essentially dehydrate the clay, it is suggested that the indiscriminant use of ethanol as a washing agent to remove excess salts from soils and clays, may render the final experimental results meaningless. A case in point is some work done by Sumner (1963) on four tropical soils. He noted that two (10 ml.) washings with 80% EtOH greatly reduced the positive and negative charges on the soil as measured by $\frac{N}{2}$ NH_4Cl retention.

It has been pointed out that the x-ray data for ethanol and glycol systems can be explained by coordination complexes without having to inject O-H...O-clay type bonds as suggested by Emerson (1957) and Brindley and Ray (1964). One of the strongest, though indirect, proofs that cation-dipole interactions are of major importance is the differential response of homoionic montmorillonite systems to adsorption-desorption of ethanol and glycol. Therefore, it is not surprising that McNeal (1964) noted marked differences in the amount of glycol retained by montmorillonite saturated with various cations.

Accepting this thesis requires a break with the 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."

CONCLUSIONS

1. Homoionic montmorillonites were essentially dehydrated by equilibration with: a) ethanol vapor at a relative pressure of unity or b) ethylene glycol vapor at 115°C for 24 hours.

2. The adsorption of ethanol and ethylene glycol and their subsequent replacement by atmospheric moisture is a reversible process. However, the adsorption-desorption of these two compounds is a function of the saturating cation with respect to time, quantity, and type of complexes formed.

3. The rate of loss of ethanol from Cu-montmorillonite during rehydration is a diffusion controlled process. The replacement of ethylene glycol by water obeys the conditions of second order chemical kinetics.

4. The lack of uniformity in the shifting of O-H vibrations (stretching and deformation) of adsorbed ethanol and ethylene glycol suggest that cation-dipole type bonds, rather than O-H...O-clay type interactions, are of major importance in the binding of these compounds on montmorillonite surfaces saturated with polyvalent ions. More direct proof of ion-dipole type interactions are the infrared bands at 2750 and 2650 cm^{-1} which are directly attributable to the O-H stretching modes of coordinated glycol.

5. There was no evidence of a C-H...O-clay type bond with either ethanol or ethylene glycol.

6. X-ray data for ethanol and ethylene glycol systems can be explained by coordination type complexes as easily as by O-H...O-clay type interactions.

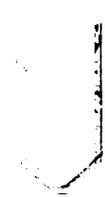


LITERATURE CITED

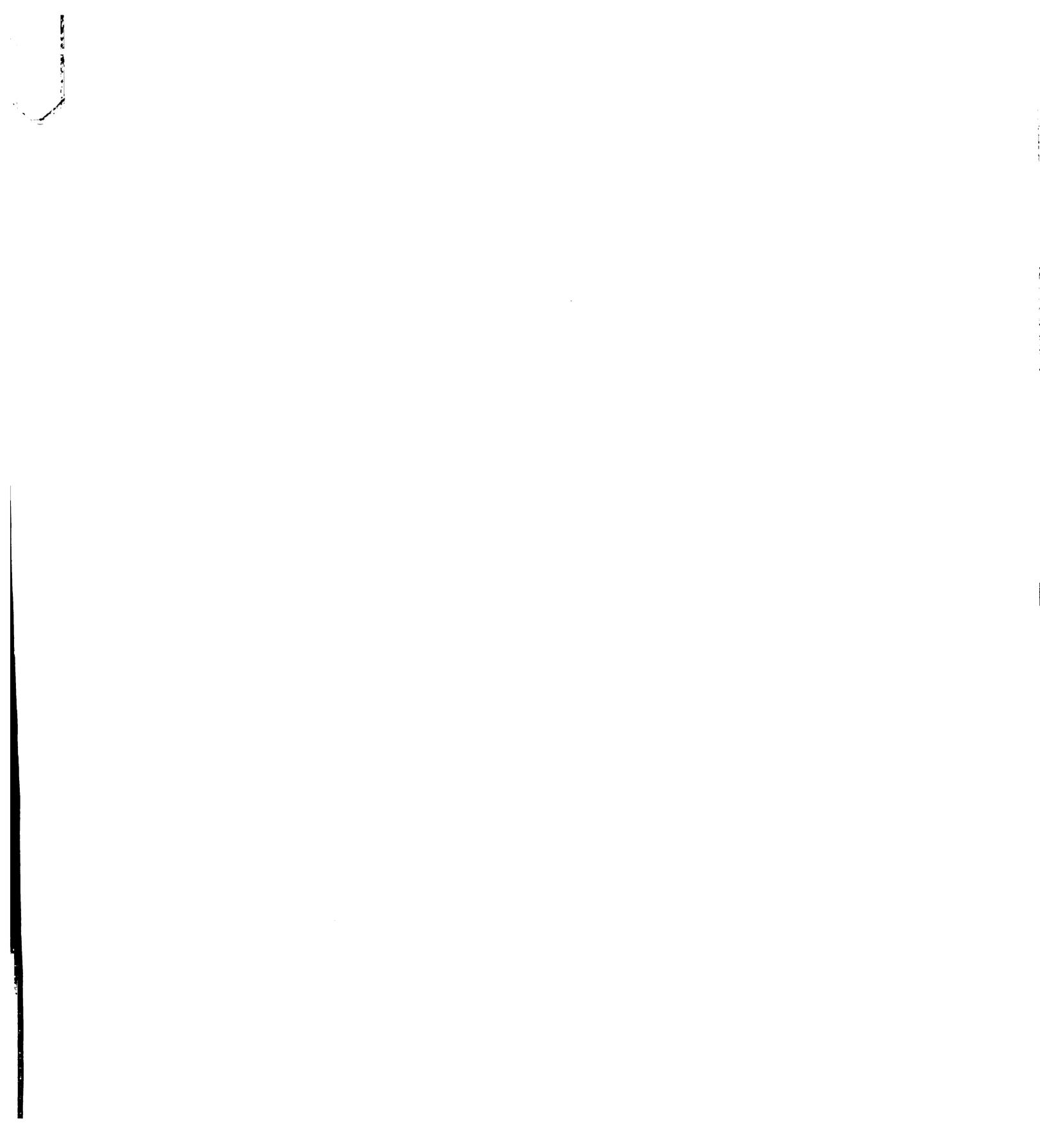
- Anderson, D. M. and G. Sposito. 1963. Rate of adsorption of water vapour by degassed Arizona bentonite. *Nature* 199:1085-1086.
- Barrer, R. M. and D. M. MacLeod. 1954. Intercalation and sorption by montmorillonite. *Trans. Faraday Soc.* 50:980-989.
- Barrer, R. M. and J. S. S. Reay. 1957. Interlamellar sorption by montmorillonite. *Proc. 2nd Int. Congr. Surface Activity II*:79-89.
- Barrow, G. M. 1952. Heat capacity, gas imperfection, infrared spectra, and internal rotation barriers of ethyl alcohol. *Jour. Chem. Phys.* 20:1739-1744.
- Barrow, G. M. 1961. Physical Chemistry. McGraw-Hill Book Company, Inc., New York, pp. 618-640.
- Barshad, Isaac. 1952. Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances. *Soil Sci. Soc. Am. Proc.* 16:176-182.
- Barshad, Isaac. 1960. Thermodynamics of water adsorption and desorption on montmorillonite. In Clays and Clay Minerals, 8th Conf., Pergamon Press, New York, 8:84-101.
- Bellamy, L. J. 1958. The Infra-red Spectra of Complex Molecules. John Wiley & Sons, Inc., New York.
- Benesi, H. A. and A. C. Jones. 1959. An infrared study of the water-silica gel system. *Jour. Phys. Chem.* 63: 179-182.
- Boreskov, G. K., Yu. M. Shchekochikhin, A. D. Makarov, and V. N. Filimonov. 1964. Investigation of the structure of surface compounds formed in the adsorption of ethanol on the γ -oxide of aluminum, by the method of infrared adsorption spectra. *Dokl. Akad. Nauk. SSSR.*, 156:901-904.
- Bouyoucos, George John. 1936. The state in which the hygroscopic moisture exists in soils as indicated by the determination with alcohol. *Soil Sci.* 41:443-447.

- Bower, C. A. and F. B. Gschwend. 1952. Ethylene glycol retention by soils as a measure of surface area and interlayer swelling. *Soil Sci. Soc. Am. Proc.* 16: 342-345.
- Bradley, W. F. 1945. Molecular associations between montmorillonite and some polyfunctional organic liquids. *Jour. Am. Chem. Soc.* 67:975-981.
- Brindley, G. W. 1956. Allevardite, a swelling double-layer mica mineral. *Am. Mineral.* 41:91-103.
- Brindley, G. W. and R. W. Hoffmann. 1962. Orientation and packing of aliphatic chain molecules on montmorillonite. *Clay-organic studies VI, in Clays and Clay Minerals*, Pergamon Press, New York, 9:546-556.
- Brindley, G. W. and S. Ray. 1964. Complexes of Ca-montmorillonite with primary monohydric alcohols (Clay-organic studies VIII). *Am. Mineral.* 49:106-115.
- Brindley, G. W. and M. Rustom. 1958. Adsorption and retention of an organic material by montmorillonite in the presence of water. *Am. Mineral.* 43:627-640.
- Brooks, C. S. 1960. Free energies of immersion for clay minerals in water, ethanol and n-heptane. *Jour. Phys. Chem.* 64:532-537.
- Coburn, W. C., Jr. and E. Grunwald. 1958. Infrared measurements of the association of ethanol in carbon tetrachloride. *Jour. Am. Chem. Soc.* 80:1318-1322.
- Davison, W. H. T. 1955. Infrared spectra and crystallinity. Part III. Poly (ethylene glycol). *Jour. Chem. Soc.* pp. 3270-74.
- Depireux, J. 1957. Etude de la vibration caracteristique du groupe carbonyle de quelques cetones et de quelques aldehydes par spectrometrie d'absorption infra-rouge. *Bull. Soc. Chim. Belg.* 66:218-228.
- Drushel, H. V., W. L. Senn, Jr., and J. S. Ellerbe. 1963. Effect of structure on the methyl and methylene group absorptivities in aliphatic alcohols. *Spectrochim. Acta.* 19:1815-1830.
- Dyal, R. S. and S. B. Hendricks. 1950. Total surface of clays in polar liquids as a characteristic index. *Soil Sci.* 69:421-432.

- Dyal, R. S. and S. B. Hendricks. 1952. Formation of mixed layer minerals by potassium fixation in montmorillonite. *Soil Sci. Soc. Am. Proc.* 16:45-48.
- Eeckman, J. P. and H. Laudelout. 1961. Chemical stability of hydrogen-montmorillonite suspensions. *Kolloid-Zeitschrift.* 178:99-107.
- Emerson, W. W. 1957. Organo-clay complexes. *Nature* 180:48-49.
- Farmer, V. C. and M. M. Mortland. 1966. An infrared study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite. *Jour. Chem. Soc. (London).* (in press)
- Folman, M. and D. J. C. Yates. 1959. Infrared studies of physically adsorbed polar molecules and of the surface of a silica adsorbent containing hydroxyl groups. *Jour. Phys. Chem.* 63:183-187.
- Fripiat, J. J., J. Chaussidon and R. Touillaux. 1960. Study of dehydration of montmorillonite and vermiculite by infrared spectroscopy. *Jour. Phys. Chem.* 64:1234-1241.
- Fripiat, J. J. and J. Helsen. 1966. Kinetics of decomposition of cobalt coordination complexes on montmorillonite surfaces, in Clays and Clay Minerals. 13th Natl. Conf., (in press).
- Gamo, Itaru. 1961a. Infrared spectra of water of crystallization in some inorganic chlorides and sulfates. *Bull. Chem. Soc. Japan.* 34:760-764.
- Gamo, Itaru. 1961b. Infrared absorption spectra of water crystallization in copper sulfate penta- and monohydrate crystals. *Bull. Chem. Soc. Japan.* 34:764-766.
- Gillery, F. H. 1959. Adsorption-desorption characteristics of synthetic montmorillonoids in humid atmospheres. *Am. Mineral.* 44:806-818.
- Glaeser, Rachel. 1954. Complexes organo-argileux et role des cations exchangeable. Thèse (Paris).
- Greene-Kelly, R. 1957. The montmorillonite minerals (smectites), in The Differential Thermal Investigations of Clays, ed. by R. C. Mackenzie. Mineral. Soc., London, pp. 140-164.



- Greenler, Robert G. 1962. Infrared study of the adsorption of methanol and ethanol on aluminum oxide. *Jour. Chem. Phys.* 37:2094-2100.
- Haas, C. and D. F. Hornig. 1960. Inter- and intramolecular potentials and the spectrum of ice. *Jour. Chem. Phys.* 32:1763-1769.
- Hadzi, D. and D. Jeramic. 1957. The infra-red spectrum and the OH in-plane deformation frequency in $\text{CH}_3\text{CD}_2\text{OH}$. *Spectrochim. Acta.* 9:263.
- Hadzi, D., I. Petrov and M. Zitka. 1962. The influence of hydrogen bonding upon the frequency and intensity of the OD in-plane deformation vibration of some phenols and alcohols. Advances in Molecular Spectroscopy, ed. by A. Mangina, vol 2, Pergamon Press, New York.
- Hass, H. and G. B. B. M. Sutherland. 1956. The infra-red spectrum and crystal structure of gypsum. *Proc. Roy. Soc. (London)* 236A:427-445.
- Hendricks, S. B., R. A. Nelson and L. T. Alexander. 1940. Hydration mechanism of the clay mineral montmorillonite saturated with various cations. *Jour. Am. Chem. Soc.* 62:1457-1464.
- Hoffmann, R. W. and G. W. Brindley. 1960. Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite. *Geochim. et Cosmochim. Acta.* 20:15-29.
- Hoffmann, R. W. and G. W. Brindley. 1961a. Adsorption of ethylene glycol and glycerol by montmorillonite. *Am. Mineral.* 46:450-452.
- Hoffmann, R. W. and G. W. Brindley. 1961b. Infrared extinction coefficients of ketones adsorbed on Ca-montmorillonite in relation to surface coverage. *Clay-organic studies. Part IV.* *Jour. Phys. Chem.* 65:443-448.
- Hornig, D. F., H. F. White and F. P. Reding. 1958. The infrared spectra of crystalline H_2O , D_2O , and HDO . *Spectrochim. Acta.* 12:338-349.
- Huang, C. K. and P. F. Kerr. 1960. Infrared study of the carbonate minerals. *Am. Mineral.* 45:311-324.
- Hunt, J. M., M. P. Wisherd and L. C. Bonham. 1950. Infra-red absorption spectra of minerals and other inorganic compounds. *Anal. Chem.* 22:1478-1497.



- Hunt, J. P. 1963. Metal ions in aqueous solutions. W. A. Benjamin, Inc., New York.
- Jones, L. H. 1954. The infrared spectra and structure of LiOH, LiOH·H₂O, and the deuterium species. Remark on fundamental frequency of OH. Jour. Chem. Phys. 22:217-219.
- Jurinak, J. J. 1957. The effect of clay minerals and exchangeable cations on the adsorption of ethylene dibromide vapor. Soil Sci. Soc. Am. Proc. 21:599-602.
- Kanbayashi, U. and K. Nukada. 1963. Rotational isomers of ethylene glycol. Nippon Kagaku Zasshi. 84:297-300.
- Krimm, S., C. Y. Liang and G. B. B. M. Sutherland. 1956. Infrared spectra of high polymers. V. Polyvinyl Alcohol. Jour. Poly. Sci. 22:227-247.
- Kuhn, M., W. Luttkke and R. Mecke. 1959. IR-spektroskopische untersuckungen über die rotationsisomerie bei 2-substituierten Athanolen. Zeitschrift für Analytische Chemie. 170:106-114.
- Kunze, G. W. 1955. Anomalies in the ethylene glycol solvation technique used in x-ray diffraction, in Clays and Clay Minerals, NAC-NRS, pub. 395. pp. 88-93.
- Lyon, J. P. 1964. Infrared analysis of soil minerals, in Soil Clay Mineralogy. Ed. by C. I. Rich and G. W. Kunze, The Univ. of North Carolina Press, Chapel Hill. Pp. 170-199.
- 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. 44:349-367.
- Mackenzie, R. C. 1948. Complexes of clays with organic compounds. Part II. Investigation of the ethylene glycol-water-montmorillonite system using the Karl Fischer reagent. Trans. Faraday Soc. 44:368-375.
- Margottin-Maclou, M. and M. Corval. 1963. Spectres d'absorption entre 2 et 15 microns de quelques composis deutiriës. Jour. Phys. et Phys-Chim. Biol. 60:1044-1046.
- Marshall, C. E. 1936. Soil Science and mineralogy. Soil Sci. Soc. Am. Proc. 1:23-31.

- Marshall, C. E. 1964. The Physical Chemistry and Mineralogy of Soils. Vol 1: Soil materials., John Wiley & Sons, Inc., pp. 188-210.
- Martin, R. T. 1955. Ethylene glycol retention by clays. *Soil Sci. Soc. Am. Proc.* 19:160-164.
- Martin, R. T. 1962. Adsorbed water on clay: A review, in Clays and Clay Minerals, 9th Conf., Pergamon Press, New York, 9:28-70.
- McNeal, B. L. 1964. Effect of exchangeable cations on glycol retention by clay minerals. *Soil Sci.* 97:96-102.
- Mering, J. 1946. On the hydration of montmorillonite. *Trans. Faraday Soc.* 42B:205-219.
- Miller, F. A. and C. H. Wilkins. 1952. Infrared spectra and characteristic frequencies of inorganic ions. *Anal. Chem.* 24:1253-1294.
- Miyake, Akihisa. 1959. Infrared spectra of glycols coordinated to metal ions. *Bull. Chem. Soc. Japan.* 32:1381-1383.
- Miyazawa, T., K. Fukushima and Y. Ideguchi. 1962. Molecular vibrations and structure of high polymers. III. Polarized infrared spectra, normal vibrations, and helical conformation of polyethylene glycol. *Jour. Chem. Phys.* 37:2764-2776.
- Mooney, R. W., A. G. Keenan and L. A. Wood. 1952. Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by x-ray diffraction. *Jour. Am. Chem. Soc.* 74:1371-1374.
- Morin, R. E. and H. S. Jacobs. 1964. Surface area determination of soils by adsorption of ethylene glycol vapor. *Soil Sci. Soc. Am. Proc.* 28:190-194.
- Mortland, M. M. 1954. Specific surface and its relationship to some physical and chemical properties of soil. *Soil Sci.* 78:343-347.
- Mortland, M. M. and N. Barake. 1966. Interaction of ethylamine and metal ions on montmorillonite. *Trans. 8th Intern. Congr. Soil Sci.* (in press).
- Mortland, M. M., J. J. Fripiat, J. Chaussidon and J. Uytterhoeven. 1963. Interaction between ammonia and the expanding lattices of montmorillonite and vermiculite. *Jour. Phys. Chem.* 67:248-258.

- Mortland, M. M. and W. D. Kemper. 1965. Specific Surface, in Methods of Soil Analysis, Part I. Am. Soc. of Agron., Madison, Wisconsin, pp. 532-544.
- Nakagawa, I. and T. Shimanouchi. 1964. Infrared absorption spectra of aquo complexes and the nature of co-ordination bonds. *Spectrochim. Acta.* 20:429-439.
- Ockman, Nathan. 1958. The infra-red and Raman spectra of ice. *Advance in Phys.* 7:199-220.
- Orchiston, H. D. 1953. Adsorption of water vapor: I. Soils at 25 C. *Soil Sci.* 76:453-465.
- Orchiston, H. D. 1954. Adsorption of water vapor: II. Clays at 25°C. *Soil Sci.* 78:463-480.
- Orchiston, H. D. 1955. Adsorption of water vapor: III. Homoionic montmorillonites at 25°C. *Soil Sci.* 79:71-78.
- Orchiston, H. D. 1959. Adsorption of water vapor: V. Homoionic illites at 25°C. *Soil Sci.* 87:276-282.
- Plyler, E. K. 1952. Infrared spectra of methanol, ethanol, and n-propanol. *Jour. Res. Nat. Bur. Standard.* 48:281-286.
- Pozefsky, A. and N. D. Coggeshall. 1951. Infrared absorption studies of carbon-hydrogen stretching frequencies in sulfurized and oxygenated materials. *Anal. Chem.* 23:1611-1619.
- Puri, B. R. and K. Murari. 1964. Studies in surface area measurements of soils: 2. Surface area from a single point on the water isotherm. *Soil Sci.* 97:341-343.
- Quirk, J. P. 1955. Significance of surface area calculated from water vapor sorption isotherms by use of the B.E.T. equation. *Soil Sci.* 80:423-430.
- Redington, R. L. and D. E. Milligan. 1962. Infrared spectroscopic evidence for the rotation of the water molecule in solid argon. *Jour. Chem. Phys.* 37:2162-2166.
- Ross, G. H. and M. M. Mortland. 1966. A soil beidellite. *Soil Sci. Soc. Am. Proc.* 30: (in press).
- Ross, S. D. and J. Goldsmith. 1964. Factors affecting the infrared spectra of planer anions with D_{3h} symmetry-I. Carbonates of the main group and first row transition elements. *Spectrochim. Acta.* 20:781-784.

- Rundle, R. E., K. Nakamoto and J. W. Richardson. 1955. Concerning hydrogen positions in aquo-complexes- $\text{CuCl}_2 \cdot \text{H}_2\text{O}$. Jour. Chem. Phys. 23:2450-2451.
- Russell, J. D. and V. C. Farmer. 1964. Infrared spectroscopic study of the dehydration of montmorillonite and saponite. Clay Min. Bull. 5:443-464.
- Stuart, A. V. and G. B. B. M. Sutherland. 1956. Effect of hydrogen bonding on the deformation frequencies of the hydroxyl group in alcohols. Jour. Chem. Phys. 24:559-570.
- Sumner, M. E. 1963. Effect of alcohol washing and pH value on leaching solution on positive and negative charges in ferruginous soils. Nature 198:1018-1019.
- Szymanski, H. A., D. N. Stamires and G. R. Lynch. 1960. Infrared spectra of water sorbed on synthetic zeolites. Jour. Opt. Soc. Am. 50:1323-1328.
- Tahoun, S. A. and M. M. Mortland. 1966. Complexes of montmorillonite with primary, secondary, and tertiary amides. II. Coordination of amides on the surface of montmorillonite. Soil Sci. 102: (in press).
- Tarte, P. 1958. Recherches sur les fréquences des de déformation OH-I. Spectre infrarouge des sels basiques de cuivre. Spectrochim. Acta. 13:107-119.
- Tarte, P. and R. Deponthiere. 1957. Spectres infrarouges des alcools ordinaires et deuterés dans le groupe hydroxyle. Bull. Soc. Chim. Belg. 66:525-542.
- Tensmeyer, L. G., R. W. Hoffmann and G. W. Brindley. 1960. Infrared studies of some complexes between ketones and calcium montmorillonite. Clay-organic studies. Part III. Jour. Phys. Chem. 64:1655-1662.
- Tettenhorst, R., C. W. Beck and G. Brunton. 1962. Montmorillonite-Polyalcohol complexes, in Clays and Clay Minerals, Pergamon Press, New York, 9:500-519.
- Toth, S. J. 1955. Colloid chemistry of soils, in Chemistry of Soil, ed. by F. E. Bear. Reinhold Inc., New York, pp. 85-106.
- Uvarou, A. V. 1963. Infrared study of the interaction of adsorbed water and ethanol vapours with surface hydroxyls on alumina. Russian Jour. Phys. Chem. (English trans.) 37:634-635.

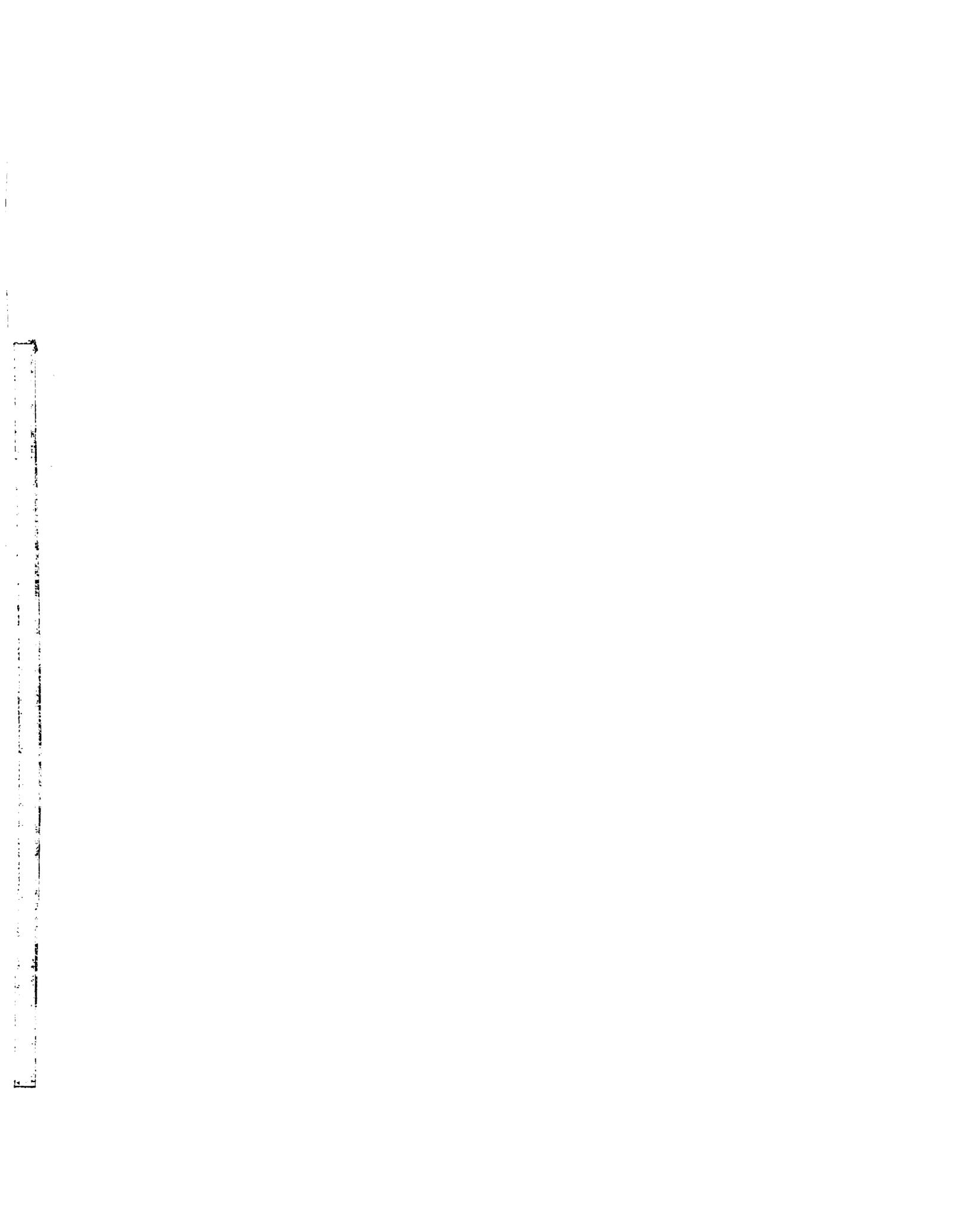
APPENDIX

Table 4. A comparison between infrared and gravimetric techniques for determination of the water content of homoionic montmorillonite.

Weight of Peak Area (mg.)	Adsorbed ¹ Water ---(g./100 g. clay)----	Adsorbed ² Water -----	Variation %
<u>Cu-montmorillonite</u>			
312.0	11.22	11.17	+ 0.45
245.2	8.00	8.27	- 3.26
214.6	6.52	6.45	+ 1.08
168.7	4.58	4.64	- 1.29
152.9	4.20	4.15	+ 1.20
<u>Al-montmorillonite</u>			
280.0	10.60	10.90	- 2.75
250.1	8.42	7.68	+ 3.38
194.9	4.30	4.79	-10.68
171.4	2.42	2.62	- 7.63
165.4	1.70	1.54	+10.39
144.8	0.85	0.82	+ 3.66
<u>Ca-montmorillonite</u>			
351.7	15.00	15.45	- 2.91
295.0	11.20	10.90	+ 2.75
240.5	7.55	7.42	+ 1.75
212.5	5.70	5.67	+ 0.53
175.1	4.22	4.25	- 0.70
161.8	3.95	3.93	+ 0.50
<u>Na-montmorillonite</u>			
131.7	4.62	4.62	0.00
64.1	2.20	2.29	- 3.93
43.9	0.68	0.76	-10.52
32.1	0.40	0.36	+11.11
27.0	0.34	0.36	- 5.56
<u>NH₄-montmorillonite</u>			
97.0	4.80	4.77	+ 1.47
70.7	3.55	3.70	- 4.05
52.8	2.65	2.60	+ 1.92
38.3	1.90	1.78	+ 6.74
26.7	1.40	1.53	- 8.50

¹Determined from plots given in figure 2.

²Determined from quartz helix distension data.



MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03071 3535