A SPECTROSCOPIC STUDY OF THE ADSORPTION OF PHENOL AND SELECTED AROMATIC ETHERS ON HECTORITE

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DENNIS B. FENN

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This is to certify that the

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ABSTRACT

A SPECTROSCOPIC STUDY OF THE ADSORPTION OF PHENOL AND SELECTED AROMATIC ETHERS ON HECTORITE

By

Dennis B. Fenn

The nature of the interaction of phenol and selected aromatic ethers with homoionic hectorite was studied by spectroscopic techniques. The only direct phenol-cation interaction observed occurred with Cu(II) or Ag(I)-hectorite, where complexation occurred between the cation and the π-electron system of the phenol molecule. Partial dehydration to uncover at least one ligand site on the cation was necessary before complexation would occur. Data obtained with a large number of other inorganic cations showed little or no direct phenol-cation interaction. Postulated binding mechanisms of phenol on these systems include hydrogen bonding to the silicate structure, hydrogen bonding through a water bridge to exchangeable cation, and weak π-electron interaction with the silicate structure. Alkyl ammonium montmorillonites adsorbed phenol by ion-dipole interaction between the cation and the phenol molecule and by weak π-electron and hydrogen bonding interactions with the silicate structure. Anisole was

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found to form a type II π complex with Cu(II)-hectorite under dehydrating conditions. When this complex was exposed to the atmosphere for several hours, it underwent a dimerization reaction to form 4,4'-dimethoxybiphenyl which then forms a type II complex with the Cu(II)-hectorite. A reaction mechanism is proposed. Physically sorbed anisole and a type I π complex are also identified on Cu(II)-hectorite. Ag(I)-hectorite formed a type I π complex with anisole. No physically bound anisole was present in the Ag(I)-hectorite system. Adsorption of anisole on all other kinds of homoionic hectorite studied was by physical means only and is independent of the cation, indicating association with the layer silicate surface. Butyl phenyl ether formed a type II π complex with Cu(II)-hectorite, but no dimerization reaction was noted in this system. Phenyl ether and benzyl methyl ether form a type I π complex with Cu(II)-hectorite. No type II analog was noted. ESR spectra of each of the ether-Cu(II)-hectorite systems showed a single, narrow band near the g value of a "free" spinning electron. Both the type II complexes and the systems containing only the type I complex exhibited this ESR band.

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By
Dennis B. Fenn

A THESIS

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This thesis is dedicated to my wonderful wife. Without her support, encouragement, patience and active interest this thesis would have been an impossibility.

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The author expresses sincere appreciation to his major professor, Dr. M. M. Mortland, for his active interest, stimulating discussions, enlightening suggestions and constant support during this study. His knowledge and interest in the science of clay surface chemistry has been a great inspiration.

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Thanks is expressed to my wife for her efforts in typing this manuscript.

TABLE OF CONTENTS

TABLE

1. Assi
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phen
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Cu(I
coor
or A

2. Chan
(V)1
plan
aren
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3. Sele
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4. Sele
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LIST OF TABLES

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2. Infr
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3. ESR
Cu(I
trea
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4. Ultr
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LIST OF FIGURES

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FIGURE

6. KBr p
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7. Ultra
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INTRODUCTION

Clay minerals interact with numerous organic compounds to form complexes of varying stabilities and properties. These interactions are often of great importance in nature and industry. In soils, for example organic matter in various stages of decomposition is often strongly adsorbed to clay minerals. This adsorbed organic matter helps to stabilize soil aggregates and build soil structure, thus greatly influencing the moisture and aeration properties of the soil. Also, the interaction between soil clay minerals and applied organic pesticides or fertilizer has proven to be an important consideration that can not be overlooked.

In industry, clay-organic complexes are utilized on a large scale in cosmetics, paints, paper, medicine, lubricants, pollution control systems, etc.

Clay-organic research has developed along two major pathways. The first approach has been to study the nature of the interaction between soil clays and soil organic matter. This important work has been handicapped by incomplete knowledge of the actual composition of the organic matter itself, making interpretation of results conditional and sometimes ambiguous. Progress is being made in this

area, however. The second approach has been to study the complexation between pure clays and simple organic compounds, deducing the nature of their interaction from the changes in certain properties of the compounds. This second method has resulted in considerable knowledge about the binding mechanisms of organic molecules on clay surfaces and has found many new industrial uses for clay-organic complexes. This study utilizes the latter approach.

Research into the variables contributing to the physical and chemical properties of clays has shown that the type of exchangeable cation occupying the exchange sites of the clay is often a major determining factor. Transition metal cations contain unfilled d electron orbitals and possess relatively strong coordinating properties compared to the alkali and alkaline earth metals. Studies on the interaction between the clay surface, the exchangeable cation, the cation hydration sphere, and other organic and inorganic ligand molecules are being conducted by numerous clay surface chemists.

Developments in the last decade have shown that infrared spectroscopy is perhaps the most potent single method for evaluating interactions between organic molecules and the silicate surface. The method allows for the in situ observation of the interaction between atoms at the clay surface and does not require the long range repetitive

regularity necessary for detailed X-ray analysis. One important hindrance in the method is the fact that mineral lattice vibrations dominate certain portions of the spectrum. The design and use of special cells with temperature and vapor pressure controls have been an important development in infrared studies of clay-organic complexes. Infrared spectroscopy was an important tool utilized in this study, along with X-ray diffraction, ultraviolet-visible spectroscopy and ESR spectroscopy.

In conducting this study we attempted to answer the following questions:

(1) How are phenol and anisole adsorbed and retained on the clay surface?

(2) What is the effect of type of exchangeable cation on the adsorption of phenol and anisole?

(3) How effectively can phenol and anisole compete with water for coordination sites on the cation?

(4) What reactions, if any, involving phenol or anisole are catalyzed by the clay system?

Substituted aromatics are an important constituent of soil organic matter and hence are important in the association of organic matter with soil clays. Many industrial processes produce phenols as a constituent of the waste products, and as a result many rivers and lakes show appreciable phenol contents. Information on the mechanisms of adsorption of these compounds on soil clays and bottom

sediments can be of great value in understanding clay-organic interactions in nature.

LITERATURE REVIEW

General Clay-Organic Interactions.

Numerous reviews of clay-organic complexes can be found in the literature. The important binding mechanisms involved in clay-organic complexes were reviewed by Mortland (1970). He found the following mechanisms documented in the literature: (1) cationic, including ion exchange by organic cations, protonation of organic molecules at the clay surface and hemisalt formation; (2) anionic; (3) ion-dipole coordination; (4) hydrogen bonding, including water bridging, organic-organic hydrogen bonding, and hydrogen bonding to surface oxygens and hydroxyls; (5) van der Waal's attraction; (6) pi bonding; (7) entropy effects; and (8) covalent bonding. The nature of the organic molecule, the kind of exchangeable cation, the type of clay mineral and the degree of hydration are all important factors in determining which of the binding mechanisms will operate in a given system. Greenland (1965) has also reviewed clay-organic bonding mechanisms.

Brindley (1970) in a review of clay-organic complexes pointed out the importance of the nature of the clay mineral in organic complex formation. Smectites and vermiculites

have been extensively studied; but kaolinite, halloysite, and many non-silicate layer structures have recently been shown to take up organic molecules. Brindley points out the importance of residual water in the association of organic molecules and exchangeable cations. In some cases organic molecules are protonated by disproportionation of the residual water on the cation, and in other cases a hydrogen bonded "water bridge" has been shown to form between the organic molecule and the hydrated cation. Brindley reviewed literature showing that small polar molecules can form complexes on the clay surface by solvating the exchangeable inorganic cations, but when polarity arises from -NH or -OH groups hydrogen bonding may also be involved. The importance of quantitative methods for establishing the number of adsorbed organic molecules per unit cell is emphasized by Brindley in his review.

Theng (1971) reviewed the mechanisms of formation of colored clay-organic complexes. He concluded that most color reactions of clay can be ascribed to a charge transfer reaction between the mineral and the adsorbed species. The active sites on the clay were found to be aluminum exposed at crystal edges and exchangeable transition metal cations in the higher valency state, both of which can act as electron acceptors. The nature of the exchangeable cation, the solvent, and the pH of the system influence the rate and intensity of color formation. Theng also

concluded that the mechanisms underlying the formation of colored clay-organic complexes are analogous to those involved in the polymerization of adsorbed organic monomers by clays. Theng felt this indicated the wide applicability of the charge transfer theory to the activation of organic species at clay mineral surfaces.

Suito (1971) reviewed the Japanese literature on clay-organic complexes. Japanese researchers have investigated many of the colored clay-organic complexes found in Theng's (1971) review, as well as clay-organic polymers, effect of the type of clay mineral on complexation, industrial applications of clay-organic complexes, humic acid-clay complexes, and the structure and orientation of adsorbed molecules. A text by van Olphen (1963) also describes various aspects of clay surface chemistry.

Numerous Australian, English, and Russian laboratories, among others, are studying clay-organic complexes. It is obviously not a narrow, isolated field of endeavor, nor one of minor importance or application.

Spectroscopic Techniques.

The study of clay-organic complexes has been greatly enhanced by the development of various spectroscopic techniques of study. X-ray diffraction has long been a widely used tool in clay research. As an example of its usefulness in clay-organic studies, Greene-Kelly (1955)

used X-ray diffraction to determine the orientation of aromatic compounds adsorbed on montmorillonite. From X-ray spacings Greene-Kelly was able to show that two orientations are common. The first, generally stable at low surface concentrations, had the plane of the ring of the aromatic molecule parallel to the silicate sheet. At higher surface concentrations the molecules reoriented so that their planes were perpendicular to the plane of the silicate sheet. Greene-Kelly also showed that the contact distances between the surface oxygens of the silicate sheet and the atoms of the organic molecules are shorter than the normal van der Waal's distance.

The most powerful tool to date for studying clay-organic complexes is infrared spectroscopy. The theoretical basis for infrared spectroscopy has existed for more than fifty years, but only in the last fifteen years have instruments and sample preparation procedures been developed for use on a practical basis in clay-organic studies.

Sidorov (1956), in an early work using infrared spectroscopy to study adsorption of small molecules on porous glass, found that adsorption occurred on two types of sites. One site was the surface OH group (as shown by the shifting of the ν OH band), and the other was tentatively identified as the surface silica atoms. Upon adsorption, the ν OH band was shifted to lower energy,

indicating that hydrogen bonding had occurred. Molecules held in this fashion were weakly adsorbed and could be driven off by mild heating and the surface OH band was restored to its original position. The presence of adsorbed molecules remaining bound on the second type of site after mild heating was indicated by the presence of their absorption bands in the infrared spectra. A complete review of the early work on the infrared spectra of adsorbed molecules has been given by Sheppard (1959).

In a work important to the study of arene-clay complexes, Kross, Fassel and Margoshes (1956) reported that a property common to all of the substituents which cause a positive shift in the CH out-of-plane vibration of substituted benzenes is that they are electrophilic in nature, i.e., they tend to deplete the aromatic nucleus of π-electronic charge. Their experimental observations were consistant with the theory of "orbital following" during molecular vibrations. The depletion of π-electron density of the aromatic nucleus leads to a decreased ability of the carbon bonding orbitals to follow the out-of-plane movement of the hydrogen atoms. This results in higher bending frequencies because vibrations occur with greater difficulty as orbital overlap decreases. The formation of a π complex on the clay surface should deplete some π-electron density from the aromatic system and likewise cause a high energy shift in the CH out-of-plane vibration.

With the growing use of infrared spectroscopy in silica gel and metal surface chemistry, it became obvious that the technique had merit for clay research as well. Farmer and Russell (1964, 1967) reported on ten years of infrared research on clay minerals by their laboratory. Farmer and Russell had found infrared spectroscopy useful in identifying different clay minerals, judging the types of isomorphous substitution within a mineral, and studying the interlamellar adsorption of water and other polar molecules.

Farmer (1968) extensively reviewed the literature on the application of infrared spectroscopy to clay mineral studies. He stated that the factor that makes the method so useful is that one may study the in situ residence of adsorbed molecules on clay minerals. No extraction procedures are necessary.

In a classic demonstration of the usefulness of infrared spectroscopy in studying clay-organic complexes, Mortland (1966) reported on a study of urea complexes on montmorillonite. Urea was observed to become protonated in H-, Fe-, and Al-montmorillonite films and to form a hemisalt complex when excess urea was present. The fully protonated urea disappeared during dehydration but formed again upon rehydration of the films. This reversible reaction demonstrated the important role of water in clay surface acidity. Mortland reported that indications were

that urea was coordinated to the exchangeable cation through the carbonyl oxygen in Cu(II)-, Mn(II)-, and Ni(II)-montmorillonite. Decomposition of urea to ammonium ion was observed with Cu(II)-montmorillonite. Mortland also found that urea may be bonded to the metal ion in Mg-, Ca-, Li-, Na-, and K-montmorillonite by coordination and possibly by ionization of the N-H bond. These results suggested the importance of ion-dipole interactions in urea complexes on montmorillonite.

In a paper further extending the usefulness of infrared spectroscopy in clay-organic studies, Serratosa (1965) proposed that organic molecules sorbed on layer silicates usually adopt a single preferred orientation. For those molecules for which the assignation of the absorption bands to different vibrational modes has been well established, the orientation of the adsorbed molecules in the interlamellar region could be inferred from the observed dichroism of specific absorption bands. Serratosa proposed that the clay film be mounted in the infrared beam at incident angles of 0^{o} and 40^{o} for measuring the dichroism of selected bands.

Several valuable textbooks on infrared adsorption of aromatic molecules in the liquid and adsorbed state, such as those by Hair (1967), Rao (1963) and Little (1966). were utilized in this study.

Another spectroscopic technique finding application in clay surface chemistry is electron spin resonance. Van Reijen (1971) describes the general application of ESR-methods in chemisorption and catalysis. In an interesting recent application of ESR to clay surface studies, Clementz, Pinnavaia, and Mortland (1973) investigated the stereochemistry of hydrated Cu(II) ions on the interlamellar surfaces of layer silicates by observing the anisotropic components of the g factor in the ESR spectra of oriented samples at room temperature. When a monolayer of water occupied the interlamellar regions, the ion had axial symmetry and the symmetry axis was perpendicular to the silicate layers. Clementz, et. al., suggested that the Cu(II) ion was likely coordinated to four water molecules in the xy plane and to two silicate oxygens along the z axis. Under conditions where two layers of water occupied the interlamellar region, the ion was in an axially elongated tetragonal field of six water molecules and the symmetry axis was inclined with respect to the silicate layers at an angle near 45^{o}. When several layers of water molecules occupied the interlamellar region, the $Cu(H_2O)_6^{2+}$ ion tumbled rapidly and gave only a single isotropic ESR signal analogous to that normally observed for the ion at temperatures above $50^{o}K$.

Rupert (1973) studied the ESR absorption of interlamellar complexes formed between arene molecules and

Cu(II)-montmorillonite. Complexes of the sort termed "type II" by Mortland and Pinnavaia (1971) were formed with benzene, biphenyl, naphthalene and anthracene by azeotropic dehydration. It was shown that the type II complex is characterized by a narrow ESR band which has a g-factor of 2.0024, very close to the value of 2.0023 for a "free spinning" electron, as well as by a characteristic infrared spectrum (Doner and Mortland, 1969). Rupert interpreted the data as suggesting that the d^9 Cu(II) ion functioned as an electron acceptor for the transfer of a π-electron from the arene. According to Rupert electron exchange may then occur between radical cations, or between radical cations and neutral, diamagnetic species on the clay surface resulting in the single, exchange-narrowed ESR band.

Ultraviolet-visible spectroscopy has also been used to study many of the highly colored clay-organic complexes. Jaffe and Milton (1962) give a complete discussion of the ultraviolet-visible properties of benzene and its derivatives.

Arene-Clay Complexes.

The group of molecules known as the arenes have been studied and the vibrational modes well documented by chemical spectroscopists. In addition, the arenes often form highly colored complexes on the clay surface. These two facts, along with the fact that aromatic compounds are

present in soil organic matter have prompted research into arene-clay complexes.

Farmer and Mortland (1966) found that pyridine molecules formed strong hydrogen bonds with pyridinium ions in the interlamellar space of montmorillonite, causing a marked perturbation of vibrations involving the NH^+ group. Water molecules directly coordinated to Ca^{2+} and Mg^{2+} formed strong hydrogen bonds with pyridine which readily displaces water from outer spheres of coordination around these cations. Pyridine coordinated to Cu^{2+} ions both directly and through a water bridge. Hydrogen bonding in these systems was reported by Farmer and Mortland to be stronger than in aqueous pyridine due to the increased acidity of water under the polarizing forces of the cation.

Yariv, Russell and Farmer (1966) studied the adsorption of benzoic acid and nitrobenzene on montmorillonite. They found that nitrobenzene and benzoic acid are coordinated through water molecules to the more highly polarizing exchangeable cations on montmorillonite but are directly coordinated to NH_4^+ and K^+. When the adsorption complexes were dehydrated by heating, the nitrobenzene and benzoic acid became directly coordinated to all of the exchangeable cations studied. The authors did not feel that the π-electrons of the ring were involved in the adsorption process of these molecules.

Serratosa (1968) studied the adsorption of benzonitrile on montmorillonite. He reported that on Mg^{2+}-montmorillonite, the benzonitrile molecules coordinate regularly about the exchangeable ions. Serratosa proposed that the CH group of benzonitrile is the point of coordination.

Yariv, Heller, Sofer and Bodenheimer (1968) studied the adsorption of aniline on homoionic montmorillonite. They reported that aniline was protonated on H^{+}- and Al^{3+}-montmorillonite, sorbed through water bridges on alkali metal and alkaline earth montmorillonite, and bonded through both water bridges and direct coordination on transition metal saturated montmorillonite. Complete dehydration prevented sorption of aniline on any of the homoionic montmorillonites.

None of the previously mentioned papers on arene adsorption reported any interaction involving the π-electrons of the arene. None of the authors, however, were looking for this type of interaction. Their reported data was concerned entirely with the vibrations of the functional group on the arene. Doner and Mortland (1969), however, reported the formation of a π complex between benzene and Cu(II)-montmorillonite. Doner and Mortland reported a dark red complex that was distinguished by infrared bands at 780, 1482, and 1535 cm^{-1} as well as a very intense adsorption in the entire region above 1700 cm^{-1}.

The complex formed only under dehydrating conditions. Mortland and Pinnavaia (1971) further found that two types of π complexes could be formed depending upon the degree of hydration of the exchangeable Cu(II) ion. They characterized a green complex, labeled "type I," which formed under a higher degree of hydration than the red complex, labeled "type II." The green complex was characterized by bands at 706, 1470, and 1586 cm^{-1}. It did not show the intense adsorption above 1700 cm^{-1} as in the red, type II complex previously characterized by Doner and Mortland (1969). The two complexes could be interconverted simply by adding or removing controlled amounts of coordinated water. Mortland and Pinnavaia propose that in the type II complex the aromaticity of the benzene is lost and the planarity of the ring distorted. They propose that in the type I complex the aromaticity and planarity of the ring are preserved.

Pinnavaia and Mortland (1971) reported that toluene and other methyl substituted benzenes formed π complexes with Cu(II)-montmorillonite. The complexes corresponded to the type I complex of benzene on Cu(II)-montmorillonite. No type II analog was found with the methyl substituted benzenes.

Clementz and Mortland (1972) studied the adsorption of benzene and substituted benzenes on Ag(I)-montmorillonite. They found that a type I complex is formed between the arene

and Ag(I)-montmorillonite. Unlike on the Cu(II)-montmorillonite, no physically bound arene was present in addition to the ligand arene on Ag(I)-montmorillonite. Stoichiometric determinations indicated that a 2:1 benzene: Ag(I) complex had formed.

Phenol Adsorption Studies.

The importance of understanding and characterizing the possible binding mechanisms of phenol on clay surfaces is demonstrated in two recent articles. Schnitzer and Kodama (1972) report that out of 19.2 millequivilants of pH dependent exchange capacity per gram of fulvic acid, 3.3 millequivilants arise from phenolic OH groups. Martin, Haider and Wolf (1972) reported on the synthesis of phenols by soil micro-organisms in relation to humic acid formation. It is obvious that phenols are an important constituent of soil organic matter, and information on its adsorption on clay surfaces will be of important value to the soil organic chemist.

A complete description of the vibrational modes of a mono-substituted benzene has been given by Randle and Whiffen (1955) and Whiffen (1956). The vibrational modes described in the text of this thesis are pictured in these articles. Davies (1948) tabulated the vibrational bands of phenol, monomer and associated, in the region 600-1400 cm^{-1}. Margoshes and Fassel (1955) studied the CH out-of-plane region of aromatic compounds. They found this region sensitive to the type of functional group on

the benzene. Phenol absorbed at 753 cm^{-1}. Goulden (1954) studied the OH-vibration frequencies of carboxylic acids and phenols. Phenol absorbed at 3609 cm^{-1} and had a pKa of 9.95 at 25°. Evans (1960) and Green (1961) reported complete vibrational frequency assignments for the spectrum of phenol. These papers were used as the source for assigning the vibrational modes of adsorbed phenol in this study. Gordy and Nielsen (1938) studied the absorption of the OH group of phenol in solutions of benzene, nitrobenzene, bromobenzene, dioxane and ethylacetate. They found the absorption intensity to be a function of concentration, indicating that hydrogen bonding was occurring as the concentration of phenol was increased. Bellamy and Pace (1966) studied the nature of hydrogen bonding in phenols. They found that dimers of phenols are open chained rather than cyclic. It was also shown that the free OH groups of the dimers were able to form stronger hydrogen bonds than the original monomers. The findings of Bellamy and Pace confirmed the previously observed fact that hydrogen bonds linking trimers and higher polymers are usually stronger than the hydrogen bonds of phenol-dimers.

Abramov, Kiselev and Lygin (1964) reported on the adsorption of phenol on a zeolite. They found that marked changes occurred in the vibrational frequencies of the OH group of phenol but only slight changes in the vibrational frequencies of the benzene ring. The aerosil hydroxyl

bands were displaced and broadened upon adsorption of phenol, indicating the formation of a hydrogen bond. The extent of displacement of the phenolic OH bands were less than in solid phenol (3250 cm^{-1}), indicating that phenol formed weaker hydrogen bonds with the zeolite surface than intermolecular hydrogen bonds with other phenol molecules. The small changes in the ring vibrational frequencies suggested to Abromov, et. al., that the interaction of the π-electrons of the ring with the surface hydroxyls is weaker than the interaction of the unshared pairs of electrons on the oxygen atom of phenol with the surface hydroxyls.

Venuto and Wu (1969) studied the adsorption of phenol and anisole on Faujasite catalyst. They found that both phenol and anisole were preferentially adsorbed relative to benzene. A temperature higher than 200^{o} was required to desorb the phenol or anisole. The adsorption occurred near the catalytic sites on the Faujasite and blocked the reactivity of the surface towards alkylation of benzene.

Anisole Adsorption Studies.

Green (1962) and Stephenson, Coburn and Wilcox (1961) have published the complete assignments of the infrared spectrum of anisole. These two papers were used in assigning the vibrational modes of adsorbed anisole in this study.

Low and Cusumano (1969) studied the adsorption of anisole on porous glass. They found that anisole was weakly

held to the surface in two ways. The first mechanism of adsorption was by weak π-electron interaction with surface hydroxyls, and the OH stretching absorption band occurred at 3600 cm^{-1}. The second mechanism of adsorption was by hydrogen bonding of the anisole oxygen to the surface hydroxyl and was characterized by an OH absorption band at 3400 cm^{-1}. Low and Cusumano also felt that the interaction of an anisole molecule with the surface by both mechanisms simultaneously was a common occurrence.

Romm and Guryanova (1968) reported that solutions of gallium chloride or aluminum bromide form a doner-acceptor complex with anisole that leads to the disruption of the pπ-conjugation of the ring. Romm and Guryanova propose that both pπ-conjugation and complex formation involve the unshaired pair of p-electrons on the oxygen atom of anisole. In the complex with aluminum or gallium halides, this pair of electrons, being strongly bound to the acceptor, cannot take part in pπ-conjugation.

Venuto, Hamilton, Landis and Wise (1966) have examined the catalytic alkylation of aromatic molecules by crystalline alumino-silicates. The catalytic effect of zeolites and clays are very important industrially and whenever an aromatic molecule is adsorbed on a clay surface one must carefully examine the evidence for some catalytic reaction that may have occurred.

In conclusion it appears that a great many adsorption mechanisms involving the functional groups on an arene, the π-electrons of an arene, the exchangeable cation and the clay surface are possible and the spectroscopic evidence must be carefully studied if the correct mechanisms operating in a given system are to be identified.

MATERIALS AND METHODS

Clay Sample.

The clay used in this study was #Bl-26 Hectorite obtained from the Bariod Division of National Lead Company. The whole cell chemical formula for this hectorite is:

$$M^{+}_{0.42} (Mg_{5.42} Li_{0.68} Al_{0.02}) (Si_{8.0}) O_{20} (F, OH)_4$$

Homoionic Clay Suspensions.

Homoionic samples of the <2μ fraction of the hectorite were prepared by washing the clay mineral three times with five symmetries of a 1N chloride salt solution of the desired cation and then removing the excess salt by dialysis until the $AgNO_3$ test for Cl^- was negative. When Ag(I)-hectorite was prepared, the same procedure was utilized except that $AgNO_3$ salt solution was used as the Ag^+ source.

Clay Film Preparation.

Thin, self supporting clay films were prepared by depositing about five milliliters of clay suspension (ca. 1 mg/cm^2) on a polyethylene sheet, allowing it to air dry, and then carefully peeling away the thin, transparent clay film. Films prepared in this manner are highly ordered,

with the silicate sheets lying parallel to the film surface.

Clay-Organic Complexation.

The homoionic clays were allowed to adsorb the arene of interest by placing the clay film in a 50 milliliter weighing bottle with a 10 milliliter beaker of P_2O_5 dessicant and a few grams of the arene. At least 24 hours of equilibration time were allowed before any determinations were made on the film.

X-ray Diffraction.

The X-ray diffraction spectra were obtained by air drying a few milliliters of the homoionic clay suspensions on glass slides and exposing them to the arene vapors and P_2O_5 dessicant. After several days of equilibration, the X-ray diffraction patterns were determined on a Phillips X-ray Diffractometer using copper radiation and a nickel filter.

Electronic Spectra.

Ultraviolet-visible spectra in the region 200-800 mu were obtained on a Beckman DK-2A ratio recording spectrophotometer. A dilute suspension of the homoionic clay was deposited on a quartz disk and air dried. The disk was placed over the arene and P_2O_5 for several days, then coated with a thin layer of mineral oil to cut down on scattering losses, and the spectra obtained. An identical film on a

quartz disk but not exposed to the arene vapors was coated with mineral oil and placed in the reference beam to compensate for absorption by the clay mineral.

Ultraviolet-visible spectroscopy was also utilized in stoichiometric determinations. A clay film of known weight was exposed to the arene vapors and P_2O_5 dessicant for a suitable period. The film was then placed under vacuum with constant degassing for ten minutes at room temperature to remove any condensed arene. Then exactly 50 milliliters of methanol was added to extract the adsorbed arene. The absorption spectrum of an aliquot of this solution was then obtained using ultraviolet-visible transparent quartz cells and pure methanol as the reference. From a previously determined standard curve, the arene concentration was determined and the stoichiometry calculated.

Infrared Spectroscopy.

Infrared spectra in the region 4000-600 cm^{-1} were obtained on a Beckman IR-7 spectrophotometer. After a clay film had been prepared and exposed to the arene vapors, it was placed in a special brass cell equipped with a heating element, a vacuum stopcock, and a pair of infrared transparent NaCl windows in order to protect it from atmospheric moisture.

The highly ordered nature of the clay film enabled one to investigate pleochroic effects by observing absorption

intensities of certain bands when the clay film is positioned at 40^{o} and 90^{o} with respect to the path of the infrared beam. This method is useful in determining the orientation of the adsorbed species relative to the clay mineral layers (Serratosa, 1965).

To determine the infrared spectra of pure compounds or crystalline reaction products, I utilized the standard KBr pellet technique or ground a small amount of compound in nujol mineral oil and coated it on a small NaCl disk.

Electron Spin Resonance Spectra.

ESR X-band spectra were obtained with a Varian E-4 spectrometer. ESR spectra of randomly oriented samples of the homoionic clay systems were obtained by exposing freeze dried clay samples to the arene vapors and P_2O_5 dessicant and then placing the complexed clay in an ESR tube.

RESULTS AND DISCUSSION

Phenol Study

X-ray Diffraction.

The homoionic hectorites were deposited on glass slides and exposed to phenol in an oven at 100°C for 24 hours. The resulting diffraction patterns showed a (001) spacing of $\sim$14.8 A° for all exchangeable cations studied, but the systems were highly interstratified and no firm conclusions on the orientation and packing of phenol in the interlamellar regions could be reached from this data.

Infrared: Cu(II) and Ag(I).

A thin Cu(II)-hectorite film possesses the pale blue color characteristic of hydrated Cu^{2+}. When the film is placed over phenol, it turns light brown; and when it is placed over phenol and P_2O_5, it turns black. The infrared spectra of the above three systems are shown in Figure 1. Figure 2 shows the infrared spectra of Ag(I)-hectorite in the hydrated state and also over phenol and P_2O_5. Table 1 lists the assignments of the various peaks of Figure 1 and Figure 2.

Figure 1B is the spectrum of phenol adsorbed on Cu(II)-hectorite where no P_2O_5 dessicant was present. Water is still

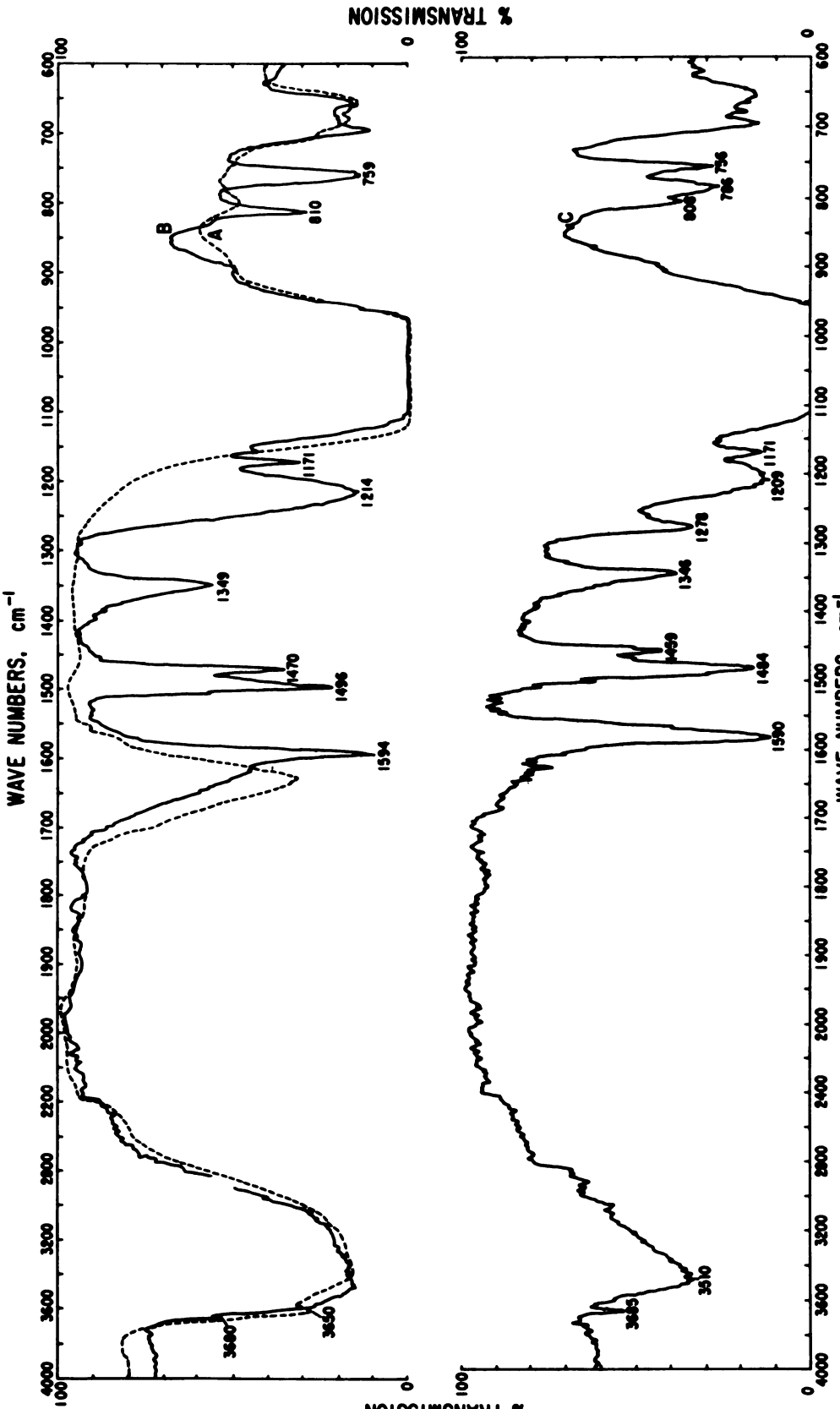


Figure 1: Infrared spectra of a Cu(II)-hectorite film over (A) no treatments; (B) phenol only; and (C) phenol and P_2O_5 and then heated to 100° for one hour under constant degassing.

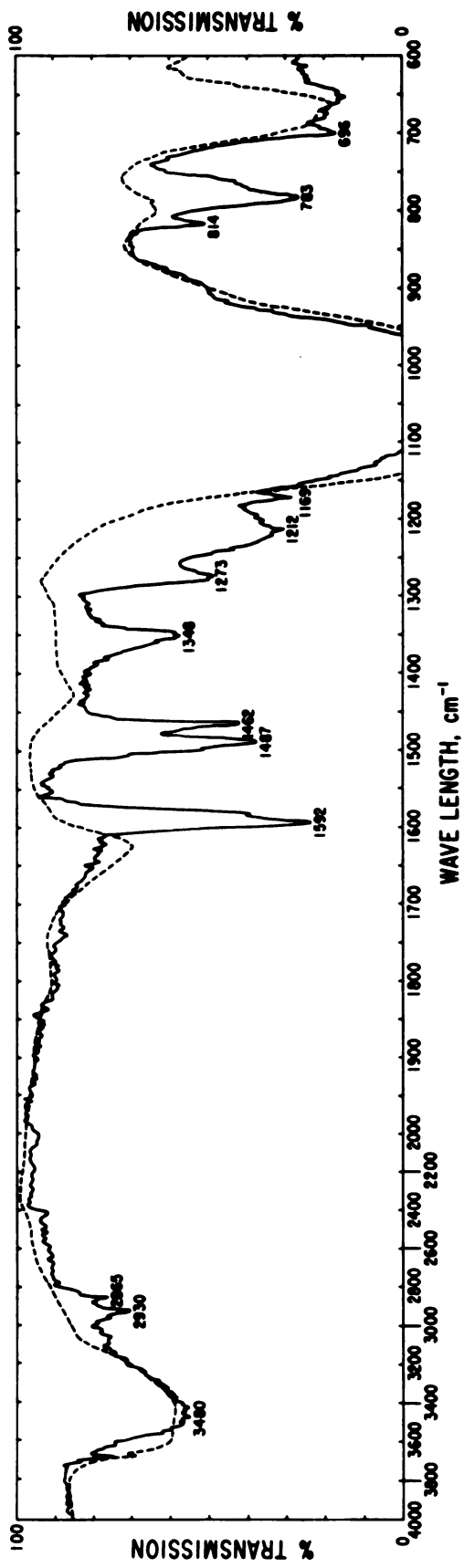


Figure 2: Infrared spectra of a Ag(I)-hectorite film over no treatments (dashed line) and over phenol and P_2O_5 then heated to 100^0 for one hour under constant degassing (solid line).

Table 1: Assignments of selected vibrational frequencies (cm^{-1}) of phenol in the solid state, as a physically bound species on Cu(II)-hectorite and as a coordinated ligand on Cu(II)- or Ag(I)-hectorite.

Solid*	Physical, Cu(II)	Ligand, Cu(II)	Ligand, Ag(I)	No.*	Assignment*
691	694	694	696	$\phi 4$	ring stretch b_2
754	759	786	783	$\gamma 10_b$	CH out of plane b_2
812	810	808	814	$\nu 12$	X sensitive a_1
888	---	---	---	$\gamma 17_b$	CH bend b_2
1152	1155	1153	---	$\beta 9_a$	CH bend b_1
1169	1171	1171	1169	$\beta 9_a$	CH bend a_1
1230	1214	1209	1212		δOH with ring stretch character
1252	---	1278	1273	$\nu 7_a$	X sensitive a_1
1370	1349	1346	1348	$\nu 14$	ring stretch with OH character
1473	1470	1459	1462	$\nu 19_b$	ring stretch b_1
1501	1496	1484	1487	$\nu 19_a$	ring stretch a_1
1598	1594	1591	1592	$\nu 8_a$	ring stretch b_1
3043	---	---	---	$\nu 13$	CH stretch b_2
3070	---	---	---	$\nu 2$	CH stretch b_1
3225	---	3510	3480		OH stretch

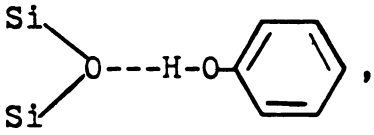
*Band frequencies and assignments taken from Green (1961) and Evans (1960).

present on the clay as evidenced by the H_2O deformation band at about 1620 cm^{-1}. This is primarily water coordinated to the Cu(II) ions. The phenol adsorbed, therefore, is not interacting directly with the Cu(II) ions, but with the silicate structure and the cation hydration sphere. Similar spectra were obtained with phenol adsorbed on hectorite saturated with a variety of different exchangeable cations, i.e., Co(II), Ni(II), Fe(III), Al^{3+}, Mg^{2+}, Na^{+}, and Li^{+}.

As seen in Table 1, each of the vibrational modes involving the phenolic OH group undergoes energy shifts when phenol is physically bound on the clay. It is apparent that the OH group of phenol is involved in the binding process of phenol on hectorite. The highly associated solid phenol exhibits an OH stretching vibration at 3225 cm^{-1} while the monomeric phenol vapor absorbs at 3661 cm^{-1}. The OH stretching region of phenol physically bound on Cu(II)-hectorite, shown in Figure 1B, has a very broad band centered around 3500 cm^{-1} but tailing toward the lower frequencies as far as 2700 cm^{-1}. Coordinated water is still present on the cation and is absorbing in this region as well. The broadness of the band, however, is an indication that several binding mechanisms of different energies, involving water and the hydroxyl group of phenol, are operating. In the absence of water the OH stretching vibration of adsorbed phenol, as seen in Figures 1C and 2B, is a broad band centered near 3500 cm^{-1}, which is

intermediate between solid phenol and monomeric phenol vapor.

Farmer and Russell (1971) report a peak at 3480 cm^{-1} in monohydrated hectorite which they attribute to the OH stretch of water molecules hydrogen bonded to oxygen of the Si-O-Si structure linkages. It appears likely, therefore, that hydrogen bonding of phenol to the oxygens of the silicate structure,



, (1)

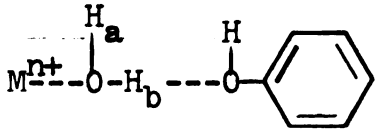
is an important physical binding mechanism.

Farmer and Mortland (1966) and Farmer and Russell (1971) report that treatment of a Mg^{2+}-smectite with pyridine displaced almost all of the outer sphere of coordinated water, giving the following ionic complex involving a water bridge:

$$Mg^{2+}\text{---}(O\overset{H_a}{\underset{|}{}}\text{-}H_b\text{---}NC_5H_5)_6. \qquad (2)$$

The OH_b group of the coordinated water formed a strong hydrogen bond with pyridine and absorbed in the infrared at 2800-2850 cm^{-1}, while the absorption due to the OH_a group occurred near 3630 cm^{-1}. The location of the OH stretching vibrations in this mechanism are very much a function of the hydration properties of the cation. As seen in Figure 1B, water is still present on the hectorite

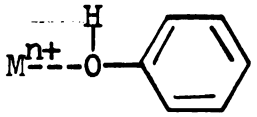
even after adsorption of the phenol. It appears likely that the coordination of phenol to the exchangeable cation through a water bridge,



(3)

is another possible physical binding mechanism.

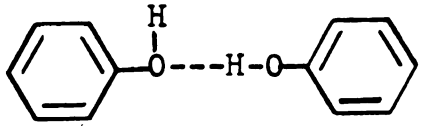
Dowdy and Mortland (1967, 1968) studied the interactions of alkyl alcohols with clay surfaces and report that alcohols can compete with water for ligand positions around the cation and that the OH stretching band of directly coordinated alkyl alcohols is a function of the exchangeable cation. These results suggest that direct coordination of phenol to the exchangeable cation,



(4)

is another possible interaction. Phenol, however, was unable to compete with water for direct coordination sites on any of the exchangeable inorganic cations studied, with the exception of Ag(I), without the aid of P_2O_5 dessicant. Also, the OH stretching vibration of physically bound phenol on Cu(II)-hectorite, Figure 1B, does not differ significantly from the OH stretching vibration of phenol physically adsorbed on the other homoionic hectorite systems studied. Therefore, it is concluded that direct coordination of phenol to the exchangeable cation through the oxygen of the hydroxyl group, as shown in Diagram 4, does not take place.

Phenol is known to form dimers and polymers. Huggins and Pimental (1956) report that the OH stretching vibration of the phenol dimer,



(5)

occurs at 3484 cm^{-1}. It is possible that adjacent phenol molecules, bound to the surface by one of the previously mentioned mechanisms, could dimerize and contribute to the infrared adsorption in the OH stretching region.

Compared to solid phenol, the CH out-of-plane (γ10b) and C-C stretching (ν8a and ν19a) vibrations undergo an $\sim$5 cm^{-1} shift when phenol is physically bound to Cu(II)-hectorite, Figure 1B. These shifts cannot be explained solely on the basis of hydrogen bonding of the hydroxyl group and suggest that a weak π-electron interaction exists between the phenyl ring and the silicate structure. Mortland and Pinnavaia (1971) noted a 13 cm^{-1} shift in the CH out-of-plane vibration of benzene physically bound to montmorillonite, which they attribute to π-electron perturbation. The CH out-of-plane vibration is known to be quite sensitive to perturbations of the π-electron cloud.

It thus appears that phenol is physically sorbed by weak π-electron interaction with the silicate oxygens accompanied by hydrogen bonding to the silicate oxygens, intermolecular hydrogen bonding and/or hydrogen bonding to water molecules directly coordinated to the exchangeable

metal cation.

Figure 1C, Cu(II)-hectorite over phenol and P_2O_5, and Figure 2B, Ag(I)-hectorite over phenol and P_2O_5, are very similar and represent phenol as a coordinated ligand on the exchangeable cation. The CH out-of-plane (γ10b) vibration undergoes a high-energy shift of 32 cm^{-1} on Cu(II)-hectorite and 29 cm^{-1} on Ag(I)-hectorite compared to solid phenol. These results are definite evidence for π-electron interaction between the exchangeable cation and the phenol.

Karagounis and Peter (1959) studied the infrared spectra of phenol adsorbed on several salts including AgI and AgCl. The C-C stretching vibration near 1500 cm^{-1} (ν19a) was shifted down about 5 cm^{-1} on all of the salts studied. This contrasts with the data here where the same band was shifted down about 14-17 cm^{-1} on Ag(I) and Cu(II)-hectorite. The shifts obtained in this study on hectorite with other types of cationic saturation, however, were similar to those obtained by Karagounis and Peter. The uniformity of their infrared spectra, regardless of the kind of salt used as an adsorbant, suggests that Karagounis and Peter were not obtaining π complexes and that the surface of the smectite provides a unique environment for such interactions.

The partial dehydration of the Cu(II) ion by P_2O_5 has evidently exposed coordination sites on the cation and

allowed interaction between the lowest unfilled orbitals of the metal and the π-electrons of the phenol. Doner and Mortland (1969) and Mortland and Pinnavaia (1971) reported that the degree of hydration greatly affected the chemisorption of benzene on Cu(II)-montmorillonite and that partial dehydration of the Cu(II) must occur before a complex will form. Complete dehydration, however, will prevent complexation, as reported by Yariv, et. al. (1968), while studying the sorption of aniline on montmorillonite. Clementz and Mortland (1972) studying benzene adsorbed on Ag(I)-montmorillonite reported that benzene can successfully compete with water for ligand sites on the Ag(I) without degassing or P_2O_5 dessication, but only a type I complex is formed.

Pinnavaia and Mortland (1971) reported that the presence of alkyl groups on the benzene ring restricted the complexation with Cu(II)-montmorillonite to the type I analog only. Clementz and Mortland (1972) report that Ag(I)-montmorillonite will only form a type I complex with arenes. Table 2 compares their results with benzene and methyl substituted benzenes with the phenol data of this study. It is readily apparent from the analogous shifts in the C-C stretching (ν19a) and CH out-of-plane (γ10b) vibrations that phenol forms a type I π-complex with Cu(II) or Ag(I) on hectorite.

Table 2: Changes in the C-C stretching (ν19a) and the CH out-of-plane (γ10b) vibrations of arenes on Cu(II)- or Ag(I)-smectite compared to the liquid state.

	$-\Delta$C-C stretch (ν19a), cm^{-1}		$+\Delta$CH out-of-plane (ν11 or γ10b), cm^{-1}	
Compound	Cu(II)[a]	Ag(I)[b]	Cu(II)[a]	Ag(I)[b]
Phenol (Solid)	17	14	32	29
Benzene	8[c]	7	31[c]	29
Toluene	8	8	36	28
o-Xylene	12	14	30	28
m-Xylene	8	8	34	30
p-Xylene	14	15	34	30
Mesitylene	10	8	53*	*
Ethylbenzene	**	12	**	35

[a] data taken from Pinnavaia and Mortland (1971) except phenol

[b] data taken from Clementz and Mortland (1972) except phenol

[c] $\Delta\nu$ for type I benzene complex

* obscured by a vibration of silicate structure

** data not available

Figure 2 shows that only one form of adsorbed phenol is present on the Ag(I)-hectorite. Unlike on the Cu(II)-hectorite, no physically bound phenol is formed on Ag(I)-hectorite. Phenol coordinated to the monovalent Ag evidently covers the interlamellar surface area and blocks the physical adsorption sites on the silicate structure. In addition, unlike on the Cu(II)-hectorite, phenol is able to compete with water molecules for ligand positions around Ag(I) without the aid of P_2O_5, although adsorption is faster under dessicant conditions. The Ag(I) has a much lower solvation energy than Cu(II), accounting for the ability of phenol to displace the water.

Pleochroic studies on the Cu(II) and Ag(I) ligand phenol systems showed that the C-C stretching (ν 19a) vibration, an in-plane vibration where the dipole change is in the plane of the molecule, undergoes a 50% increase in absorption when the orientation of the clay film is changed from 90° to 40° with respect to the spectrophotometer beam. This suggests that the phenol molecules are oriented in the interlamellar regions at an angle more toward the vertical than the horizontal.

Stability studies on the Cu(II)-hectorite showed that ligand phenol is stable at $200^{\circ}C$ but decomposes at $300^{\circ}C$ as evidenced by infrared spectroscopy. The ligand phenol also is unstable in the open air. Atmospheric moisture replaces ligand phenol and after a few hours of exposure to

room air conditions the infrared spectrum of Figure 1C will become identical to the spectrum of Figure 1B, indicating a loss of all ligand phenol.

Stoichiometric studies on the Cu(II)-hectorite-type I phenol complex, Figure 1C, indicated that a total of about five molecules of phenol are adsorbed on the hectorite per exchangeable Cu^{2+} ion. This value contains both ligand phenol and physically bound phenol. It was not possible to determine the coordination number for ligand phenol alone on Cu(II)-hectorite. In the Ag(I)-hectorite system, however, Figure 2B, where only ligand phenol is present, the stoichiometry is on the order of one molecule of phenol adsorbed per exchangeable Ag^{+} ion.

Electron Spin Resonance Spectra.

The ESR spectra of freeze dried Cu(II)-hectorite and of the type I phenol-Cu(II)-hectorite complex are shown in Figure 3. Both the $g_{\parallel}$ and $g_{\perp}$ components of the d^9 Cu(II) ion signal are apparent in Figure 3A. In Figure 3B, however, the Cu(II) signal has disappeared and only a single narrow signal with a g value of 2.0023 is found. The g value for a "free spinning" electron is also 2.0023. Similar ESR signals have been reported by Rupert (1973) for several arene-Cu(II)-montmorillonite complexes but only where a type II complex had formed. Rupert proposes that the d^9 Cu(II) ion functions as an electron acceptor for the transfer of a π-electron from the arene to form a radical cation which

then gives the ESR signal. Rupert attributes the lack of any hyperfine splitting to rapid electron exchange between radical cations and between radical cations and neutral diamagnetic species on the clay surface, resulting in the single exchange narrowed ESR signal. The fact that the type I phenol-Cu(II)-hectorite complex, where a complete electron transfer between the arene and the Cu(II) ion has not occurred, also exhibits this ESR signal indicates that Rupert's explanation is not completely satisfactory and that more research is needed in this problem.

Ultraviolet-Visible Spectra.

Figure 4B shows the ultraviolet-visible spectrum of phenol crystals dissolved in distilled water. It shows peaks at 273 mu and 278 mu. The ultraviolet-visible spectrum of the type I phenol-Cu(II)-hectorite complex is shown in Figure 4A. As can be seen, a single peak occurs at 475 mu accompanied by a broad region of absorption below 400 mu. The shift towards the visible region and the absorption broadening upon complexation are indications of a charge transfer process, in agreement with the complex conclusions from the infrared study of the phenol-Cu(II)-hectorite complex.

Infrared: Co(II)-, Ni(II)-, Fe(III)-, Al^{3+}-, Mg^{2+}-, Na^{+}-, Li^{+}-Hectorite.

The sorption of phenol by each of the above kinds of

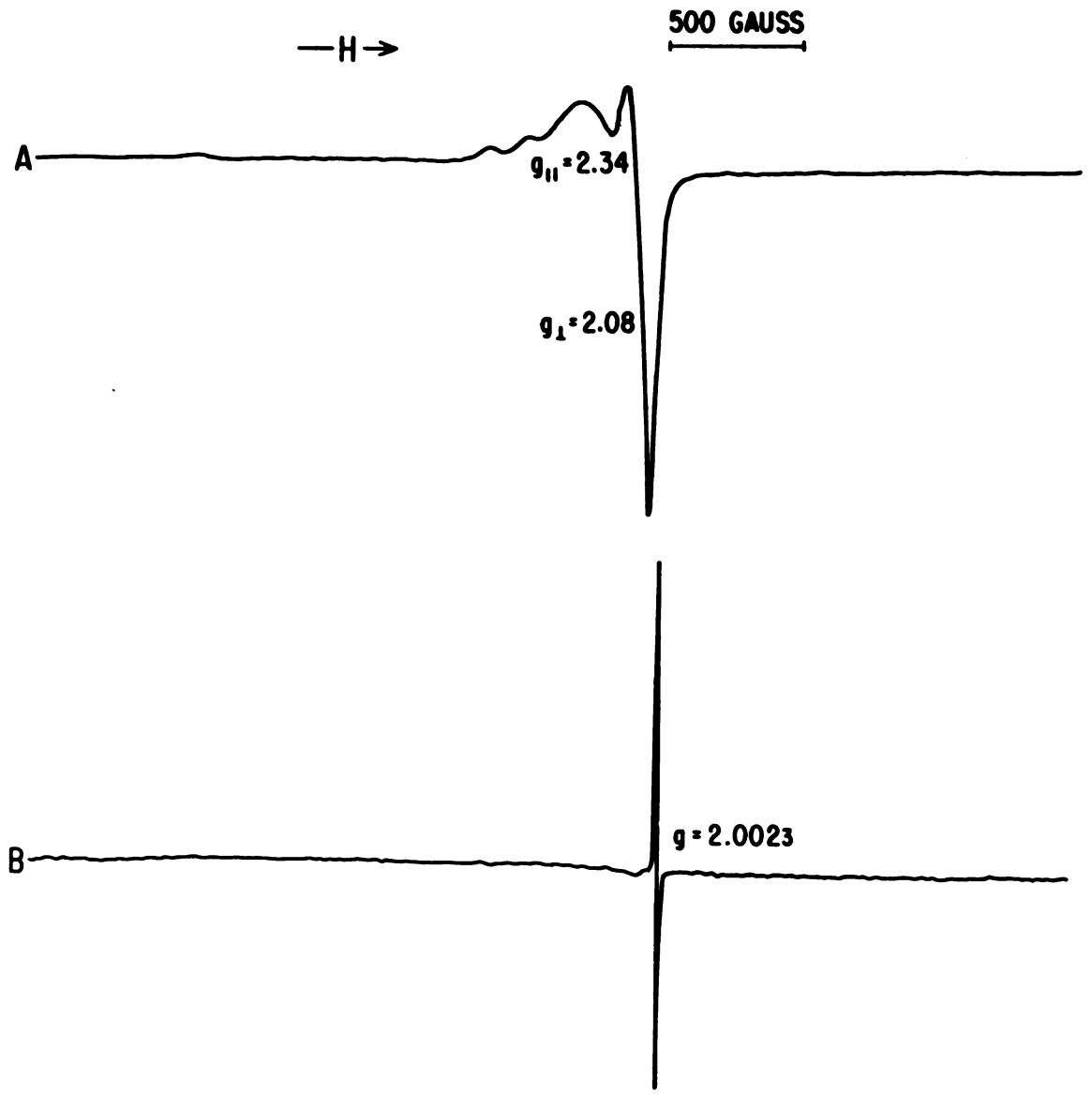


Figure 3: ESR spectra of freeze dried Cu(II)-hectorite over (A) no treatments; and (B) phenol and P_2O_5.

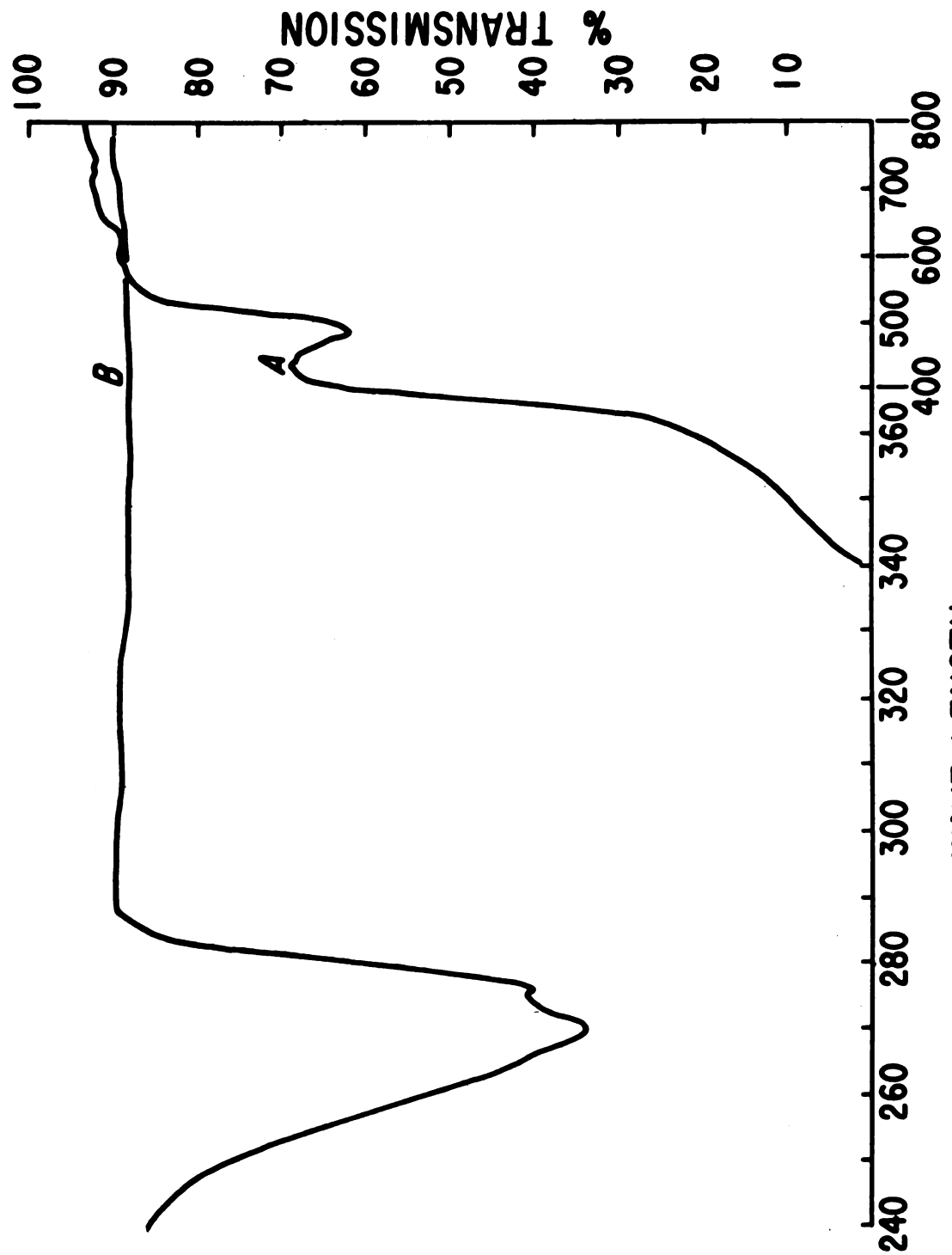


Figure 4: Ultraviolet-visible spectra of (A) Cu(II)-hectorite deposited on a quartz disk and exposed to phenol and P_2O_5 for 10 days; and (B) phenol dissolved in distilled water.

homoionic hectorite was studied, and no evidence of a π complex was noted in any of the systems. Table 3 summarizes the results for the most important diagnostic bands. Each of the homoionic systems retained a varying amount of coordinated water, depending on the hydration properties of the cation, even after the adsorption of phenol over P_2O_5. The OH deformation vibration is shifted 15-30 cm^{-1} to lower energy which suggests some weak hydrogen bonding of the hydroxyl group, particularly in the Co(II), Ni(II), and Fe(III) systems. The water bridging mechanism of Diagram 2 would seem to be the most likely interaction. The 5-10 cm^{-1} shift in the C-C stretching (ν 19a) vibration also suggests some weak π-electron interaction with the silicate structure.

Infrared: NH_4^+-, $(CH_3)_3NH^+$-, $(CH_3)_4N^+$-Montmorillonite.

Ammonium and substituted ammonium montmorillonites (Upton, Wyoming) were exposed to phenol and P_2O_5. Table 4 summarizes the important infrared diagnostic bands. Ammonium ions would be expected to hydrogen bond to phenol and the OH deformation band, although partially obscured by the clay mineral absorption, occurs at 1210 cm^{-1} in the phenol-NH_4^+-montmorillonite complex. This is 20 cm^{-1} lower than in the highly associated solid phenol.

As seen in Table 4, the infrared spectra of phenol adsorbed on trimethyl- and tetramethyl-ammonium montmorillonite shows a 13-14 cm^{-1} high energy shift in the CH

Table 3: Selected infrared bands (cm^{-1}) of homoionic hectorite exposed to phenol and P_2O_5 for 24 hours and then heated to 100° for one hour under constant degassing.

Vibration	No.	Solid Phenol	Co(II)	Ni(II)	Fe(III)	Al^{3+}	Mg^{2+}	Na^{+}	Li^{+}
CH out-of-plane	γ 10b	754	753	752	753	754	755	754	756
OH deformation	--	1230	1199	1197	1198	1215	1209	1200-1210	1205
Ring stretch w/OH character	ν 14	1370	1363	1364	1358	1349	1358	1350	1356
Ring stretch a_1	ν 19a	1501	1490-1496	1490	1494	1493	1496	1497	1497

Table 4: Selected infrared bands (cm^{-1}) of three ammonium cations on montmorillonite after 24 hours exposure to phenol and P_2O_5.

Vibration	No.	Solid Phenol	NH_4^+	$(CH_3)_3NH^+$	$(CH_3)_4N^+$
CH out-of-plane	γ 10b	754	760	767	768
OH deformation	--	1230	1210	1220	1215
Ring stretch with OH Character	ν 14	1370	1350	1354	1351
Ring stretch a_1	ν 19a	1501	1497	1491	1493

out-of-plane vibration and an 8-10 cm^{-1} low energy shift in the C-C stretching vibration. These shifts are intermediate between those of the ligand phenol on Cu(II)- and Ag(I)-hectorite, and those of phenol physically bound on the other homoionic hectorite systems reported in this study. This evidence suggests that, while no charge transfer type π complex is formed, there is a significant ion-dipole interaction between the substituted ammonium cation and the phenol molecule.

The OH deformation vibration, as seen in Table 4, is less affected by the adsorption on the substituted ammonium systems than it is in the inorganic homoionic systems studied (Table 3). However, the 10-15 cm^{-1} low energy shift of the OH deformation band upon adsorption does suggest that hydrogen bonding mechanisms are operating in the physical adsorption of phenol on the substituted ammonium montmorillonite.

AROMATIC ETHER STUDY

Adsorption of Anisole on Cu(II)-Hectorite.

The infrared spectrum of liquid anisole is shown in Figure 5A. A thin Cu(II)-hectorite film possesses the pale blue color characteristic of hydrated Cu^{2+}, and its spectrum is shown in Figure 5B. When a Cu(II)-hectorite film is placed over anisole vapors (Figure 5C), with no external dehydrating treatments, it shows no apparent color change. The absorption bands in Figure 5C correspond closely to infrared bands of liquid anisole (Figure 5A), indication that this form of adsorbed anisole is physically bound to the clay mineral structure. Anisole is unable to favorably compete directly with water for ligand positions on the cation. When a Cu(II)-hectorite film is placed over anisole vapors and P_2O_5 dessicant, it turns a deep blue color (Figure 5E). If the film is then exposed to atmospheric moisture for a few seconds, the deep blue color disappears and the film becomes tan in color (Figure 5D).

The tan anisole complex, Figure 5D, appears to be a type I analog. There is no indication of the broad, intense adsorption above 1800 cm^{-1} as in the type II spectrum of benzene (Doner and Mortland, 1969) but the CH out-of-plane

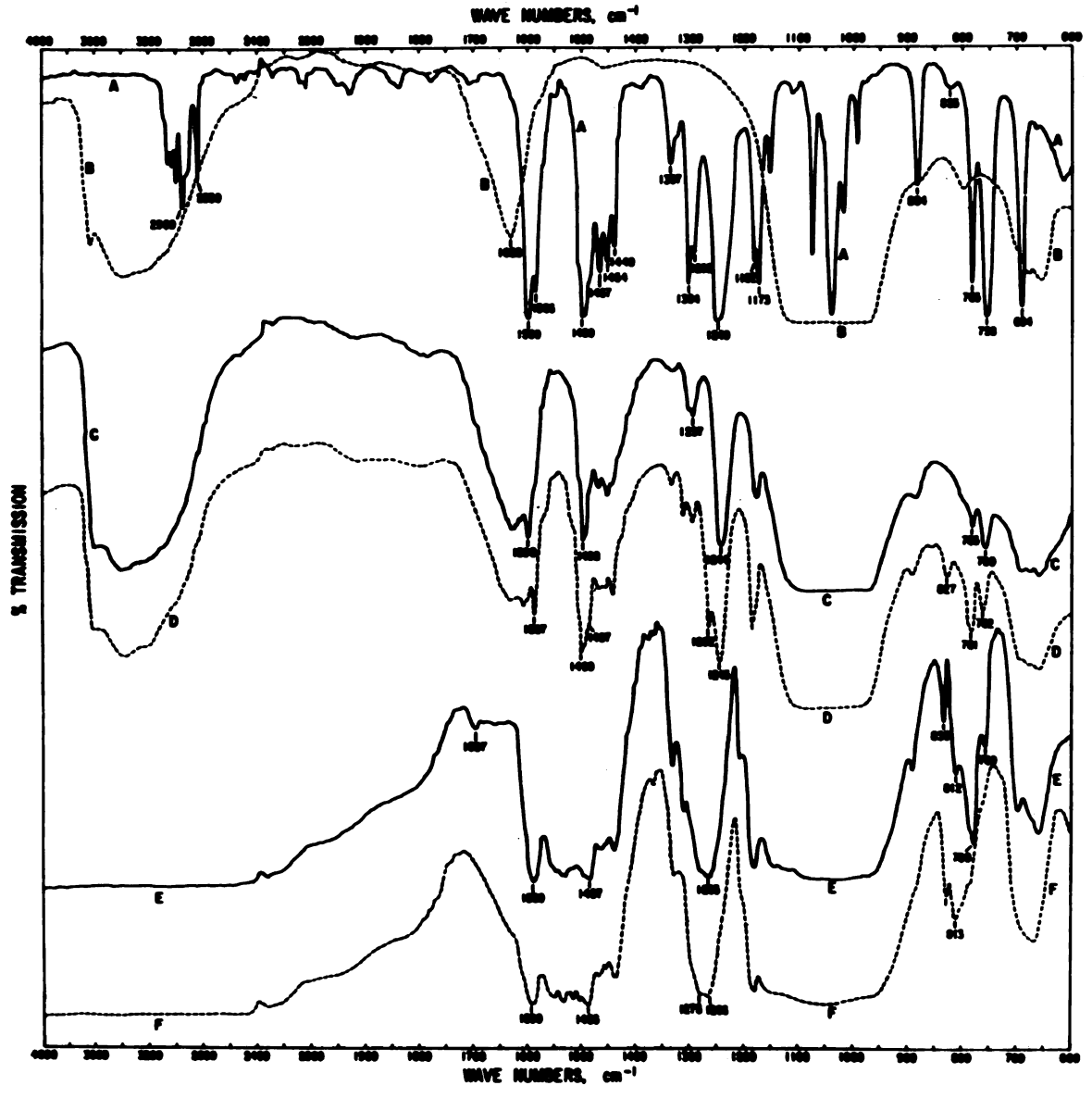


Figure 5: Infrared spectra of (A) liquid anisole; (B) an air dry Cu(II)-hectorite film; (C) physically bound anisole on Cu(II)-hectorite; (D) type I (tan) anisole complex on Cu(II)-hectorite; (E) type II (blue) anisole complex on Cu(II)-hectorite; and (F) type II (green) 4,4'-dimethoxybiphenyl complex on Cu(II)-hectorite.

vibration is shifted up 23 cm^{-1} to 781 cm^{-1} compared to liquid anisole. The $\nu 16$ C-C stretching vibration has been shifted down 11 cm^{-1} to 1587 cm^{-1}, and a new band appears at 1262 cm^{-1}. This latter band likely arises from a 13 cm^{-1} high energy shift of the C-O-CH_3 stretching mode upon formation of a type I complex.

The blue anisole complex, Figure 5E, is obviously a type II analog. The very intense absorption above 1800 cm^{-1} corresponds directly with that of the type II benzene complex, which Mortland and Pinnavaia (1971) attribute to a low energy electron transition arising from the d-π Cu(II)-benzene interaction. The CH out-of-plane region of liquid anisole, Figure 5A, shows a band at 758 cm^{-1}. In Figure 5E we find a band at 760 cm^{-1} corresponding to physically sorbed anisole, a strong band at 780 cm^{-1} which is attributed to a type I complex, and a band at 812 cm^{-1} which is attributed to the $\gamma 4b$ CH out-of-plane vibration characteristic of the type II anisole complex. This represents about a 60 cm^{-1} high energy shift of the CH out-of-plane mode upon type II complexation. The C-C stretching region of liquid anisole shows several clearly defined bands and shoulders. Formation of the type II complex produces shifts in the energies of these bands which overlap with absorption bands of the other two forms of adsorbed anisole present, creating the broad absorption region found between 1400 cm^{-1} and 1600 cm^{-1}.

Three forms of adsorbed anisole then may be identified on Cu(II)-hectorite, namely, physically sorbed, type I (tan), and type II (blue). Table 5 contains the assignments of the infrared bands for these three forms of adsorbed anisole.

If a tan type I complexed film is not put in the infrared cell but mounted directly in the infrared beam, it will shortly turn green and exhibit the type II anisole spectrum. The heat of the infrared beam is evidently enough to partially dehydrate the film and convert the type I to the type II anisole complex. A similar effect was noted with the biphenyl-Cu(II)-montmorillonite complex (J. P. Rupert, 1973). If the film is removed from the infrared beam it turns tan once again.

Pleochroic studies on the type II anisole complex show no changes in intensity of any of the in-plane or out-of-plane vibrational modes, which indicates that the anisole is lying in the interlamellar regions with the plane of its ring at or near an angle of 45° to the clay plates.

Stoichiometric studies on the type II system, which also contains physically sorbed and type I anisole, indicated that a total of about five molecules of anisole are adsorbed on the hectorite per exchangeable Cu^{2+} ion.

Identification of the Green Type II Complex.

When the blue, type II anisole-Cu(II)-hectorite complex is placed out in the air it adsorbs atmospheric

Table 5: Assignments of selected vibrational frequencies (cm^{-1}) of anisole as a liquid, as a physically bound species on all kinds of homoionic hectorite studied, as a type I ligand on Cu(II)-hectorite, and as a type II ligand on Cu(II)-hectorite.

Liquid*	Physically Bound	Type I Cu(II)	Type II Cu(II)	No.*	Assignment*
690	696	-	699	$\nu 8$	δ C-C
752	760	781	812	$\nu 4$	γ C-H
783	785	-	-	$\nu 2$	ν C-O-CH_3
825	-	827	835	$\nu 11$	γ C-H
880	885	885	890	$\nu 11'$	γ C-H
1180	1178	1182	1180	-	methyl bending ?
1247	1244	1262	1265	$\nu 12$	ν C-O-CH_3
1292	1297	1294	1280	$\nu 3$	β C-H
1304	1305	1313	1312	-	methyl bending
1332	-	1335	1333	$\nu 9$	ν C-C
1442	1445	1442	1440	-	?
1454	1454	1454	**	$\nu 13'$	ν C-C
1469	1470	1470	**	-	methyl bending
1499	1498	1487	**	$\nu 13$	ν C-C
1588	-	-	**	$\nu 16'$	ν C-C
1599	1598	1587	1589	$\nu 16$	ν C-C

* Assignments taken from Green (1961) and Stephenson, Coburn and Wilcox (1961).

** Broad overlapping of bands makes assignment difficult.

moisture and reverts to the tan type I complex. If this type I complex is left out in the air overnight it turns to a green color. The infrared spectrum of this green complex is shown in Figure 5F. It is characterized by an 813 cm^{-1} CH out-of-plane vibration and an intense absorption above 1700 cm^{-1}. It is obviously a type II analog, but one that forms out in the atmosphere with no external dehydration treatments. The spectrum resembles the parent anisole in many respects, but the complex is stable when immersed in distilled water. The fact that the green color forms only after the type II anisole complex is placed out in the air suggests that the reaction pathway is through either the type I complex or the physically bound anisole. Its formation is evidently promoted by one or more of three factors, namely: light, atmospheric moisture or oxygen. Light was eliminated as a factor when the green complex was found to form on films treated in the dark. When a film was complexed with anisole and placed in a vacuum cell over pure oxygen, the blue type II color remained stable and no green complex was formed. Oxygen alone, therefore, cannot be the critical factor. The presence of water must be important. It is known that the acidity at a clay surface is greater than that measured in a bulk solution (Mortland and Raman, 1968). It was felt that perhaps we were witnessing a surface acidity effect, where as atmospheric moisture was readsorbed and the type I

anisole complex and physically bound anisole became predominate, the acidity at the clay surface initiated a reaction leading to the type II green complex. To test this hypothesis a blue, type II anisole complexed film was placed over the vapors of concentrated HCl for a few seconds. The film very rapidly turned dark green, and the infrared spectrum corresponded to that in Figure 5F, confirming the hypothesis that the reaction is acid catalyzed and that clay surface acidity is a controlling factor in the formation of the green complex.

It was found that the green complex could be extracted with methanol in a few hours. The methanol could be distilled off, and a highly crystalline product of light brownish color remained. The product had a melting point of 176°C, and the mass spectral analysis indicated a molecular weight in excess of 207. The infrared spectrum of the compound is shown in Figure 6. The anisole has undergone a dimerization reaction to form 4,4'-dimethoxybiphenyl (m.w. 214, m.p. 173°) which then forms a type II complex with the Cu^{2+}-hectorite. Figure 6 corresponds exactly with the infrared spectrum of the authentic compound. The nmr spectrum of the isolated product also corresponds to that of the authentic compound. The following mechanism, similar to the one proposed by Kovacic and Kyriakis (1963) for the formation of p-polyphenyl in solution, is suggested:

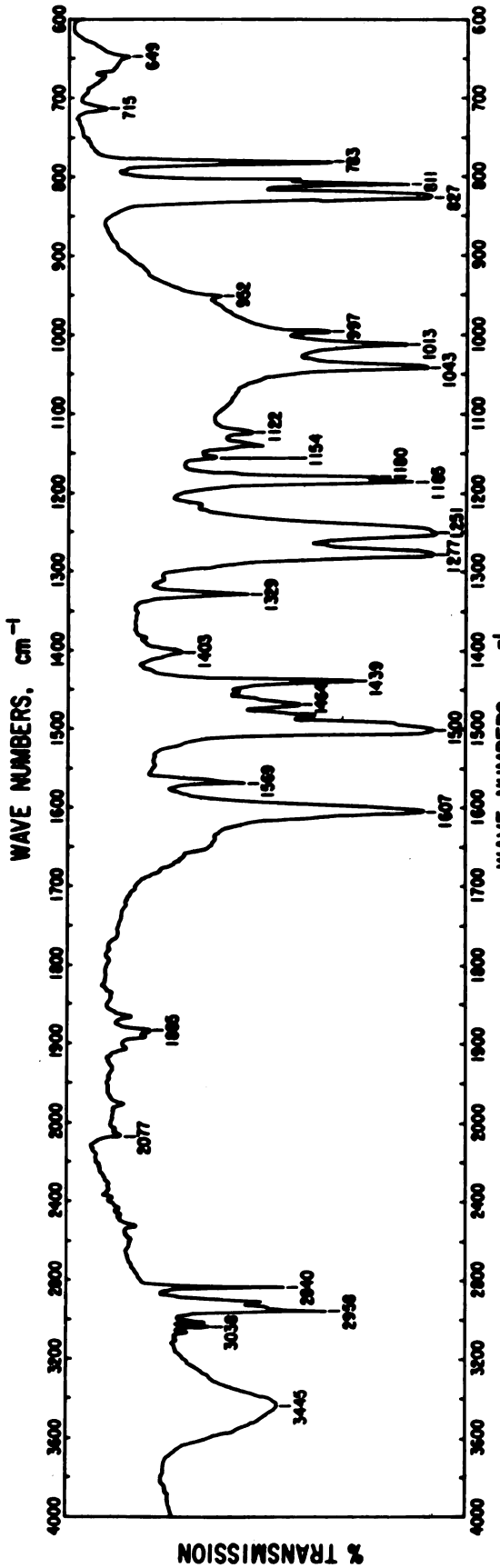
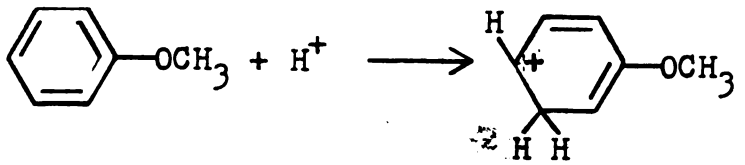
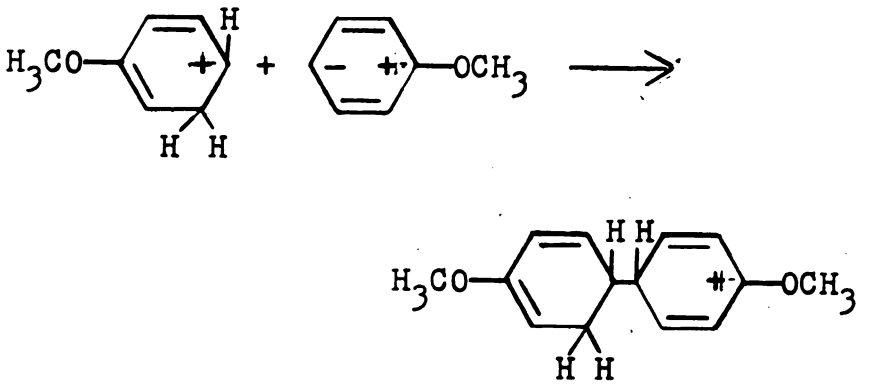
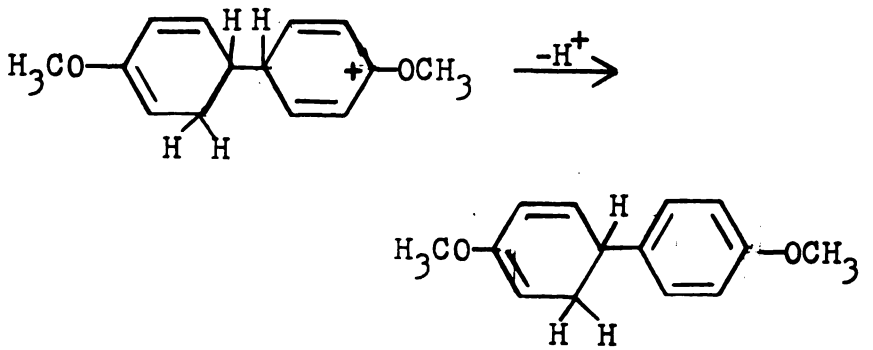
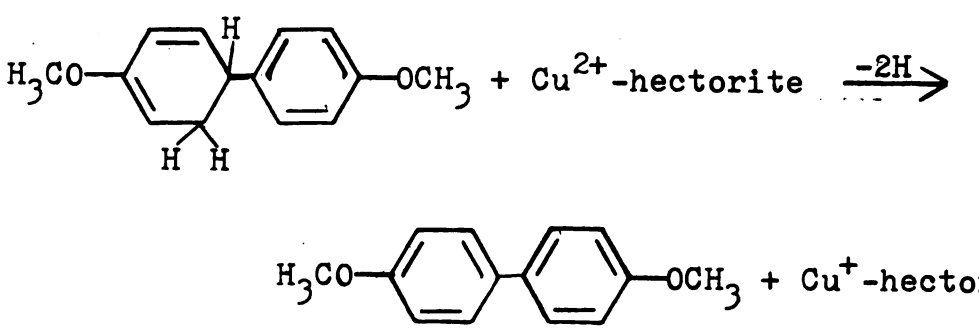


Figure 6: KBr pellet infrared spectra of crystals distilled from methanol extract of green, type II, Cu(II)-hectorite complex.

(1) 

(2) 

(3) 

(4) 

In the presence of oxygen and in a hydrated condition on the clay surface, it is likely that Cu(I) will be rapidly oxidized back to the Cu(II) state. To test this hypothesis a blue, type II anisole complexed film was placed in a flask over nitrogen gas and a drop of water. No oxygen was allowed in the system. As the clay rehydrated, the blue complex disappeared and the film became tan in color. After twenty-four hours the film was still light tan, indicating that no green complex had formed in the absence of oxygen. When the film was taken out of the flask and placed in the air it turned green within a few minutes. These results suggest that the dimerization reaction had occurred on the Cu(II)-hectorite film under a nitrogen atmosphere but that the green, type II complex could not form because step 4 of the proposed mechanism had left copper in the +1 oxidation state. Type II complexation requires copper in the +2 oxidation state. When the film was placed out in the air, the Cu(I) was rapidly oxidized to Cu(II) and the green complex could then form.

Ultraviolet-Visible Spectra.

The ultraviolet-visible spectra of the deeply colored anisole and 4,4'-dimethoxybiphenyl complexes are shown in Figure 7. Liquid anisole, Figure 7A, absorbs at 265, 271, and 278 mu. The blue anisole-Cu(II)-hectorite complex, Figure 7B, however, shows a strong band at 612 mu and a broad region of absorption below 360 mu. This intense

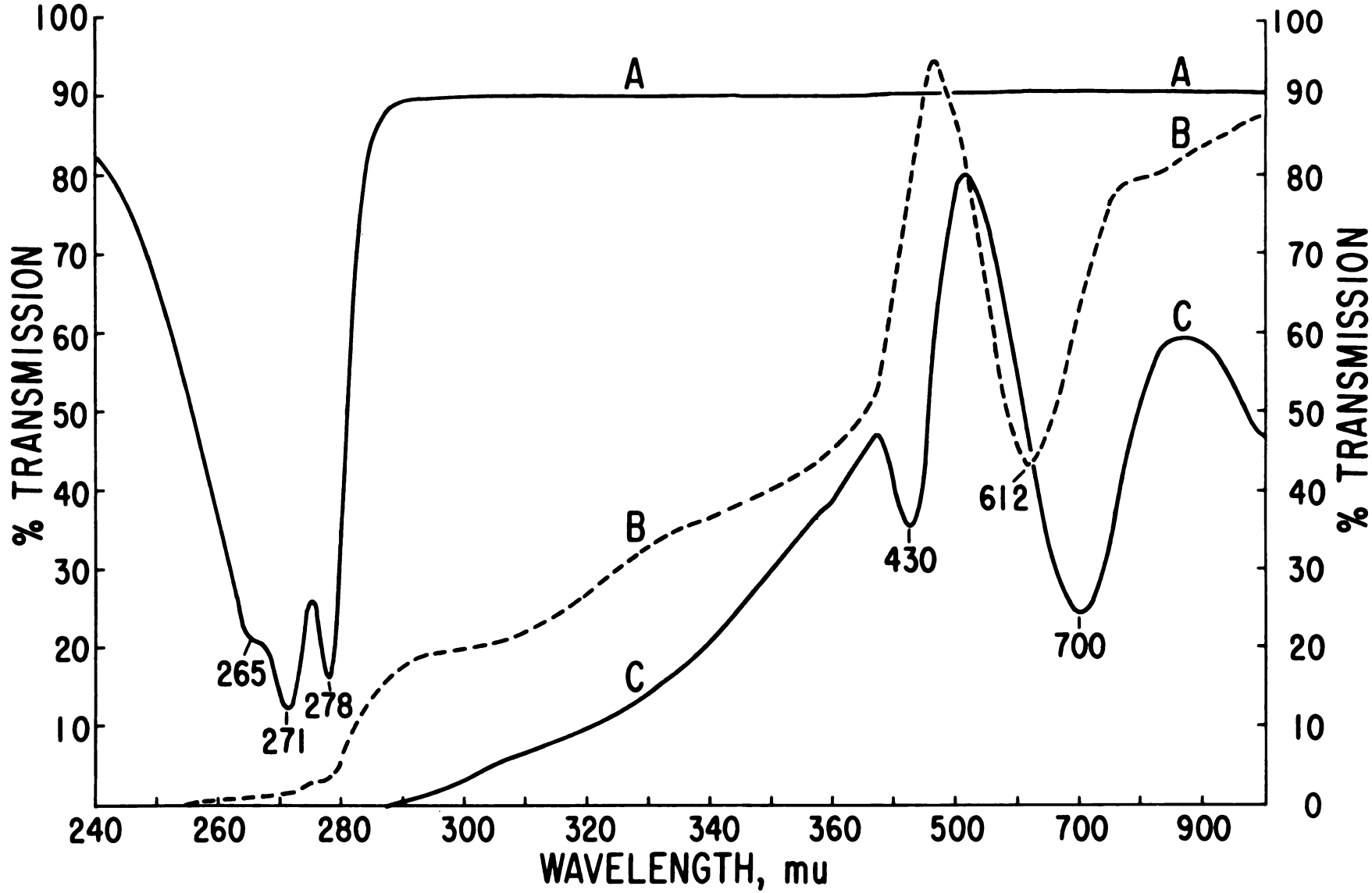


Figure 7: Ultraviolet-visible spectra of (A) anisole dissolved in distilled water; (B) blue, type II anisole-Cu(II)-hectorite complex (dashed line); and (C) green, type II 4,4'-dimethoxybiphenyl-Cu(II)-hectorite complex.

ultraviolet absorption, the shift into the visible region and the broad absorption above 1700 cm^{-1} in the infrared region (Figure 5E) all agree with the previous work of Pinnavaia and Mortland (1972) on the benzene-Cu(II)-montmorillonite complex and are further evidence for a charge transfer type interaction between the π-electrons of the arene and the exchangeable Cu(II) ions. The spectrum of the green type II complex is shown in Figure 7C. As can be seen, the spectrum is much different from that of the anisole complex, Figure 7B. This is further evidence that a reaction has taken place, and the green complex no longer contains anisole. The broad ultraviolet absorption, the two bands in the visible region and the infrared spectra, Figure 5F, are all analogous to the anisole system, however, and suggest that the 4,4'-dimethoxybiphenyl complex is similar in nature to the other type II arene-Cu(II)-smectite complexes reported to date.

Adsorption of Anisole on Other Kinds of Homoionic Hectorite.

The adsorption of anisole on other kinds of homoionic hectorite was also studied. Figure 8 shows representative spectra from this study. As can be seen in Figure 8A, the Ag(I)-hectorite forms a type I complex with anisole. The CH out-of-plane band at 780 cm^{-1}, the C-O-CH_3 mode at 1262 cm^{-1} and the C-C stretches at 1487 cm^{-1} and 1587 cm^{-1} all correspond to the type I Cu(II)-anisole complex bands in Figure 5D. As was noted in previous studies on Ag(I)-hectorite-arene

complexes (Clementz and Mortland, 1972 and Fenn and Mortland, 1972), no physically bound arene is adsorbed on the Ag(I)-hectorite. Twice as many Ag(I) ions are needed to satisfy the hectorite exchange capacity than Cu(II) ions. The formation of the type I complex by anisole molecules on Ag(I)-hectorite effectively covers the interlamellar surface area and blocks the physical adsorption sites on the silicate structure.

As shown in Figures 8B and 8C, both Na^+-hectorite and Co(II)-hectorite adsorb anisole by physical means only. The adsorption process appears to be independent of the exchangeable cation since similar spectra were obtained for all the kinds of homoionic hectorite studied where physically sorbed anisole was present. The band at 1696 cm^{-1} in Figures 5E and 8C, however, appears only in the transition metal saturated hectorite but not in the alkali metal or alkaline earth saturated hectorite studied. It is possible that this band is masked by the H_2O deformation band of residual water on the alkali metal or alkaline earth homoionic hectorite. The band is in the C-O stretching region, but the other bands show no indication of any ketone or quinone formation from anisole. The origin of this weak band cannot yet be explained and requires further study.

Adsorption of Other Aromatic Ethers on Homoionic Hectorite.

The critical influence of the strong inductive effect of the methoxy group on the coordination of anisole with

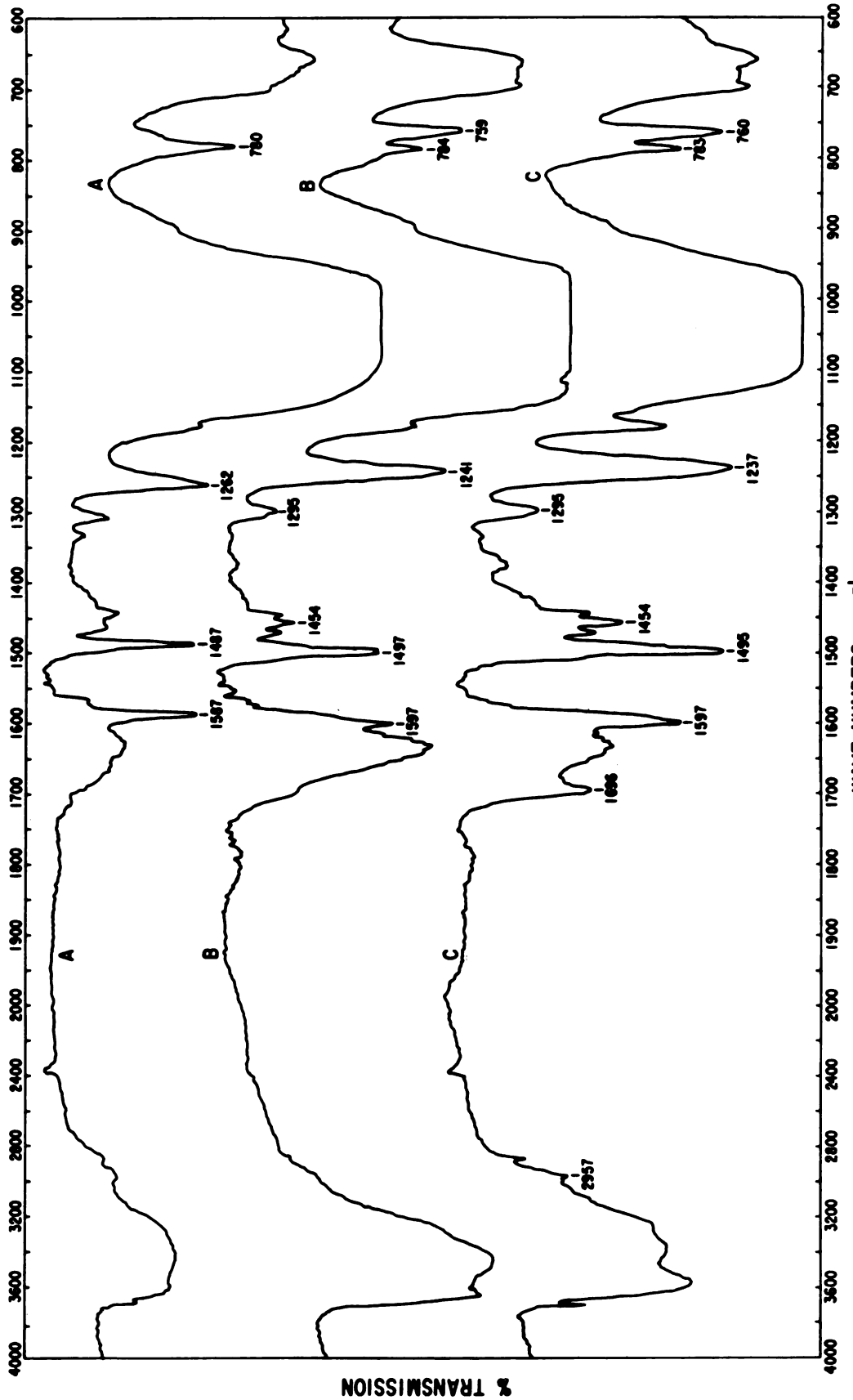


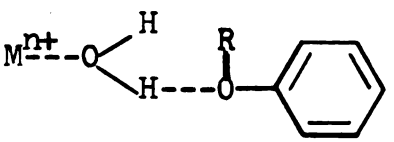
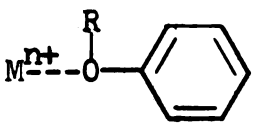
Figure 8: Infrared spectra of (A) anisole over Ag(I)-hectorite and P_2O_5; (B) anisole over Na^+-hectorite and P_2O_5; and (C) anisole over Co(II)-hectorite and P_2O_5.

exchangeable Cu^{2+} is evident. No other substituted benzenes studied to date have been capable of forming a type II complex with the Cu(II)-smectites except where the substitution was with other benzene rings such as in biphenyl, naphthalene or anthracene (J. P. Rupert, 1973).

Butyl phenyl ether, benzyl methyl ether and phenyl ether were also studied in order to further investigate the effects of the ether linkage on the formation of the type II complex with Cu(II)-hectorite. Figure 9 shows the spectra obtained in the study of butyl phenyl ether.

As can be seen in comparing the spectrum of liquid butyl phenyl ether (Figure 9A) with that of butyl phenyl ether adsorbed on Ni(II)-hectorite (Figure 9B), only physically bound ether is present. The CH out-of-plane vibration is shifted up 8 cm^{-1} from 755 to 763 cm^{-1}, and the ν19a C-C stretch is shifted down 6 cm^{-1} from 1498 cm^{-1} to 1492 cm^{-1} compared to liquid butyl phenyl ether. These small shifts indicate that the adsorption process may involve a weak π-electron interaction between the silicate surface and the butyl phenyl ether. The positions of the above peaks are independent of the exchangeable cation. The C-O-R stretching vibration at 1248 cm^{-1} in liquid butyl phenyl ether does show some cation dependence, however. With butyl phenyl ether adsorbed on Ni(II)-hectorite (Figure 9B), the C-O-R stretch occurs at 1233 cm^{-1}; while on Al^{3+}-hectorite it occurs at 1217 cm^{-1}, and on Na^{+}-hectorite

The band is at 1244 cm^{-1}. These results suggest that the physical adsorption process may involve either (A) hydrogen bonding to coordinated water on the cation; or (B) direct coordination between the cation and an unshared pair of electrons on the ether linkage, depending on the cation. These two processes are shown below:

(A)  , (B)  .

In Figure 9C we find that Ag(I)-hectorite forms a type I complex with butyl phenyl ether. The CH out-of-plane vibration is shifted from 755 cm^{-1} up to 780 cm^{-1}, a difference of 24 cm^{-1}. The ν19a C-C stretch is shifted down 10 cm^{-1} to 1488 cm^{-1}. Once again there is no physically bound arene formed on Ag(I)-hectorite.

In Figure 9D it appears that butyl phenyl ether was able to form a type II complex with Cu(II)-hectorite, although the complex was less stable than the anisole type II complex. The CH out-of-plane region of Figure 9D shows a band at 757 cm^{-1} due to physically bound butyl phenyl ether, a band at 770 cm^{-1} arising from a type I complex and bands at 793 cm^{-1} and 843 cm^{-1} which are characteristic of the type II butyl phenyl ether complex on Cu(II)-hectorite. A strong band at 1299 cm^{-1} is characteristic of the type II complex and possibly arises from 51 cm^{-1}

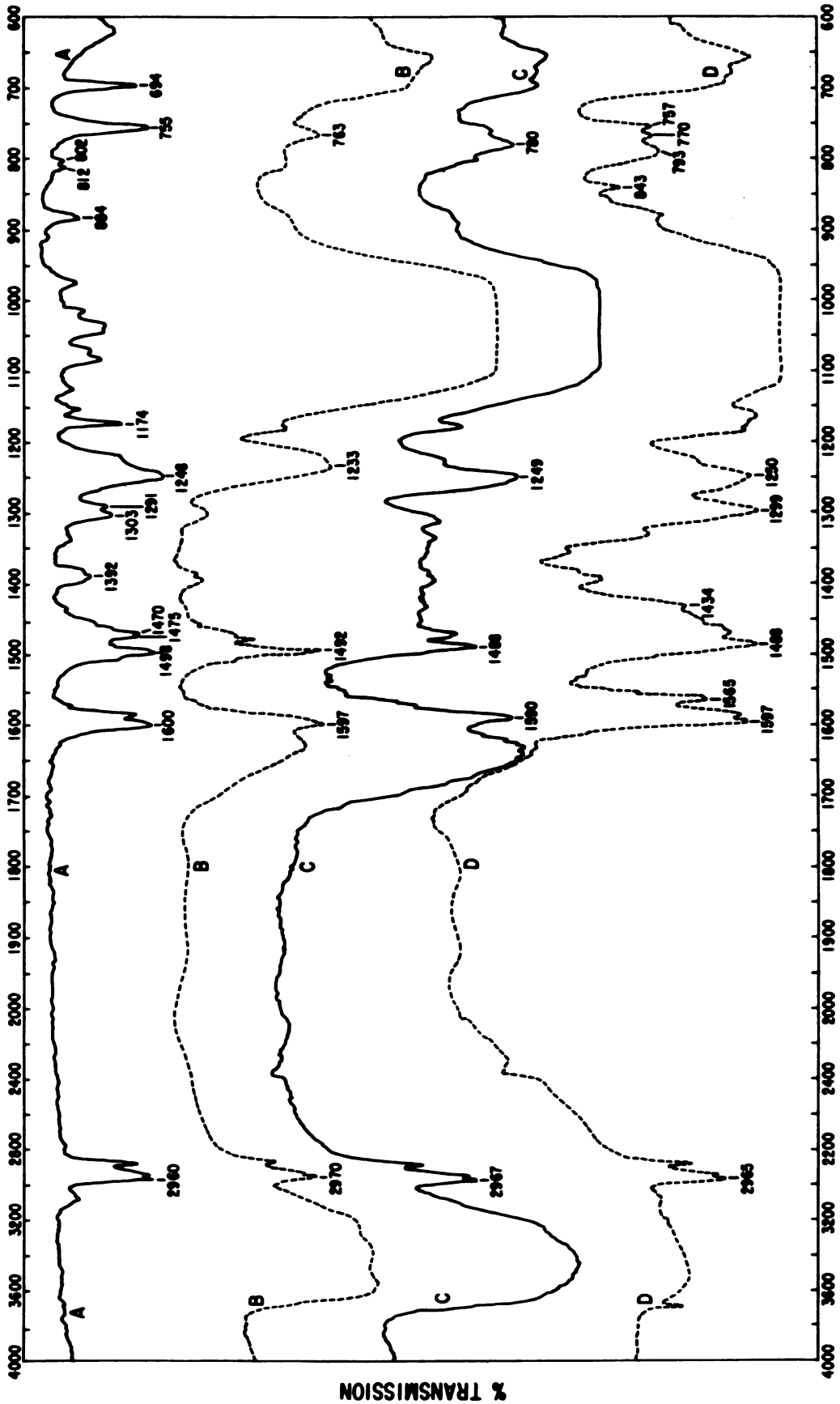


Figure 9: Infrared spectra of (A) liquid butyl phenyl ether; (B) butyl phenyl ether over Ni(II)-hectorite and P_2O_5; (C) butyl phenyl ether over Ag(I)-hectorite and P_2O_5; and (D) type II (purple) butyl phenyl ether on Cu-hectorite.

high energy shift of the ν12 C-O-R stretching vibration which occurs at 1248 cm^{-1} in liquid butyl phenyl ether. The ν8a C-C stretch has shifted down from 1600 cm^{-1} to 1565 cm^{-1} in the type II complex. A comparison of Figure 9D with Figure 9B in the region above 2400 cm^{-1} shows additional evidence for the type II butyl phenyl ether complex on Cu(II)-hectorite. The broad absorption remains intense out to 4000 cm^{-1} in the spectrum of Figure 9D where the type II complex is present but not in Figure 9B where only physically bound butyl phenyl ether is present.

Phenyl ether and benzyl methyl ether did not form type II complexes with Cu(II)-hectorite. In the benzyl methyl ether system, a methylene group is situated between the ring and the methoxy group. This CH_2 group prevents the unshared pairs of electrons on the ether oxygen from participating in resonance with the π-electrons of the benzene ring. In phenyl ether there is no shielding methylene groups but both rings compete for resonance with the linking oxygen. Resonance between the ring and the ether oxygen, therefore, appears to be critical in the formation of the type II complex by anisole and butyl phenyl ether on Cu(II)-hectorite. Benzyl methyl ether did form a type I complex with Cu(II)-hectorite as evidenced by shifts in the CH out-of-plane and C-C stretching vibrations upon complexation which were comparable to shifts in previously studied type I complexes. With phenyl

ether, the thin Cu(II)-hectorite film turned a light green color indicating complexation, possibly a type I analog, had occurred. This complex was extremely unstable, however, and good infrared spectra could not be obtained. ESR data on phenyl ether with freeze dried Cu(II)-hectorite is discussed next in this paper and further indicates a complex is formed between Cu(II)-hectorite and phenyl ether.

Electron Spin Resonance: Aromatic Ethers Adsorbed on Cu(II)-Hectorite.

The ESR spectra of the adsorbed ethers are shown in Figure 10, and the respective g values are listed with each figure. As can be seen the values are all very close to the g value of 2.0023 for a "free spinning" electron, although the last digit in the g values of Figures 10B--10F is not highly significant. There is no evidence of any hyperfine splitting of the narrow band. The phenyl ether and benzyl methyl ether strongly show the presence of Cu^{2+} spins. These systems are obviously interstratified, and the complex has not maximized on all the available ligand sites. Weaker Cu^{2+} signals are noted in the butyl phenyl ether and the 4,4'-dimethoxybiphenyl complexes also. In addition to the "free" electron signal in the ESR spectra of the type I complexes of benzyl methyl ether and phenyl ether, a sharp peak of similar g value has been observed in the ESR spectra of the type I Cu(II)-hectorite complexes of toluene (Cady, personal communication) and phenol. It is

clear, therefore, that this narrow ESR signal is not a singular property of the type II complex since several type I complexes on Cu(II)-hectorite also exhibit the signal. Rupert (1973) proposes that the d^9 Cu(II) ion functions as an electron acceptor for the transfer of a π-electron from the arene to form a radical cation which then gives the ESR signal. The lack of hyperfine splitting in the spectrum is attributed to rapid electron exchange between radical cations or between radical and neutral, diamagnetic species resulting in the single, exchange-narrowed ESR band. Rupert, however, only observed signals on type II Cu(II)-montmorillonite-arene complexes. The fact that the signal is also found in Cu(II)-hectorite systems containing only type I complexes but not in the type I Ag(I)-hectorite complexes (D. M. Clementz, unpublished data) suggests the need for further research on this "free" electron signal in arene-Cu(II)-smectite complexes.

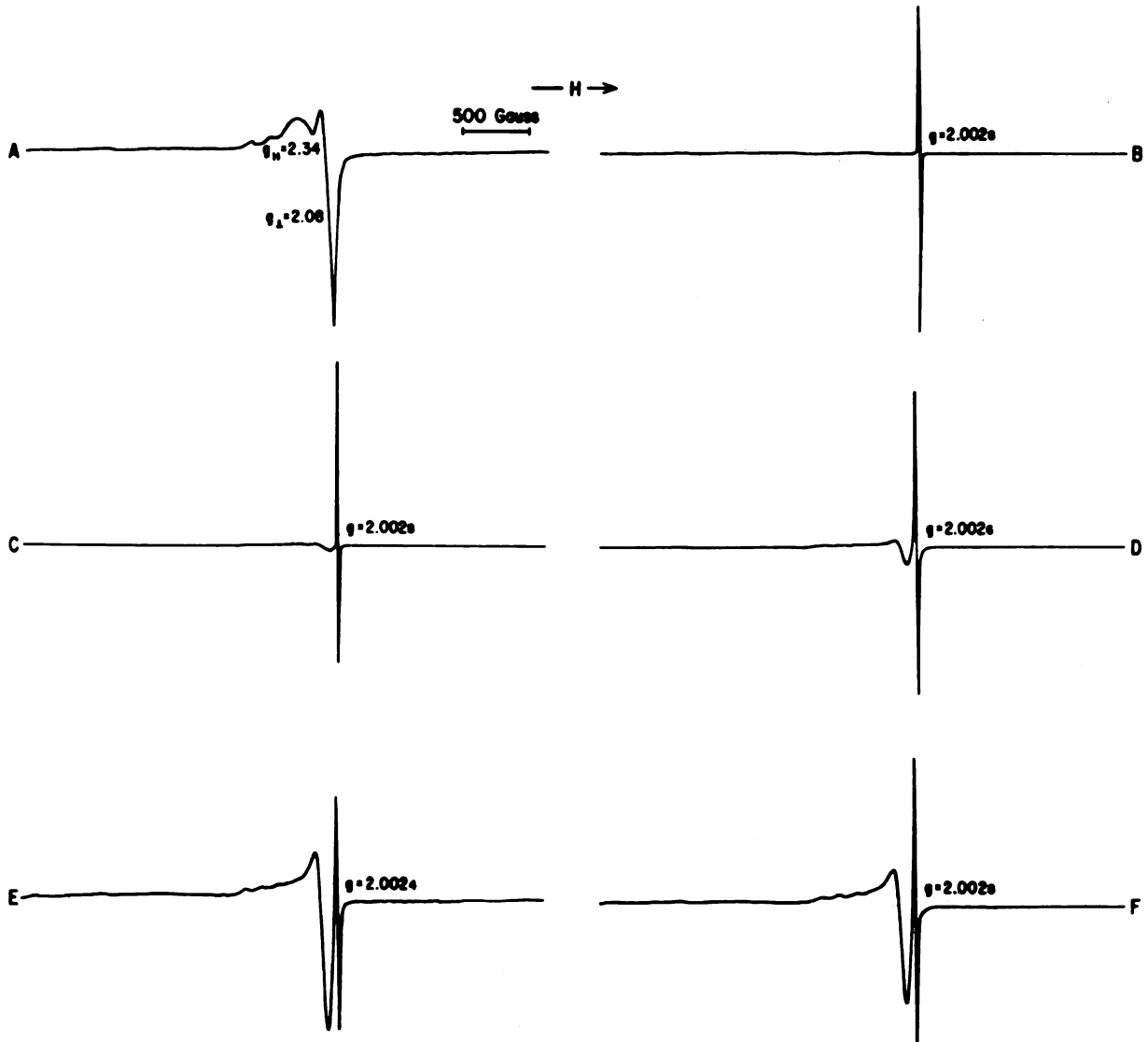


Figure 10: ESR spectra of freeze dried Cu(II)-hectorite over (A) no treatments; (B) anisole and P_2O_5 (blue complex); (C) green, 4,4'-dimethoxybiphenyl complex; (D) butyl phenyl ether and P_2O_5 (purple complex); (E) benzyl methyl ether and P_2O_5 (brown complex); and (F) phenyl ether and P_2O_5 (green complex).

SUMMARY AND CONCLUSIONS

1. Cu(II)-hectorite forms a type I π-complex with phenol in the presence of P_2O_5 dessicant. The complex is distinguished by a 32 cm^{-1} high energy shift in the γ10b CH out-of-plane vibration and a 17 cm^{-1} low energy shift in the ν19a C-C stretching vibration. The complex is black in color. Physically bound phenol is present simultaneously with the complex on Cu(II)-hectorite.

2. Ag(I)-hectorite forms a type I π-complex with phenol. The complex is distinguished by a 29 cm^{-1} high energy shift in the γ10b CH out-of-plane vibration and a 17 cm^{-1} low energy shift in the ν19a C-C stretching vibration. No physically bound phenol is formed on the Ag(I)-hectorite.

3. Stoichiometric studies indicate that about five molecules of phenol are adsorbed per exchangeable Cu^{2+} ion. This total includes ligand phenol and physically bound phenol. On Ag(I)-hectorite about one molecule of phenol was adsorbed per exchangeable Ag^{+} ion. Pleochroic studies indicate that the phenol molecule is oriented in the interlamellar region on an angle more toward the vertical than the horizontal.

4. The ESR spectrum of the phenol-Cu(II)-hectorite complex shows a single, sharp signal at a g value of 2.0023.

5. Co(II)-, Ni(II)-, Fe(III)-, Al^{3+}-, Mg^{2+}-, Na^{+}-, and Li^{+}-hectorite all adsorb phenol by physical processes only. No ligand phenol was formed on any of the above homoionic hectorites. Suggested adsorption mechanisms include hydrogen bonding to oxygen of the silicate structure, hydrogen bonding through a water bridge to the exchangeable cation, and weak π-electron interaction with the silicate structure.

6. Trimethyl ammonium- and tetramethylammonium-montmorillonite adsorb phenol by an ion-dipole interaction between the substituted ammonium cation and the phenol molecule. Hydrogen bonding and a weak π-electron interaction with the silicate structure are also probably occurring.

7. Three forms of adsorbed anisole are present on Cu(II)-hectorite over P_2O_5 dessicant, namely: physically bound anisole, a type I complex (tan) and a type II complex (blue). The type I complex is characterized by a 29 cm^{-1} high energy shift in the $\nu 4$ CH out-of-plane vibration, a 12 cm^{-1} low energy shift in the $\nu 13$ C-C stretching mode and a 15 cm^{-1} high energy shift in the $\nu 12$ C-O-CH_3 vibration. The type II complex is characterized by a 60 cm^{-1} high energy shift in the $\nu 4$ CH out-of-plane vibration and an intense absorption above 1700 cm^{-1} which obscures the rest of the spectrum.

8. When a type II anisole complexed film is placed out in the air, the blue color rapidly disappears and the film becomes tan in color. After several hours in the air the film will turn green and exhibit a type II spectrum. A dimerization reaction has occurred to form 4,4'-dimethoxybiphenyl from anisole and the product then forms the type II complex with Cu(II)-hectorite in the presence of oxygen.

9. The dimerization reaction proceeds through the type I anisole complex and/or physically bound anisole and is catalyzed by acidity at the clay surface. Oxygen is necessary to oxidize Cu(I) back to Cu(II) before type II green complex will form after the dimerization reaction has occurred.

10. Butyl phenyl ether forms a type II complex on Cu(II)-hectorite over P_2O_5 dessicant, and forms a type I complex on Ag(I)-hectorite.

11. Benzyl methyl ether and phenyl ether formed type I complexes with Cu(II)-hectorite but not type II complexes. This points out the importance of the special inductive effect of the -OR group on the activity of the phenyl ring. Anisole and butyl phenyl ether are the first known substituted benzenes to form the type II complex.

12. The ESR spectra of each of the Cu(II)-hectorite-arene complexes studied showed a single, sharp signal near a g value of 2.002. This was true of both the type II and type I complexes.

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