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THE POLYMERIZATION OF ANILINE ON TRANSITION-METAL CATION EXCHANGED HECTORITE FILMS

By

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ABSTRACT

McMANAMAN, CHARITY The polymerization of aniline on transition-metal cation exchanged hectorite films. Department of Chemistry, June 1999.

Inorganic-organic materials often exhibit enhanced flexibility and thermal stability over their individual inorganic and organic precursors. We are studying the polymerization of organic aniline monomers on inorganic hectorite clay thin film supports. Previous research has shown that aniline polymerizes on the surface and intergallery regions of Cu(II)-exchanged hectorite films. We have synthesized a library of first row transition-metal exchanged hectorite thin film hosts and are probing the effects of the different transition metal cations on aniline polymerization. We have used infrared spectroscopy, X-ray diffraction and digital photography to characterize the extent of aniline polymerization on the films. Utilizing the transition metal to control the extent of polymerization allows the optimization of stability and permeability necessary for materials applications including catalytic converters and chemical sensing devices.

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Thanks especially to my advisor Dr. Michael Hagerman, without whom this research would not have been possible. For the opportunity to see a project from the beginning, its metamorphosis, and the results come to life.

CONTENTS

CONTENTS

TABLES

FIGURES

APPENDIX: INFRARED SPECTRA

APPENDIX: INFRARED SPECTRA

APPENDIX: INFRARED SPECTRA

1. INTRODUCTION

Inorganic/organic composites are materials that combine the useful properties of both inorganic and organic compounds. Inorganic compounds are generally chosen to provide a sturdy support surface for the organic compound, which is chosen for its useful optical, electronic or chemical sensing properties. One method of combining organic and inorganic compounds is to synthesize a film by alternating the inorganic and organic layers. In a second inorganic/organic synthesis method, an organic guest is inserted between the pre-existing layers of an inorganic host solid or placed on the host surface.

In one example of alternating organic/inorganic layered materials, Kotov, Maganov, and Tropsha produced inorganic-organic layered films in a layer-by-layer synthesis of three different montmorillonite/ polyelectrolyte films on a poly-(ethyleneterephthalate) substrate (PET)[1]. In 50 montmorillonite/polymer layers, the films proved crack-resistant and oxygen permeation through the films decreased up to 6.6 times over the PET substrate, while leaving the permeation rate of water through the membrane unaffected. The organic polymer gave the film flexibility, and the specific polymer directed the amount of montmorillonite clay deposited in each layer. The amount of polar montmorillonite, in turn, controlled the number of nonpolar oxygen molecules that passed through the water-permeable membrane. The inorganic/organic composite allowed control over the oxygen-permeability of a stable membrane, leading to their potential application as gas separation membranes.

Mallouk and Gavin demonstrated the use of another inorganic/organic layered composite, organometallic thin films, as chemical sensors[2]. In a layer-by-layer adsorption scheme, they synthesized $Cu_2(O_3PC_6H_4)_2$, a pillared organometallic film, on the gold electrodes of the sensitive 5MHz quartz crystal microbalance. The mass change upon ammonia adsorption showed that two ammonia molecules bound to each copper site. By changing the ammonium functional groups and the size of the bis(phosphate) pillars, they created a $Cu_2(O_3P(CH_2)_8PO_3)$ thin film carbon dioxide sensor. These layered solids exhibit the potential flexibility and sensitivity of organic/ inorganic systems.

Giannelis has noted that polar guest molecules placed between the pre-existing layers of an inorganic host such as a mica-type silicate also make successful organic/inorganic hybrids^3. Mica-type silicates are inorganic materials consisting of layers held loosely together by weak dipolar and van der Waals forces. Each layer consists of an inner layer of octahedrally bonded metal cations sandwiched between two layers of tetrahedrally bonded silicate groups, as shown in Figure 1. Between the layers are spaces called intergallery regions. The depth of a single layer plus the intergallery region represents the unit cell, or d-spacing, and can be determined with powder X-ray diffraction in multilayered materials.

The layers of mica-type silicates have inherent negative charge that is balanced by hydrated cations in the intergallery regions. These intergallery cations can be replaced by other cations in simple ion-exchange reactions. Polar molecules placed in the intergallery regions are held in the intergallery regions or on the surface by van der Waals forces, dipole-dipole interactions or hydrogen bonding to hydroxyl groups on the silicate layer. The fracture toughness of silicates containing organic polymer in the intergallery regions is greater than the fracture toughness of the silicate alone^3. Vaia et al. found that polystyrene placed between inorganic clay layers stabilized the polymer at temperatures

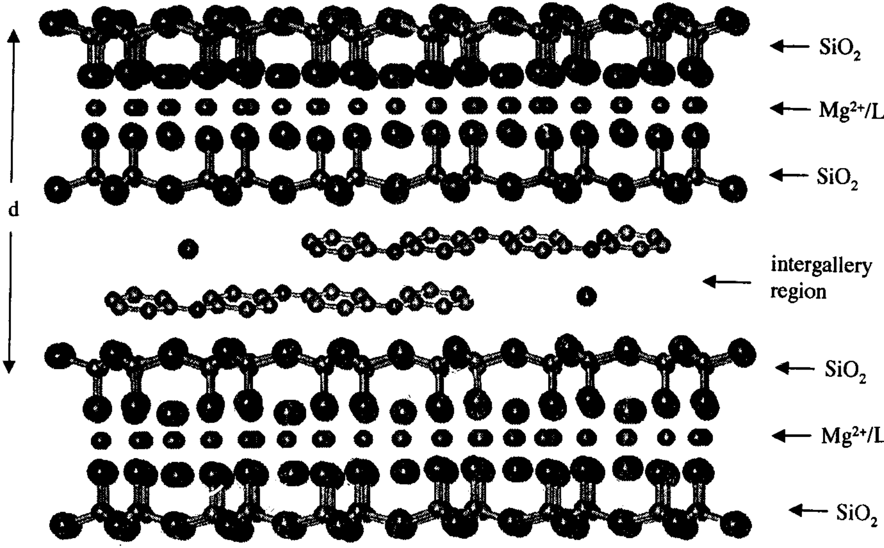


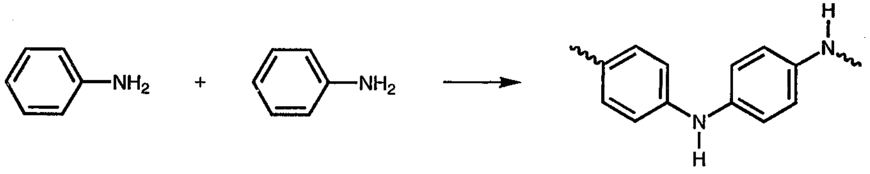
Figure 1. Structure of Hectorite, a mica-type silicate, showing aniline in the intergallery regions[5]. d-spacing indicated by d.

above the glass transition temperature of bulk polystyrene[4]. The strength and thermal stability of organic/inorganic films make them useful for applications such as integrated circuits, which require high processing temperatures.

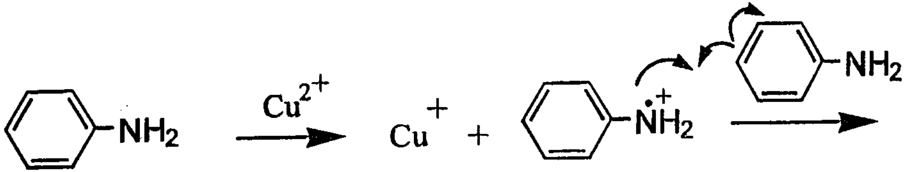
In order to create a sturdy, useful inorganic/organic composite material with a simple synthesis technique, we have chosen sodium hectorite, a mica-type silicate, as our inorganic host. Lithium(I) and magnesium(II) are the octahedrally bonded metal cations in the layers of hectorite and sodium ions occur naturally in the intergallery regions[5]. As Eastman et al. have demonstrated, sodium hectorite can be exchanged in copper(II) solutions and washed to form copper(II) hectorite. This copper(II) hectorite suspended in deionized water leaves a thin, light blue film after drying[6].

For our organic component, we have chosen aniline. Previous work by Porter et al. has shown that aniline vapor readily polymerizes on the surfaces of copper(II)-exchanged hectorite films, leaving them stiff and black[5,6,8]. Electrochemical studies have shown that the first, rate-limiting step of aniline polymerization is likely the formation of a primary radical cation[7], as the mechanism in Figure 2 shows[8].

It is thought that the reduction of the transition metal cation exchanged into the hectorite film catalyzes the polymerization of aniline by oxidizing neutral aniline to the primary radical cation[8]. By exchanging transition metal cations of widely varying reduction potentials into the hectorite, we were able to test this hypothesis by comparing the polymerization of aniline on films synthesized with each transition-metal cation. Bulk polyaniline is found in three oxidation states: the nonconducting leucoemeraldine form, the metal-like emeraldine form, and the semi-conducting pernigraniline form[9]. While the conductive form of emeraldine polyaniline exhibits a shine, polyaniline of



a. Overall polymerization reaction.



b. Initial steps in the proposed mechanism of aniline polymerization in the presence of transition-metal cation[8].

Figure 2. Aniline polymerization.

mixed oxidation states are generally a dull black color. These appearance generalities are useful in determining the character of the polymer synthesized.

We have studied the polymerization of aniline on various transition metal hectorite films by three methods: X-ray diffraction (XRD), infrared spectroscopy (IR) and visual analysis. Visual analysis was used to identify the oxidation of aniline from its yellow neutral monomer form to its black oxidized form. This enabled a comparison of oxidation speeds among the cation-exchanged films. A digital camera was used to record the appearance of each cation-exchanged film before and after aniline polymerized on the surface.

X-ray diffraction spectroscopy tells us the film d-spacing, or the combined thickness of one silicate layer and intergallery region[10] (see Figure 1). Previous studies have shown that aniline enters the intergallery regions of a copper(II) hectorite film upon exposure of the film to aniline vapor[5]. Aniline in the film intergallery regions increases the d-spacing from 12Å to 15Å. This has been hypothesized to correspond to one to two layers of aniline replacing water in the intergallery regions.

Infrared spectroscopy is used to identify the molecules and chemical bonds present in a sample[11]. A different frequency of infrared light is absorbed by the vibration of each type of chemical bond. The molecules present are identified by the frequencies of light they absorb. Polyaniline was identified on the film surfaces by the absorption of infrared frequencies due to the carbon-nitrogen-carbon bond present only in polyaniline and by the absence of the major aniline monomer absorbance frequencies (Figure 2).

The goal of our research is to create an inorganic/organic material with a use as a chemical sensor or gas permeation membrane. We use the inorganic hectorite film as our support surface, the transition metal cation to regulate the amount of organic polymerized upon the film surface and will choose an organic monomer that provides the chemical properties required. The goal of this project has been to establish a method of creating cation-exchanged hectorite films, to establish the role of the transition-metal cation in determining the amount of aniline polymerized on the film surface and to prove aniline polymerization through spectroscopic techniques.

2. METHODS

We first synthesized copper(II) hectorite films and later synthesized hectorite films from solutions of the vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and zinc(II) cations. We also attempted to produce sodium ion and [ruthenium(II) (bipyridyl)$_3$] hectorite films. After quality films were poured, at least one sample of each was exposed to aniline under ambient conditions. The films, prior to and subsequent to aniline exposure, were characterized by visual and textural analysis, infrared spectroscopy and X-ray diffraction.

Synthesis

The first copper(II) hectorite films were made from a 1.0M solution of copper(II) sulfate. Hectorite films were later made from the following 0.50M solutions: sodium sulfate, vanadyl(II) sulfate, chromium(III) chloride, manganese (II) sulfate, iron(III) chloride, iron(III) nitrate, cobalt(II) chloride, nickel(II) sulfate, nickel(II) nitrate, copper(II) sulfate and zinc(II) nitrate. Hectorite films were also synthesized from 0.10M solutions of chromium(III) chloride and vanadyl(II) sulfate.

Copper(II) Exchange: In a glass beaker, 50.mL of a 1M $CuSO_4$ solution were added to 0.2g of hectorite clay. The mixture was covered and stirred for three days to allow the copper cations to replace sodium ions in the intergallery regions of the clay. The mixture was poured into test tubes and centrifuged. The supernatant was poured off and the clay was washed with deionized water. The clay was centrifuged and washed at least four times, or until the supernatant tested negative for sulfate.

Pouring the Film: After the last supernatant was poured off, deionized water was added to the test tube to three times the volume of the wet clay and mixed thoroughly. With a glass transfer pipette, the mixture was carefully pipetted into a one-inch-diameter puddle in a plastic weigh boat. The best results were obtained when the weigh dish rested undisturbed on a flat surface. The water evaporated from the puddle in about two days, leaving a colored film. The films were stored in the labeled weigh boats in a lab drawer.

Sulfate Test: Two drops of 0.10M barium chloride were added to 0.5mL of supernatant. A milky white precipitate is a positive test for sulfate.

Other Cation Exchanges: Films were synthesized from cation exchanges with the following solutions: 0.50M $VOSO_4$, 0.50M $CrCl_3$, 0.50M $MnSO_4$, 0.50M $FeCl_3$, 0.50M $Fe(NO_3)_3$, 0.50M $CoCl_2$, 0.50M $NiSO_4$, 0.50M $Ni(NO_3)_2$, 0.50M $CuSO_4$ and 0.50M $Zn(NO_3)_2$. Because the vanadyl and chromium films dried badly, hectorite exchanges were also performed with 0.10M $VOSO_4$ and 0.10M $CrCl_3$. To synthesize control films, one "exchange" was set up with 0.50M Na_2SO_4 and another with only hectorite and deionized water. Attempts to make solutions of iron(II) chloride and copper(I) chloride failed because both were nearly insoluble and oxidized to iron(III) chloride and copper(II) chloride in air.

$[Ru(bpy)_3]^{2+}$ Exchange: Ruthenium bipyridyl chloride crystals were dissolved in deionized water. 0.001M and 0.0001M solutions of the ruthenium bipyridal complex were exchanged with hectorite clay for six days and films were poured from both solutions. A copper-exchanged hectorite film was placed in a plastic weigh boat containing a dilute $[Ru(bpy)_3]Cl_2$ solution for a few days. After absorbing most of the ruthenium complex from the solution, the film was removed and allowed to dry.

Aniline Exposure: The edges of a film were taped to the bottom of a watchglass that was placed over a small beaker containing a few milliliters of aniline. The watchglass and beaker were sealed with parafilm and left for a day, as shown in Figure 3. The films were left in the air for further polymerization.

Exposure to Aniline Derivatives: Copper(II) hectorite films were also placed over beakers of o-bromoaniline and 3,5-dimethylaniline for one day.

Timed Aniline Exposures: A copper(II) hectorite film was cut into five pieces. Four pieces were exposed to aniline for one, two, three and four hours before being left in the air. The

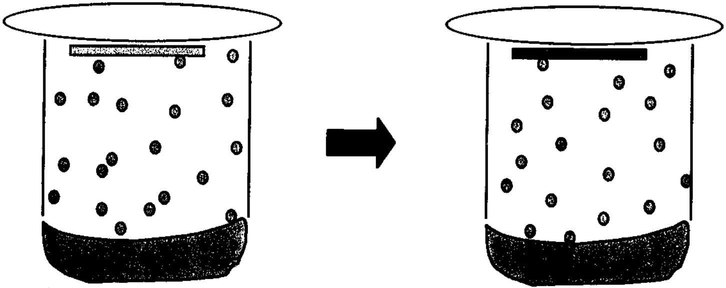


Figure 3. Method of aniline exposure. Film is taped to watchglass. Watchglass is parafilmed to beaker containing aniline.

colors of all five pieces were compared and IRs were taken of those left over aniline one hour and four hours and of the piece left in the air.

A second timed aniline exposure experiment was performed to discover when polymerization was noticeable in the infrared spectra. An infrared transmittance spectrum was taken of a copper(II) hectorite film taped to an IR card. The film and IR card were parafilmed over a beaker of aniline. The film was removed and an IR spectrum taken after thirty minutes, after every hour up to seven hours and after twelve days.

Exposure of Other Cation Films: One film synthesized from each of the following anions was exposed to aniline for 72 hours and then left under ambient conditions for six months: vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II).

Infrared Spectroscopy

Overview: Infrared Spectroscopy (IR) uses infrared light to determine the chemical bonds present in a material. Infrared light is produced by a Globar, which produces a continuous range of light between 400 and 4000 cm^{-1}. Radiation passes through the sample, where different light frequencies are absorbed by each dipolar vibration of the chemical bonds in the sample. The infrared radiation is detected by a thermocouple on the other side of the sample and translated into absorbance peaks[11]. A material can be identified by its infrared absorption spectrum.

The Multiple Internal Reflectance Accessory (MIRA) can be used to take an IR of the surface of a sample. The sample is pressed onto a crystal surface so that the incident beam is reflected from the crystal onto the sample surface multiple times, to enhance the absorbance at IR active wavelengths. Infrared reflection spectra were taken with the MIRA, but owing to poor peak resolution in the 1200 to 1500cm^{-1} region and consequent destruction of the film samples, the method was changed.

Transmittance IR spectra were taken by taping each film to a 3M Type 62 disposable IR card with the polyethylene sample surface removed. This method leaves the film intact for aniline exposure or for an X-ray diffraction sample. Most of the IR spectra were taken with 16 scans and 1cm^{-1} resolution.

MIRA Spectra: Infrared spectra of copper(II) hectorite films that had and had not been exposed to aniline were taken with the Multiple Internal Reflectance Accessory. A spectrum was also taken of parafilm for diagnostic purposes.

Aniline Derivative Exposures: Infrared transmittance spectra were taken of a copper(II) hectorite film before and after aniline exposure and of copper(II) hectorite films after exposure to o-bromoaniline and 3,5-dimethylaniline.

Standards for IR Comparison: An infrared spectrum was taken of liquid aniline between sodium chloride plates. An IR was also taken of the emeraldine form of polyaniline by suspending the solid in dichloroethylene and allowing it dry on a sodium chloride plate.

Timed Aniline Exposures: Infrared spectra were taken of the two timed aniline exposure studies. For the first, a spectrum was taken of an unexposed Cu(II) hectorite film, and of the films exposed to aniline for one and four hours. In the second study, an IR was taken of the unexposed film and of the same film after 30 minutes of aniline exposure, one hour of exposure and every hour thereafter up to seven hours of aniline exposure. Further spectra were taken after two and three weeks of exposure to aniline, and following an additional three weeks, eleven weeks and seventeen weeks under ambient conditions.

Transition-Metal Cation Comparison: For the study of the polymerization of aniline on films from different transition metal cations, an infrared transmittance spectrum was taken of each film before aniline exposure, after 24 hours one aniline exposure, and after 72 hours of aniline exposure and five months of ambient conditions. For comparison, IR transmission spectra were also taken of unexposed films that had been under ambient conditions for six months, and of a six-month old sodium hectorite film.

X-Ray Diffraction Spectroscopy

Overview: X-ray diffraction spectroscopy uses X-rays to determine the d-spacing, or total average thickness of one layer and intergallery region in the hectorite films (see Figure 1).

The d-spacing of a film increases when aniline is intercalated into the intergallery regions, because of the expansion of the intergallery region. X-ray diffraction can therefore verify aniline intercalation[5].

The X-ray diffractometer consists of a cobalt X-ray source, rotating sample holder and silicon detector. Electrons boiled off a tungsten filament are accelerated toward the cobalt target by a 45keV voltage. These electrons knock inner shell electrons from cobalt. X-rays are emitted as electrons fall from higher energy levels of cobalt to replace the lost electrons. Each emitted X-ray represents the energy difference between the higher and lower energy levels. An iron filter selects for the cobalt $K_{\alpha 1}$ and $K_{\alpha 2}$ X-rays, with a combined wavelength of 1.790Å. During an X-ray scan, the incident angle of X-rays on the sample rotates from 0° to 60° and the X-rays are detected from 0° to 120° 2θ. The detector produces a current proportional to the number of X-rays striking the silicon[11].

Because the film consists of many identically spaced layers, the reflected X-rays exhibit constructive interference at some incident angle θ. At all other incident angles, the reflected rays destructively interfere, giving a radiation peak only at the incident angle θ. According to Bragg's Law[11], constructive interference occurs when the distance from the point of incidence to the reflected wave front is ${}^{1}/_{2}n\lambda$, where n is any integer and λ is the X-ray wavelength (see Figure 4). From the reflected X-ray angle 2θ at which the peak occurs, the d-spacing, or distance from one layer of the film to the next, can be found by the equation: $d = n\lambda / 2 \sin \theta$.

The X-ray diffraction samples were attached to the opaque sides of glass sample plates with double-stick tape. The double-stick tape was pressed onto the sample plate and trimmed to approximately 1/2" x 3/4" before to film was pressed onto the tape and trimmed by pressing a sharp razor blade into the film at a right angle to the film. The most efficient

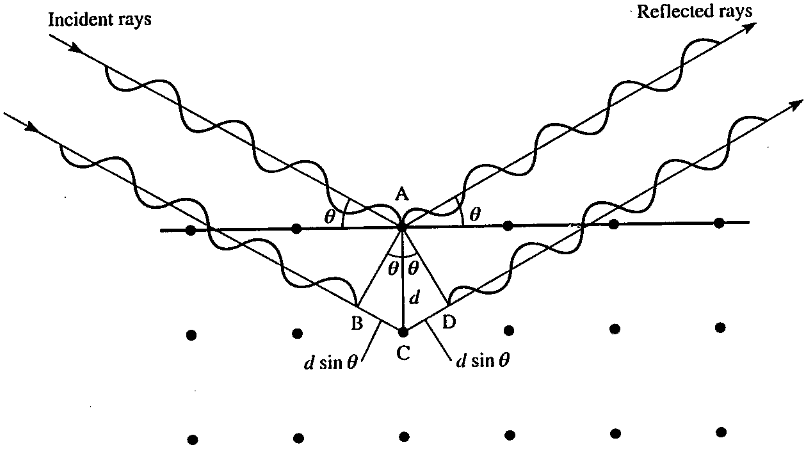


Figure 4. Bragg's Law[13]. $2d \sin \theta = n\lambda$.

X-ray diffraction method with the clearest results was to run a spectrum from 1 to 15 °2θ, with a scan speed of 0.01 °2θ per second and a time constant of 2 seconds. Removal of the double-stick tape and film from the sample holder destroyed the film.

Cu(II) Hectorite Film XRD: X-ray diffraction spectra were taken of Cu(II) hectorite films before and after aniline exposure, Cu(II) hectorite films left under ambient conditions for five days after exposure to aniline, exposed to aniline under vacuum for one week, heated after exposure to aniline and of Cu(II) hectorite films that had absorbed five and ten drops of water before the spectrum was taken. XRD spectra were also taken to compare a copper(II) hectorite film with a copper(II) hectorite film that had been exposed to aniline, ten months after the aniline exposure.

Transition Metal Cation XRD: X-ray diffraction spectra were also taken of each of the films made from the different transition metal cations, vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II). A spectrum of the double-stick tape was taken to make sure that the tape was not affecting the d-spacing data.

Visual and Textural Analysis

Each transition metal cation gives the films a slightly different overall appearance. Some are green, grey, light blue or pink. Some are smooth, while others are blotchy. Some dry and crack more easily than others. After the films have dried, their appearance is noted. Digital photographs were taken of a representative film of each transition metal cation, with and without aniline exposure.

Aniline present on the surface of a film gives it a yellow tinge, which changes to darker shades of brown and black upon oxidation. Because this is a clue to the amount of aniline oxidized on the surface of a film, the colors of films exposed to aniline were noted in the first timed aniline exposure and when films from the various cations were exposed to aniline.

Some of the films tend to dry out and crack more easily than others, and aniline exposure can affect the long-term stability of the film. Because stability is important in materials applications, the shape, flexibility and fragility of the films made with each of the transition metals were noted upon synthesis and six months later. The texture and appearance of corresponding transition-metal cation-exchanged films that had been exposed to aniline were also noted following aniline exposure and six months later.

3. RESULTS

Film Synthesis

Hectorite films exchanged with all of the following first row transition metal cations were successfully synthesized: vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II). Hectorite films exchanged with sodium ions and with the ruthenium bipyridyl complex were also synthesized.

Although the copper(II) hectorite films were synthesized with ease the first time, the iron(III) films and several others were only synthesized successfully on the second try, and the sodium and ruthenium bipyridyl films required experimentation with several cation concentrations to make films. The ruthenium bipyridyl film synthesis was unrepeatable. The quality of the films varied widely, from the consistent, flat, round iron(III) films to the curling, cracking manganese(II) films and the small, veined sodium films. Film quality also seemed to vary with the day that the film was poured. Table 1 gives the general appearance of films successfully synthesized from each cation exchange.

Table 1. Appearance of different cation-exchanged hectorite films immediately following film synthesis. The most successful cation solution concentrations are given.

Cation Exchanged	Exchange Solution	Film Color	Film Texture
Sodium	0.5M Na_2SO_4	light, light pink	non-uniform thickness, not round, very thin
Vanadyl(II)	0.1M $VOSO_4$	dark green	non-uniform thickness
Chromium(III)	0.1M $CrCl_3$	dark gray	tendency to curl
Manganese(II)	0.5M $MnSO_4$	light yellow-pink	curls and cracks
Iron(III)	0.5M $Fe(NO_3)_3$ 0.5M $FeCl_3$	yellow-orange orange	flat, round, uniform thickness
Cobalt(II)	0.5M $CoCl_2$	light pink	round, curls, uniform thickness
Nickel(II)	0.5M $Ni(NO_3)_2$ 0.5M $NiSO_4$	light yellow light yellow	non-uniform thickness
Copper(II)	1.0M $CuSO_4$ 0.5M $CuSO_4$	light blue-green	flat, round, uniform thickness
Zinc(II)	0.5M $Zn(NO_3)_2$	light peach	flat, round, smooth
Ruthenium Bipyridyl (II) Complex	0.01M $[Ru(bpy)_3]Cl_2$	bright orange	flat, round, thick

Hectorite exchanges with the less stable iron and copper cations was unsuccessful because the copper(I) chloride oxidized and did not dissolve. The iron(II) sulfate was also insoluble in deionized water.

Preliminary Aniline Exposure Studies

Various aniline exposure experiments showed that aniline oxidizes on all of the transition-metal exchanged hectorite films. This is obvious because the films become darker due to the black oxidized aniline on their surfaces. However, widely differing amounts of aniline oxidize on the surfaces of films synthesized from different cations. Longer exposures to aniline tend to increase the amount of aniline oxidized on the film surface, although some oxidation occurs under ambient conditions following the aniline exposure.

Initial studies of copper(II)-exchanged hectorite films exposed to aniline and aniline derivatives showed that different aniline derivatives oxidized on the hectorite films at different rates. All of the copper(II) hectorite films were initially the same light blue-green color. The oxidation of aniline and aniline derivatives on a film surface was accompanied by the formation of a dark organic coating on the film surface. Table 2 shows that in these initial studies, aniline vapor did not always turn the film black within the same period of time. There is a definite difference between the relatively short time required for aniline and o-bromoaniline vapor to give the hectorite film a dark coat, and the longer time required for 3,5-dimethylaniline to turn the same type of film darker.

Table 2. Copper(II) hectorite film appearance following exposure to aniline and aniline derivatives.

Organic Monomer	**Time Film Exposed**	**Appearance Afterward**
Aniline	1 day	Black
Aniline	1 day	Dark Brown
o-Bromoaniline	1 day	Black
3,5-Dimethylaniline	1 day	No change
3,5-Dimethylaniline	8 days	Dark

A study of aniline oxidation on copper(II) hectorite films over time showed that the films became gradually darker while inside the beaker with aniline, indicating a gradual process of oxidation as more aniline vapor was deposited on the film. An interesting note is that those films left in the beaker with aniline for only one hour before being placed under ambient conditions exhibited more oxidation after four hours than those films remaining in the aniline vapor for the entire four hours. This indicates one of two possible results: the amount of aniline deposited on a film per hour is a variable, and the film that was removed from the aniline vapor after one hour happened to have more aniline on its surface than the others, or that oxidation in air, where there is presumably more oxygen, is a faster process than oxidation in the container with aniline vapor. Table 3 tabulates the results of the timed aniline oxidation study.

Table 3. Appearance of copper(II) hectorite films following timed exposure to aniline.

Time Exposed to Aniline	**Film Appearance**
1 hour	slightly dark
2 hours	slightly darker than 1hr
3 hours	dark tan
4 hours	dark tan
1 hour + 3 hours ambient	nearly black

A third study compared the effects of exposing cobalt(II), nickel(II), copper(II) and zinc(II) hectorite films to aniline vapor for six days. The nickel(II) films were made from two different cation solutions, $Ni(NO_3)_2$ (aq) and $NiSO_4$(aq). Aniline oxidation on each of the different cation-exchanged films resulted in a different film shade or color, but the exposure of nickel(II) films made from different counter anions to aniline gave the same final appearance. Table 4 gives the appearances of the different films before and after exposure to aniline vapor.

This study shows that the counter anions were fully washed out of the solution-hectorite mixtures before the films were poured and therefore do not affect the oxidation of aniline on the subsequent cation-exchanged films. On the other hand, this study shows the powerful effect of the transition-metal cation on the oxidation of aniline on the film surface.

The zinc(II) hectorite film did not oxidize aniline at all during the six day study. The yellow color on its surface is neutral aniline deposited there. The nickel(II) and cobalt(II) hectorite films exhibited intermediate amounts of aniline oxidation and the copper(II) hectorite film induced a large amount of aniline oxidation.

Table 4. Appearances of various cation-exchanged hectorite films before and immediately following a six-day exposure to aniline vapor.

Cation	Exchange Solution	Appearance Before Exposure	Appearance After Exposure
Cobalt(II)	0.5M $CoCl_2$	light pink	dark purple
Nickel(II)	0.5M $Ni(NO_3)_2$	light yellow	green
Nickel(II)	0.5M $NiSO_4$	light yellow	green
Copper(II)	0.5M $CuSO_4$	light green	black
Zinc(II)	0.5M $ZnSO_4$	white	yellow

Upon threat of complete and utter laboratory boredom, some random studies were completed. From these studies, three facts have come to light: 1. a copper(II) hectorite film placed in deionized water for eight hours experiences no readily visible structure changes, 2. a copper(II) hectorite film sunk into liquid aniline for eight hours turns completely black but seems otherwise unaffected, and 3. if a lousy hectorite film is crushed with a mortar and pestle in deionized water and repoured, the result is no film at all.

Comparative Aniline Polymerization Study

In order to assess the relationship between the transition-metal cation reduction potential and the rate of aniline polymerization on the surface or in the intergallery regions of the hectorite films, one sample hectorite film from each of the transition-metal cation exchanged series from vanadyl(II) to zinc(II) was exposed to aniline for 72 hours. The films were studied in three ways: visually, with infrared spectroscopy and by X-ray diffraction.

Changes in the film appearance and rigidity were recorded after 24 hours and after 72 hours of exposure to aniline vapor. The color of all of the films changed. Except for the nickel(II) and zinc(II) films, which gained yellow color, all of the hectorite films became darker within 72 hours. This shows that aniline oxidation was occurring while the films were under aniline vapor. From the differences in the extent of the color change, one can estimate on which transition metal cation film the most aniline oxidation occurs. The stiffness of the films was more difficult to judge, which made the stiffness data erratic. Table 5 shows the changes that aniline exposure made in the appearance of each of the series of cation-exchanged hectorite films.

Table 5. Comparison of visible changes in transition-metal cation exchanged hectorite films following 24-hour and 72-hour aniline vapor exposure. On the far right are numbers from 1 to 8 estimating least to most aniline oxidation.

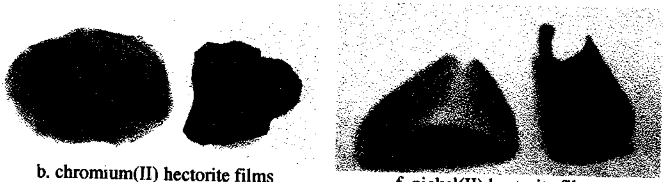
Cation	**Film Before Aniline Exposure**	**Film After 24-Hr Aniline Exposure**	**Film After 72-Hr Aniline Exposure**	
Vanadyl(II)	dark, dark green	bit darker same texture	nearly black little stiffer	8
Chromium(III)	gray	lighter slightly stiffer	green-gray slightly stiffer	3
Manganese(II)	light yellow-pink	much darker same texture	dark tan-brown-gray much stiffer	5
Iron(III)	orange	much darker stiffer	darker orange same stiffness	6
Cobalt(II)	light pink	edges a little yellowed slightly stiffer	dark pink slightly stiffer	4
Nickel(II)	light yellow	little darker stiffer	light yellow-green same stiffness	2
Copper(II)	light green	much, much darker same texture	dark, dark brown stiffer	7
Zinc(II)	light, light pink	barely darker stiffer	slightly yellow stiffer	1

Digital photographs taken of the films before and after exposure to aniline are shown in Figure 5 on the following page. The pictures convey an idea of differences in roundness and smoothness among films from the different transition metal cations and of the difference between the same film before and after aniline exposure.

In six months under ambient conditions, all of the hectorite films lost some water from their intergallery regions. This is shown by the decreased d-spacing in films after several months and by the tendency of films to curl and crack over time. Films with aniline on their surfaces experienced further polymerization, evident from their infrared spectra. Films coated with aniline also tended to better resist curling and cracking.

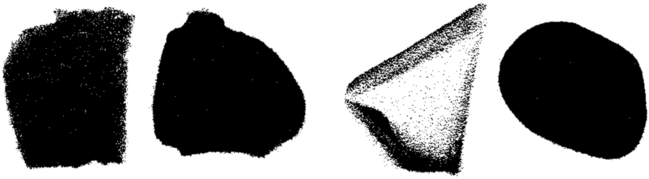
a. vanadyl(II) hectorite films

e. cobalt(II) hectorite films



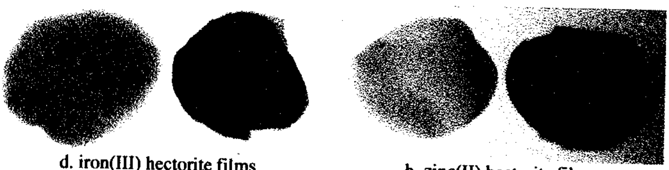
b. chromium(II) hectorite films

f. nickel(II) hectorite films



c. manganese(II) hectorite films

g. copper(II) hectorite films



d. iron(III) hectorite films

h. zinc(II) hectorite films

Figure 5. Transition-metal exchanged hectorite films. In each picture, the film shown on the left is the original appearance of the film. The film shown on the right has been exposed to aniline. All of the films are approximately six months old.

The colors and textures of the films also changed in other subtle ways. Table 6 lists the macroscopic changes that occurred over six months in the cation-exchanged films coated with aniline. The films that had not been exposed to aniline stayed their original color, but became slightly darker due to organic chemicals in the laboratory air oxidizing on the surfaces. Films with a coat of aniline experienced both color and texture changes. All of the aniline-coated films became darker, a few acquired shine, and most became stiffer over time compared with films not coated with aniline.

Table 6. Changes in hectorite films following 72 hours of aniline exposure and 6 months of ambient conditions. Comparisons are made to films not exposed to aniline but under ambient conditions for the same time period, in both cases. Where "curled" or "flat" is noted, the film not exposed to aniline did the opposite.

T.M. Cation	**Film Appearance**		
	Original Color	**72-hr Aniline**	**6 mo. Ambient**
Vanadyl(II)	dark, dark green	nearly black little stiffer	much darker, less flexible, smooth + rough sides
Chromium(III)	gray	green-gray slightly stiffer	brown, not flexible, smooth + rough sides
Manganese(II)	light yellow-pink	dark tan-brown-gray much stiffer	dark brown, less brittle, flatter
Iron(III)	orange	darker orange same stiffness	dark, dark brown, smooth + rough sides, less flexible
Cobalt(II)	light pink	dark pink slightly stiffer	shiny dark magenta, curled
Nickel(II)	light yellow	light yellow-green same stiffness	orange- brown, a little flexible, curled
Copper(II)	light green	dark, dark brown stiffer	black, not flexible, flat
Zinc(II)	light, light pink	slightly yellow stiffer	orange- brown, less flexible, smooth + rough sides

Changes in the hectorite films were also monitored by infrared spectroscopy and by X-ray diffraction, the results of which are shown in the following sections, under their respective technique.

Preliminary Infrared Spectroscopy Studies

Preliminary IR spectra showed that the presence of aniline on the surface of copper(II) hectorite films can be detected by infrared spectroscopy. The infrared spectra taken appear in Appendix A. As the infrared transmittance spectrum of a copper(II) hectorite film shows (Figure A1), the strong infrared absorption peaks from water at 3000 - 3600cm^{-1} and from silicate[14] at 1050cm^{-1} render much of the infrared spectrum useless for analysis. However, the important part of the spectrum for determining aniline deposition and polymerization occurs in a readable portion of the spectrum, from 1200 to 1800cm^{-1}. The infrared absorbance spectrum of aniline is shown in Figure A2. Table 7 summarizes the important infrared stretching bands seen in the hectorite films and in aniline and polyaniline.

Table 7. IR-active normal modes of hectorite clays, aniline and polyaniline.

Material	Normal Mode	Infrared Frequency
Hectorite Clay[14]	Si - O stretch	1020 cm^{-1}
	unknown	1450 cm^{-1}
	H-O-H bend	1630 cm^{-1}
	H-O-H stretch	3000-3500 cm^{-1}
	clay -OH stretch	3679 cm^{-1}
Aniline	C-N stretch	1280 cm^{-1}
	H-N-H bend	1460 cm^{-1}
	ring stretch	1495 cm^{-1}
	ring strech	1600 cm^{-1}
	C=C stretch	1630 cm^{-1}
Polyaniline[15]	C-N-C stretch	1290 cm^{-1}
	unknown	1445 cm^{-1}
	ring stretch	1495 cm^{-1}
	ring strech	1565 cm^{-1}
	C=C stretch	1590 cm^{-1}

Note that the C-N stretching frequency in aniline occurs at 1280cm^{-1}, while the corresponding C-N-C stretching peak in polyaniline occurs at 1290cm^{-1}. As Figure 2 shows, aniline contains only C-N bonds, while the polyaniline chain contains C-N-C bonds. Therefore, this small frequency shift is used to confirm aniline polymerization.

We used the portion of the infrared spectrum from 1200 to 1800cm^{-1} for analysis of the film and of surface aniline deposition and polymerization. Figures A3 and A4 are IR spectra of copper(II) hectorite films. The film in Figure A3 was exposed only to ambient conditions, while the film in Figure A4 was exposed to aniline vapor for 18 hours and left under ambient conditions for 3 days before the spectrum was taken. Both spectra contain the peaks at 1450 and 1630cm^{-1} from the host copper(II) hectorite film; Figure A4 also contains peaks near 1280 and 1500cm^{-1} owing to aniline deposited on the film.

An attempt was made to study the aniline deposited on the surface of the film separately from the aniline that may have entered the intergallery regions of the film by taking IR spectra with the Multiple Internal Reflectance Accessory (MIRA). Since this reflects the IR beam off the surface of the sample studied, the result would be an infrared spectrum of only the surface material. As Figure A5 shows, the fates were against us. This spectrum of a copper(II) hectorite film exhibits the high noise in the 1200 to 1800cm^{-1} region of the spectrum. Figures A6 and A7 are the infrared spectra of a copper(II) hectorite film not exposed to aniline and a film exposed to aniline, respectively. Both were taken with the MIRA, and it is obvious that these spectra contain no data of analytical value.

The noise observed in the reflected infrared spectra may be due to poor surface contact between the totally reflecting crystal of the Multiple Internal Reflectance Accessory and the textured film surface. While working with the MIRA, we did learn that purging the IR for five to fifteen minutes before taking both the background spectrum and the sample spectrum, significantly improved the signal-to-noise ratio of the sample spectrum.

For comparison purposes, all further infrared spectra were taken in absorbance mode, and the 1200 to 1800cm^{-1} region of each spectrum is displayed. Figures A8 and A9 are the infrared absorbance spectra of pure aniline monomer and of the emeraldine form of polyaniline, respectively. Table 8 lists the wavenumbers at which peaks were found in each. These were used to determine whether aniline deposited on the films was detectable by IR and whether the aniline had polymerized.

Table 8. Aniline and emeraldine polyaniline infrared spectral peaks.

Aniline		**Polyaniline**	
C-N stretch	1280 cm^{-1}	C-N-C stretch	1290 cm^{-1}
H-N-H bend	1460 cm^{-1}	unknown	1445 cm^{-1}
ring stretch	1495 cm^{-1}	ring stretch	1495 cm^{-1}
ring strech	1600 cm^{-1}	ring strech	1565 cm^{-1}
C=C stretch	1630 cm^{-1}	C=C stretch	1590 cm^{-1}

All of the peaks that appear in the infrared spectrum of aniline have a complement in the infrared spectrum of the emeraldine form of polyaniline, but the absorption frequencies have shifted in polyaniline to account for the heavier connecting chains in polyaniline. The peaks also tended to broaden, mostly due to the interacting chains of the solid polyaniline, compared to the freely rotating monomers in the liquid aniline.

In an attempt to drive aniline monomer into the intergallery regions of hectorite, one copper(II) hectorite film was exposed to aniline under vacuum for a week and another was gradually heated to 200°C. The heat did not appear to affect the copper(II) film or the aniline coating the film surface. IR spectra were taken of the film exposed to aniline under vacuum before and after the aniline exposure, as shown in Figures A10 and A11. An IR was taken of the heated film only after aniline exposure and subsequent heating (Figure A12). This IR exhibits only hectorite peaks, despite the massive amount of black aniline deposited on the film surface. They may be buried beneath the absorbance of a thick hectorite film. Figure A13 is the infrared spectrum of a copper(II) hectorite film that had been soaked in liquid aniline for several months and left under ambient conditions for a few months. As Figure A13 shows, the film exhibits sharp peaks at 1495 and 1600cm^{-1} characteristic of the aniline monomer and the peak at 1290cm^{-1} characteristic of the polymer.

Timed Aniline Oxidation and Polymerization Studies

The next study showed that the deposition of aniline on the surface of a copper(II) hectorite film over time could be followed qualitatively with infrared spectroscopy. Figure A14 is the infrared spectrum of a copper(II) hectorite film, showing the peaks from to the film at 1450 and 1630cm^{-1}. Figure A15 is the infrared spectrum of the same film after having been exposed to aniline vapor for one hour. Additional peaks at 1300, 1490 and 1530cm^{-1} indicate the presence of aniline on the film. As Figure A16, the infrared spectrum of the film after four hours of exposure to aniline shows, the absorbance of the aniline peaks increases with respect to the absorbance of the film peaks, over time. Additional peaks at 1580 and 1600cm^{-1} from the aniline also begin to appear. This is IR verification that more aniline is deposited on the film surface over longer exposure to aniline.

A later, longer study to observe IR evidence of aniline deposition and polymerization had slightly different results. Figures A17 through A25 are the infrared spectra taken of a copper(II) hectorite film before exposure to aniline and after a half-hour, one, two, three, four, five, six and seven-hour exposures, respectively. Unlike the previous study, the only apparent change over the seven hours was the growth of one sharp peak at 1495cm^{-1}, corresponding to the strongest peak in both aniline and polyaniline. The strong absorbance of the copper(II) hectorite film may be covering other aniline peaks.

Infrared spectra taken of the same film after it had been exposed to aniline for two weeks and three weeks (Figures A26 and A27, perspectively) contain peaks at 1300 and 1320cm^{-1}, and around 1520cm^{-1}, in addition to the aniline peak at 1495cm^{-1} and the host peaks. This shows that more aniline was being deposited on the film. After the film was removed from the beaker with aniline, infrared spectra were taken of the same film after 3 weeks, after 11 weeks and following 17 weeks of ambient conditions (Figures A28 through A30). In the spectrum taken after 11 weeks of ambient conditions, the sharp ring stretching peak at 1495cm^{-1} has decreased and broadened and the peak at 1300cm^{-1} has changed to a shoulder at 1295cm^{-1}. The decrease in sharp, aniline monomer-like peaks and frequency shift in the peak at 1280cm^{-1} suggest that some polymerization has occurred. There are no obvious changes between the spectra taken after 11 and 17 weeks of ambient conditions.

IR Comparison of Transition-Metal Exchanged Films

In order to accomplish a more quantitative comparison of aniline deposition and polymerization on hectorite films made from different transition metal cations, infrared spectra were taken of films made with each transition metal cation before exposure to aniline and after a 24-hour aniline exposure. Additional infrared spectra were taken of the same films at the end of 2 further days of aniline exposure and 5 months of ambient conditions. At that time, infrared specra were also taken of a second transition-metal cation exchanged film that had only experienced six months of ambient conditions, to check for any changes in the film structure apparent under infrared analysis. The transition metal cations compared were vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II).

Figures A31 through A62 are the infrared spectra of the transition-metal cation exchanged hectorite films before and after exposure to aniline and following six months of ambient conditions. All of the hectorite films that had aged for six months exhibited two broad peaks near 1640 and 1450cm^{-1}. Most of the films exhibited both these peaks before the six months of ambient conditions, but the 1450cm^{-1} peak was missing from infrared spectra of the vanadyl(II)-, iron(III)- and nickel(II)-exchanged films acquired before aging. Table 9 on the following page summarizes the infrared absorption frequencies of each film. Upon exposure to aniline, the C-N aniline stretching peak at 1280cm^{-1} appears in IR of most of the hectorite films, but is shifted to lower frequencies. This may reflect hydrogen bonding between the nitrogen of aniline and silicate hydroxyl groups of the clay[3] (see Figure 1). It is interesting to note that the aniline C-N stretching peak in only the vanadyl(II)-, iron(III)- and copper(II)-exchanged films exhibited a shift toward higher frequencies. As the emeraldine form of polyaniline exhibits a C-N-C stretching peak at 1290cm^{-1} (see Table 8), this shift toward 1290cm^{-1} may correspond with the faster polymerization of aniline on their surfaces.

As the films with aniline coating on their surfaces aged, a noticable trend was the disappearance of all the sharp aniline monomer peaks. This is noted on in Table 9 by their burial beneath the peaks that characterize the hectorite clay. As the IR spectrum of the emeraldine form of polyaniline shows, the polymer exhibits wider IR peaks because of the many varying bonds in its solid form. This same widening and shortening of aniline monomer peaks on the hectorite films may indicate linking of aniline monomers as well as the linking of aniline to the film surface.

Table 9. IR absorption frequencies of hectorite films before and following a 24-hour aniline exposure and 5 months of ambient conditions.

		Film Peaks		Aniline Peaks				
T. M. Cation	**Film**	1640 cm^{-1}	1450 cm^{-1}	1630 cm^{-1}	1600 cm^{-1}	1495 cm^{-1}	1470 cm^{-1}	1280 cm^{-1}
		H-O-H	unk.	C=C	ring	ring	H-N-H	C-N
Vanadyl(II)	Original	X						
	Aniline	X		B	X	X	X	SU
	6 Months	X	X					
	Aniline + 5mo#							
Chromium(III)	Original	X	X					
	Aniline	B	X	B	B	X	X	SD
	6 Months	X	X					
	Aniline + 5mo	X	X	B	B	X	B	B
Manganese(II)	Original	X	X					
	Aniline	B	B	X	X	X	X	SD
	6 Months	X	X					
	Aniline + 5mo	X	X	B	B	B	B	B
Iron(III)	Original	X						
	Aniline	B		X	X	X	X	SU
	6 Months	X	X					
	Aniline + 5mo*	X	X	B	X	B	X	X
Cobalt(II)	Original	X	X					
	Aniline	X	X	X	X	X	X	SD
	6 Months	X	X					
	Aniline + 5mo	X	X	B	B	B	B	B
Nickel(II)	Original	X						
	Aniline	B	B	X	X	X	X	SD
	6 Months	X	X					
	Aniline + 5mo	X	X	B	B	B	B	B
Copper(II)	Original*	X	X					
	Aniline	X	X	B	X	X	B	SU
	6 Months*	X	X					
	Aniline + 5mo	X	X	B	X	X	B	X
Zinc(II)	Original	X	X					
	Aniline	X	X	X	X	X	X	SD
	6 Months	X	X					
	Aniline + 5mo	X	X	B	B	B	B	B

Symbols: [blank] = no peak appears, X = peak appears, B = peak does not appear, wide peaks in the same region may hide peak, SU = shifted to higher wavenumbers than aniline peak, SD = shifted to lower wavenumbers than aniline peak, * = extra peaks appear, # = too low S/N to analyze.

X-Ray Diffraction Studies

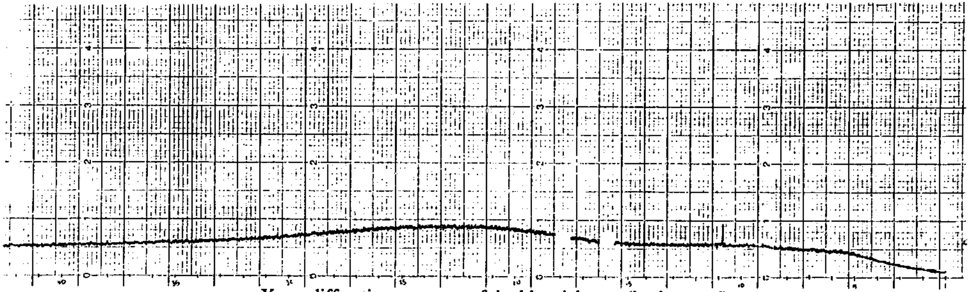
X-ray diffraction spectra were taken of hectorite films made with each of the transition metal cations, and of a copper(II) hectorite film that had been exposed to aniline. The X-ray diffraction spectra of cation-exchanged hectorite films all exhibit two broad peaks near 7° 2θ and 33° 2θ representing the (001) and (004) planes, respectively. This shows that the films consist of two-dimensional layers, and that all of the layers are oriented in the same direction, but that the layer thicknesses vary over the peak width. A control spectrum of double-stick tape gave no significant peaks. Figure 5 shows a typical X-ray diffraction spectrum of a copper(II) hectorite film and the double-stick tape control spectrum.

Preliminary studies using copper(II) hectorite films made from 1.0M $CuSO_4$ solutions showed that there was no significant difference between the d-spacings of copper(II) hectorite films left under ambient conditions and those exposed to aniline for about 4 hours at room temperature and pressure. Table 10 gives the placement of the (001) peaks and the subsequent d-spacings calculated, for two copper(II) hectorite films, one exposed to aniline and the other unexposed. Spectra taken of the same films on two different days show the slight variations in d-spacings that occur with changes in humidity.

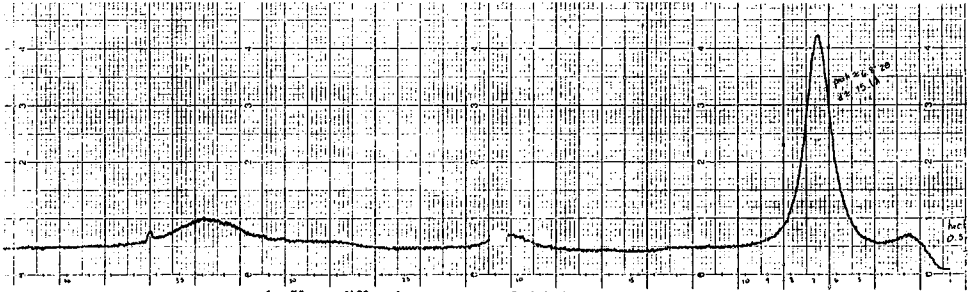
Table 10. d-spacings of copper(II) hectorite films.

Exchange Soln	Aniline Exposure?	Day	Peak	d-Spacing
1.0M $CuSO_4$	No	Day 1	7.25 °2θ	14.0 Å
1.0M $CuSO_4$	No	Day 2	6.90 °2θ	14.9 Å
1.0M $CuSO_4$	Yes	Day 1	7.20 °2θ	14.2 Å
1.0M $CuSO_4$	Yes	Day 2	6.90 °2θ	14.9 Å
0.5M $CuSO_4$	No	Day 3	7.5 °2θ	13.7 Å
0.5M $CuSO_4$	Yes	Day 4	7.4 °2θ	13.9 Å

The lack of a significant difference between d-spacings of films exposed to aniline vapor and films not exposed, shows that aniline does not intercalate between the layers of copper(II) hectorite films at room temperature and pressure. About the same results were



a. X-ray diffraction spectrum of double-stick tape (background).



b. X-ray diffraction spectrum of nickel(II) hectorite film.

Figure 6. Typical X-ray diffraction spectra.

obtained later with a copper(II)-exchanged hectorite film made from a 0.5M $CuSO_4$ exchange solution, exposed to aniline vapor for 5 hours and left under ambient conditions for 5 days before the XRD spectrum was taken.

X-ray diffraction spectra taken of hectorite films exchanged with each of the transition-metal cations showed that all of the films have about the same d-spacing, which is around 15Å. Different exchange solution concentrations between 0.1M and 1.0M do not affect the d-spacing, either. Table 11 summarizes the d-spacings calculated from XRD of each transition-metal exchanged film.

Table 11. d-spacings of transition-metal exchanged hectorite films. The solution from which the film was synthesized is listed.

T.M. Cation	**Cation Solution**	**Peak**	**d-Spacing**
Vanadyl(II)	0.1M $VOSO_4$	6.7 °2θ	15.3 Å
Chromium(III)	0.1M $CrCl_3$	6.4 °2θ	16.0 Å
	0.5M $CrCl_3$	6.5 °2θ	15.8 Å
Manganese(II)	0.5M $MnSO_4$	6.7 °2θ	15.3 Å
Iron(III)	0.5M $Fe(NO_3)_3$	6.8 °2θ	15.1 Å
	0.5M $FeCl_3$	6.9 °2θ	14.9 Å
Cobalt(II)	0.5M $CoCl_2$	6.7 °2θ	15.3 Å
Nickel(II)	0.5M $Ni(NO_3)_2$	6.8 °2θ	15.1 Å
	0.5M $NiSO_4$	6.8 °2θ	15.1 Å
Copper(II)	0.5M $CuSO_4$	7.2 °2θ	14.2 Å
	0.5M $CuSO_4$	7.5 °2θ	13.7 Å
Zinc(II)	0.5M $ZnSO_4$	6.6 °2θ	15.5 Å

In order to examine the effects of atmospheric water vapor on d-spacing, a copper(II) hectorite film was split into two pieces. Each piece was attached to a glass XRD plate. Five drops of water were placed on one piece, and ten drops of water were placed on the other. It was assumed that all of the water would be absorbed into the intergallery regions of the films. An X-ray diffraction spectrum was taken of each immediately after all of the water on that film piece was absorbed. As Table 12 shows, both pieces of film had the same d-spacing. It is probable that most of the water evaporated, instead of being absorbed by the film.

Table 12. d-spacings of copper(II) hectorite films soaked with water.

Amount of Water	Peak	D-Spacing
5 drops	7.2 °2θ	14.3 Å
10 drops	7.2 °2θ	14.3 Å

X-ray diffraction spectra were taken of two copper(II) hectorite films: one had been exposed to aniline for three days, and both had been left under ambient conditions for ten months. X-ray spectra were also taken of copper(II) hectorite films that had been exposed to aniline under a vacuum for one week, and of a copper(II) hectorite film that had been exposed to aniline and then heated above 200°C. Table 13 compares the d-spacings of copper(II) hectorite films before and after aging, after aniline exposure, and after aniline exposure under vacuum and heated conditions.

Table 13. Comparison of d-spacings in copper(II) hectorite films under various conditions.

Copper(II) Hectorite Film Conditions	Age	Peak	d-spacing
Ambient	1 month	7.5 °2θ	13.7 Å
Exposed to aniline 3 days	1 month	7.4 °2θ	13.9 Å
Ambient	10 months	8.6 °2θ	11.9 Å
Exposed to aniline 3 days	10 months	7.9 °2θ	13.0 Å
Exposed to aniline 1 week under vacuum	10 months	7.0 °2θ	14.6 Å
Exposed to aniline, later heated	10 months	8.2 °2θ	12.5 Å

The smaller d-spacings measured for films that had aged (11.9Å aged vs. 13.7Å new) is an indication that water evaporated from the intergallery regions over time. The slightly larger d-spacing in the aged film coated with aniline than the aged film unexposed to aniline (13.0Å with aniline vs. 11.9Å without) may indicate that the coating of aniline on the film surface prevented some drying. The 2.5Å difference in d-spacing between the aged film that had experienced only ambient conditions and the aged film that had been exposed to aniline under a vacuum leaves open the possibility that aniline entered the intergallery regions of the film exposed to aniline vapor under a vacuum. Aniline on the copper(II) hectorite film that was heated to 200°C obviously did not move into the intergallery regions.

4. DISCUSSION

Film Synthesis

First row transition-metal exchanged hectorite films were repeatedly and successfully synthesized from the vanadyl(II), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) transition metal cation solutions. The syntheses of sodium hectorite and ruthenium bipyridyl films were less successful. The ruthenium bipyridyl complex inhibited the formation of a smooth hectorite film on most of the synthesis attempts. The successfully synthesized sodium hectorite films were of poor quality. This shows that the intrinsic differences between transition metal cations and the smaller Group I cations affect the hectorite texture and composition differently.

There were also major differences in the quality and ease of production of hectorite films exchanged with the different transition metal cations. The iron(III), copper(II) and zinc(II) hectorite films were particularly easy to produce and of good quality (flat and uniform), while the vanadyl(II), chromium(III) and manganese(II) hectorite films were notoriously difficult to produce and of lower quality. While different cations have different exchange capacities, it appears that cations with low size-to-charge ratios are good candidates for synthesizing a cation-exchanged hectorite film. Synthesis of cation-exchanged hectorite films from second- or third-row transition-metal cations could be used to further explore the effect of the cation size, charge and valency on hectorite film synthesis.

It also became apparent that experimental technique is important in successful film synthesis. For the iron(III) hectorite films in particular, it appeared that the hectorite sediment settled to the bottom of the plastic weigh dish almost immediately upon pouring the hectorite/solution mixture, and that disturbing this layer of sediment was detrimental to final film quality. It also appeared that allowing the transition-metal cations to exchange with the hectorite clay for at least five days enhanced the final film quality.

Although copper(II) hectorite films were successfully synthesized from 1.0M exchange solutions of the copper(II) cation, other cations required lower molarity exchange solutions. For vanadyl(II) and chromium(II), 0.10M cation exchange solutions worked best, while 0.50M exchange solutions of the other transition metal cations resulted in decent-looking hectorite films. For the synthesis of a film containing the ruthenium bipyridyl complex, 0.001M and 0.0001M exchange solutions were far too dilute, but much care and luck were necessary to make a hectorite film from the 0.01M cation exchange solution.

Preliminary Aniline Exposure Studies

The initial exposures of cation-exchanged hectorite films to the vapor of aniline and aniline derivatives showed that the amount of organic material oxidized on the film surface depended on the transition metal cation, the organic monomer in question and the amount of time that the film was exposed to organic vapor.

Although one would expect that organic monomers with lower boiling points and therefore with higher vapor pressures would deposit more monomer on the surface of a copper(II) hectorite film, Table 14 shows that there is no apparent trend relating higher vapor pressure to more monomer oxidation on the film surface. This simple experiment shows that the oxidation potential of the particular organic monomer and therefore the structure of the molecule in question is as important or more important in determining the amount of organic oxidized on the film surface than the vapor pressure of the molecule. Further experiments with more aniline derivatives are necessary to confirm any trends shown.

Table 14. Comparison of organic monomer vapor pressure with copper(II) hectorite film appearance following exposure to monomer. Exposure to vapor lasted 24 hours.

Organic Monomer	Boiling Point[16]	Vapor Pressure	Film Appearance
3,5-Dimethylaniline	105°C	highest	no change
Aniline	184°C	medium	dark brown
o-Bromoaniline	229°C	lowest	black

From the first timed aniline exposure experiment (Table 3) and the 3,5-dimethylaniline exposure (Table 2), it is apparent that leaving a film over aniline or aniline derivative vapor for a longer period of time leads to more aniline oxidation on the film surface. The rapid oxidation of aniline under ambient conditions suggests that ambient oxygen also oxidizes aniline. The range of colors observed in hectorite films of different transition metal cations after exposing them to aniline for the same period of time (Tables 7 and 8) is due partly to the different colors of the underlying film and due partly to the different amounts of aniline that oxidizes on the surface of each film.

Exposing zinc(II), nickel(II), cobalt(II) and chromium(III) hectorite films to aniline for 24 hours caused the films to turn yellow. Aniline oxidation, accompanied by a change to a darker film surface color, eventually did occur on all of the transition-metal cation exchanged films. The dark color observed upon oxidation of aniline is indicative of mixed aniline oxidation states. The various colors initially observed on the various films after a 24-hour aniline exposure indicate either alternative aniline oxidation states or the aniline monomer. Further work is required to achieve pure conducting emeraldine polyaniline.

Comparative Aniline Polymerization Study

Some changes in hectorite film character upon exposure of the film to aniline were common to all of the transition-metal exchanged hectorite films. After 72 hours under aniline vapor, most of the films became darker and stiffer. After five months of ambient conditions, the films that had been exposed to aniline remained flatter and cracked less over time, while films not exposed to aniline curled and cracked. This is probably due to less water loss from those films coated with aniline. A few of the films that were exposed to aniline exhibited a shiny surface after five months; a shiny polymer is consistent with the conducting form of polyaniline useful for batteries and small electrical applications.

The comparative study shows that the rate of aniline oxidation on a film is controlled by the reduction potential of the cation exchanged into the film. In Table 5, the transition-metal cation exchanged films are ranked from least (1) to most (8) aniline oxidation occurring within 72 hours of exposure to aniline. As Table 15 shows, these rankings generally coincide with increasing reduction potential of the transition metal cation.

Table 15. Aniline oxidation compared to cation standard reduction potential. Rank is order from least to most aniline oxidation on film surface, from table 5.

Rank	Reduction	E°_{red}
1	$Zn^{2+} + 2e^- \rightarrow Zn$	- 0.762 V
2	$Ni^{2+} + 2e^- \rightarrow Ni$	- 0.257 V
3	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	- 0.424 V
4	$Co^{2+} + 2e^- \rightarrow Co$	- 0.282 V
5	$Mn^{2+} + 2e^- \rightarrow Mn$	- 1.180 V
6	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+ 0.771 V
7	$Cu^{2+} + e^- \rightarrow Cu^+$	+ 0.159 V
8	$VO_2^+ + e^- \rightarrow VO^{2+}$	+ 1.000 V

Although the trend is not perfect, it is apparent that the reduction potential of the cation influences the rate of aniline oxidation. Cations with more positive reduction potentials correspond to more initial aniline oxidation on the film surface. This evidence supports previous work by Porter et al. showing that the oxidation of aniline to a radical cation is the first step in polymerization[8], as shown in Figure 2. Imperfection in the trend of more positive reduction potential leading to more aniline polymerization is due partly to the lack of control over the number of transition-metal cations that exchange for sodium ions in the hectorite intergallery regions. Since each cation has a different exchange capacity in the hectorite clay and the redox reaction is occurring on a surface, not in a 1.0M solution, the E°_{red} of the cation is only an approximation of the reduction potential of the corresponding hectorite film.

Infrared Spectroscopy Studies

The first infrared spectroscopy studies showed simply that the presence of aniline on the surface of a copper(II)hectorite film could be detected by transmittance infrared spectroscopy with useful resolution. The signal-to-noise ratio in the infrared spectra taken with the Multiple Internal Reflectance Accessory was so high that one could not tell whether aniline existed on the surface of the copper(II) hectorite film. This signal-to-noise ration was probably due to low surface contact between the textured film and the flat reflecting crystal of the accessory.

In the second timed study of the deposition of aniline on a copper(II)hectorite film (Figures A16-A29), the final infrared spectrum of the film after exposure to aniline and 17 weeks of ambient conditions (Figure A29), exhibited shorter, broader peaks from the aniline than existed just after the film had been removed from aniline vapor (Figure A26). It is apparent from the IR spectra of aniline and of polyaniline that polyaniline exhibits much shorter and broader infrared peaks, due to the many molecular interactions in the solid form. This same shortening and broadening of aniline IR peaks on the hectorite film surface suggests extra interactions among aniline molecules and between aniline and the film. It is possible that the differences in aniline peaks between Figures A26 and A29 represent the beginning steps of aniline polymerization on the hectorite film surface.

Further evidence for delayed polymerization of aniline comes from infrared spectra taken in the comparative aniline polymerization study. Sharp aniline stretching peaks are visible in all of the IR spectra taken of the different transition-metal exchanged hectorite films immediately after the 24-hour exposure to aniline. Infrared spectra taken following five months of ambient conditions show that these peaks have shortened, broadened and, for most of the films, disappeared beneath the infrared absorbance of the film itself. Table 16 gives the films for which the sharp aniline peaks at 1495 and 1600cm^{-1} have disappeared after six months of ambient conditions. The signal-to-noise ratio of the vanadyl-exchanged film was too high to extract any meaningful data.

Additional evidence for aniline polymerization comes from the C-N-C stretching peak that occurs at 1290cm^{-1} in the emeraldine form of polyaniline. In the infrared spectrum of the copper(II)hectorite film exposed to aniline and left under ambient conditions for six months, the peak at 1290cm^{-1} grew significantly. This probably

Table 16. Disappearance of aniline IR peaks at 1495 and 1600cm^{-1} and appearance of emeraldine polyaniline peak.

Rank	T.M. in Film	Aniline Disappears	C-N-C Peak Appears	
			24 hrs aniline	5 mo. ambient
1	Zinc(II)	yes	no	no
2	Nickel(II)	yes	no	no
3	Chromium(III)	no	no	no
4	Cobalt(II)	yes	no	no
5	Manganese(II)	yes	no	no
6	Iron(III)	yes	yes	no
7	Copper(II)	yes	yes	yes
8	Vanadyl(II)	cannot tell	yes	low S/N

indicates sufficient emeraldine form of the aniline polymer on the copper(II) hectorite film to make the peak visible. For the vanadyl(II) hectorite film, the IR peak at 1290cm^{-1} appeared immediately following the 24-hour exposure to aniline, suggesting that the vanadyl cation was a strong enough oxidizing agent to catalyze significant polymerization in a short period of time. For the iron(III) hectorite film, there is a shoulder at 1290cm^{-1} on the IR spectrum taken after the 24-hour aniline exposure, also suggesting swift aniline polymerization. This shoulder is not apparent following 5 months of ambient conditions.

The C-N-C stretching peak does not appear in IR spectra taken of the other hectorite films. This may be due to the fact that the cations in the other IR films had negative reduction potentials, making the films unable to oxidize sufficient aniline to drive the polymerization reaction far forward. Infrared absorption by the hectorite film may also cover small polyaniline absorption peaks on films exchanged with transition-metal cations having negative reduction potentials.

On most of the films, the aniline C-N stretching peak at 1280cm^{-1} shifted to lower frequencies. According to Giannelis et al., hydrogen bonding is one of the intermolecular forces that holds organic polymers in the intergallery regions of hectorite clay[3]. This may be extrapolated to assume that the clay surface also contains hydroxyl groups bound to the silicate layers. These hydroxyl groups can also hydrogen bond to the nitogen of aniline, shifting the C-N stretching peak to slightly lower frequencies from the additional weight of the attachment of nitrogen to hydrogen.

We have so far studied only the emeraldine, or most basic form, of polyaniline. It is possible that the polymer is present one of the more acidic forms or in a mixture of forms on the surface of each film. The broadening occurring in the aniline peaks over time is due to the linking of aniline monomers. Monomers at different positions in the monomer chains experience vibrational transitions at slightly different IR absorption frequencies. There are also different lengths of monomer chains present on the film surface, further increasing the IR peak width.

X-Ray Diffraction Studies

X-ray diffraction spectra of copper(II) hectorite films taken before and immediately after exposure to aniline show that the layer thickness does not change during the exposure to aniline. This shows that aniline did not polymerize between the layers, despite the fact that the film surface was coated with aniline. Since the highly polar water molecule bonds more tightly to the charged clay layers than the less polar aniline monomer, it has been concluded that water in the intergallery regions simply does not evaporate from the intergallery region, but keeps aniline from intercalating between the layers. Previous researchers have used the alkyl ammonium cation to render the intergallery regions organophilic before attempting to place organic monomers there[3].

All of the transition-metal exchanged hectorite films have d-spacings between 13.7Å and 16.0Å. The variation in layer depth has no correlation with the size of the exchanged cation. Considering the 1.3Å variation in the d-spacing of the copper(II) hectorite films over the course of the summer, we conclude that the variation observed in d-spacing is a function of the ability of the exchanged cation to complex water molecules and of the variation in laboratory humidity.

Conclusions

This work has resulted in a few steps in the understanding of hectorite films and organic polymerization on or in the films. First, it is possible to form hectorite films from most of the first row transition metal cations. Secondly, aniline vapor will oxidize on the surface of all of these films at room temperature, and the rate of oxidation is at least partly controlled by the reduction potential of the exchanged cation. Third, aniline polymerization at room temperature occurs over the few months following aniline deposition on the film surface. Fourth, infrared spectroscopy is a useful method of studying this polymerization, and fifth, conditions stressful to the hectorite film, such as the vacuum conditions used in previous work, are necessary to induce aniline polymerization in the intergallery regions of the copper(II) hectorite films. The last area requires further research, including stressing the hectorite films with vacuum conditions during aniline exposure and heating the film above room temperature during aniline deposition. These stresses may pull water from the intergallery regions, allow aniline to enter the intergallery regions and encourage monomer linkage and polymerization. As Vaia et al. have shown, layers of organic polymer between the inorganic layers will give hectorite/polyaniline composites the thermal stability necessary to produce applications such as gas separation membranes in car exhaust manifolds and chemical sensors for computer chips[4].

5. APPENDIX

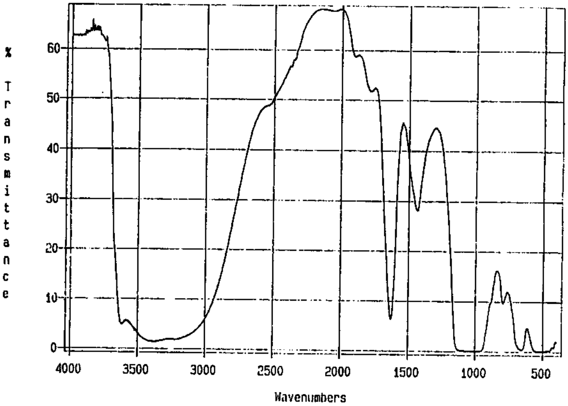


Figure A1. Infrared transmittance spectrum of Copper(II) Hectorite Film, 400-4000cm^{-1}.

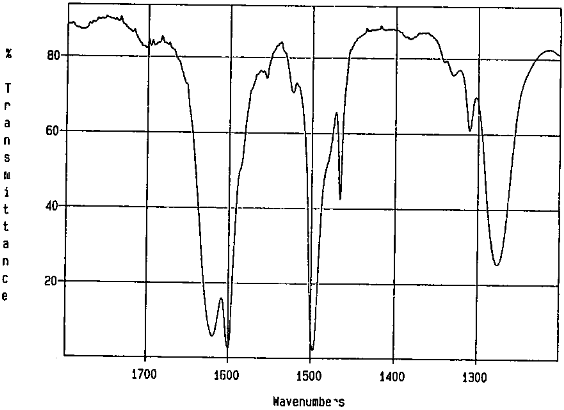


Figure A2. Infrared transmittance spectrum of Aniline, 1200-1800cm^{-1}.

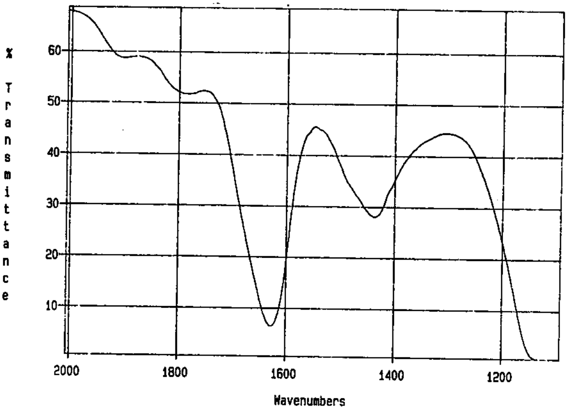


Figure A3. Infrared transmittance spectrum of Copper(II) Hectorite film, 1100-2000cm^{-1}.

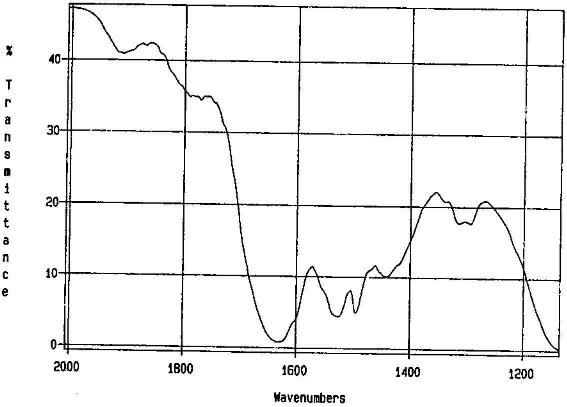


Figure A4. Infrared transmittance spectrum of Copper(II) Hectorite film exposed to Aniline for 18 hours, 1100-2000cm^{-1}.

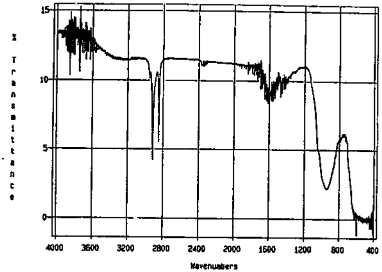


Figure A5. Infrared spectrum of Copper(II) Hectorite film, taken with Multiple Internal Reflectance Accesory, 400-4000cm^{-1}.

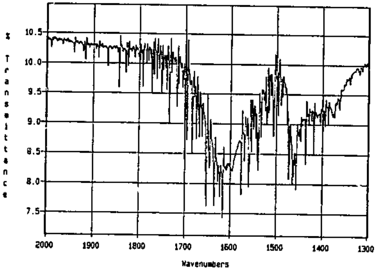


Figure A6. Infrared spectrum of Copper(II) Hectorite film, taken with Multiple Internal Reflectance Accesory, 1300-2000cm^{-1}.

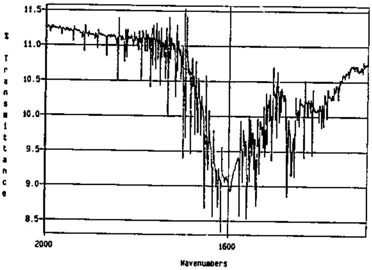


Figure A7. Infrared spectrum of Copper(II) Hectorite film exposed to Aniline, taken with Multiple Internal Reflectance Accesory, 1300-2000cm^{-1}.

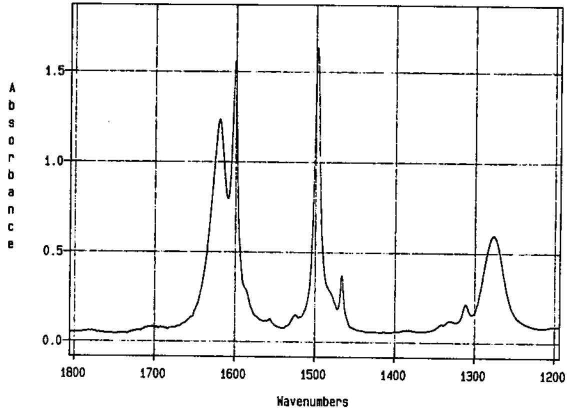


Figure A8. Infrared absorbance spectrum of aniline, 1200-1800cm^{-1}.

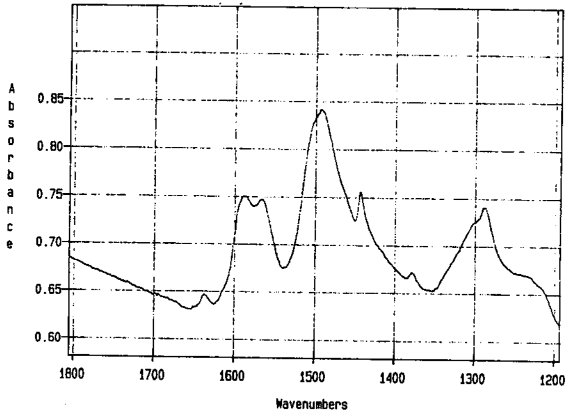


Figure A9. Infrared absorbance spectrum of Emeraldine Polyaniline, 1200-1800cm^{-1}.

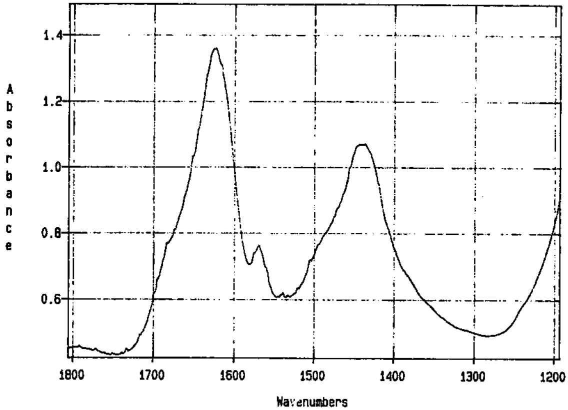


Figure A10. Infrared absorbance spectrum of Copper(II) Hectorite film, 1200-1800cm^{-1}.

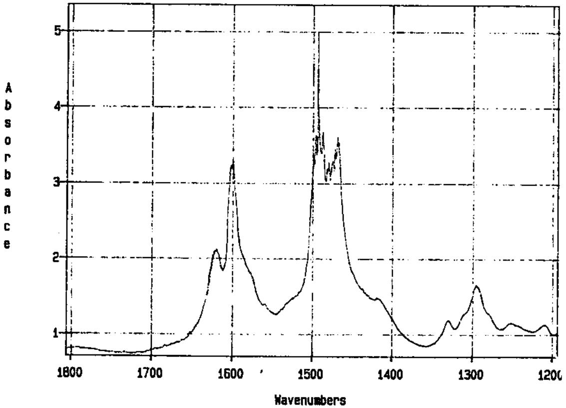


Figure A11. Infrared absorbance spectrum of Copper(II) Hectorite film exposed to aniline 1 week under vacuum, 1200-1800cm^{-1}.

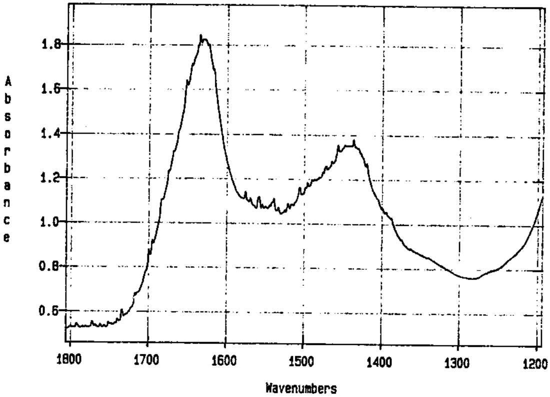


Figure A12. Infrared absorbance spectrum of Copper(II) Hectorite film exposed to aniline and later heated to 200°C, 1200-1800cm^{-1}.

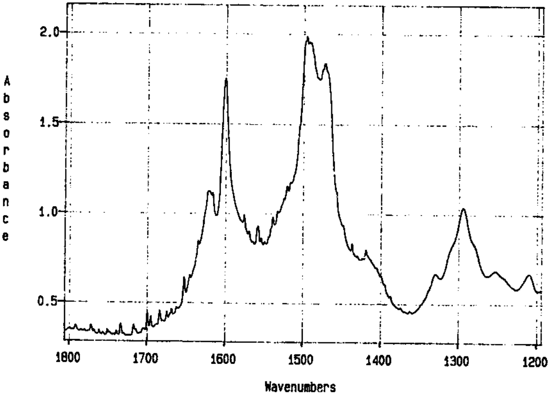


Figure A13. Infrared absorbance spectrum of Copper(II) Hectorite film soaked in liquid aniline several months, 1200-1800cm^{-1}.

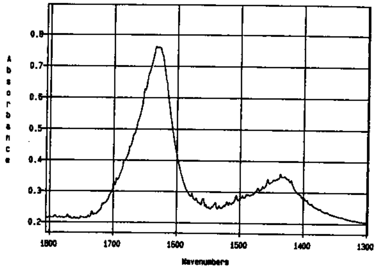


Figure A14. Infrared absorbance spectrum of Copper(II) Hectorite film, 1300-1800cm^{-1}.

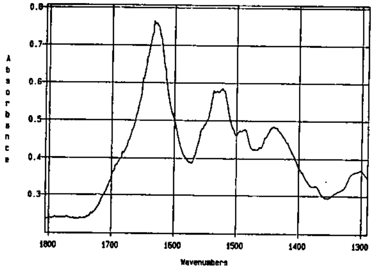


Figure A15. Infrared absorbance spectrum of Copper(II) Hectorite film exposed to Aniline 1 hour, 1300-1800cm^{-1}.

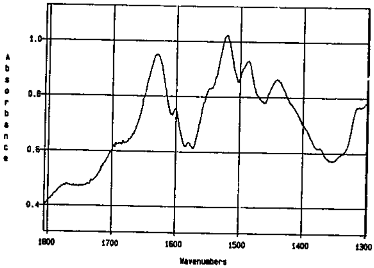


Figure A16. Infrared absorbance spectrum of Copper(II) Hectorite film exposed to Aniline 4 hours, 1300-1800cm^{-1}.

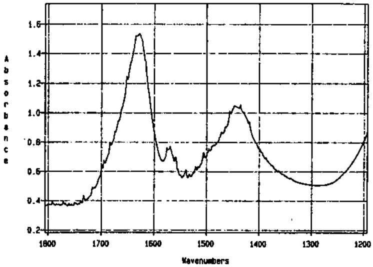


Figure A17. Infrared absorbance spectrum of Copper(II) Hectorite film, 1200-1800cm^{-1}.

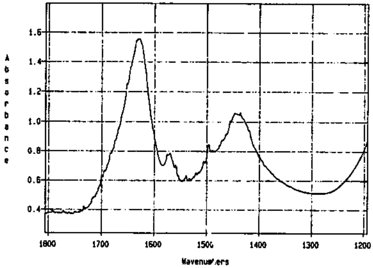


Figure A18. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 30 minutes, 1200-1800cm^{-1}.

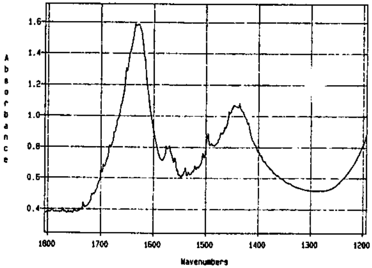


Figure A19. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 1 hour, 1200-1800cm^{-1}.

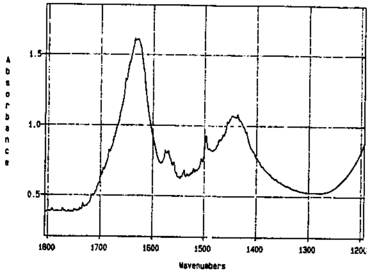


Figure A20. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 2 hours, 1200-1800cm^{-1}.

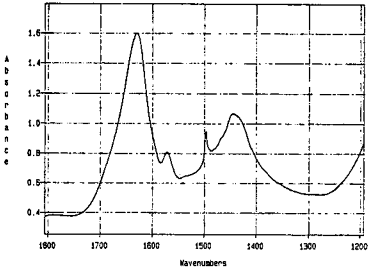


Figure A21. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 3 hours, 1200-1800cm^{-1}.

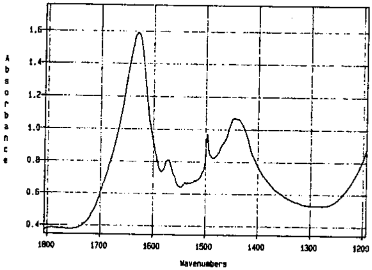


Figure A22. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 4 hours, 1200-1800cm^{-1}.

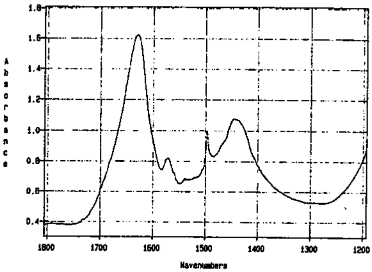


Figure A23. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 5 hours, 1200-1800cm^{-1}.

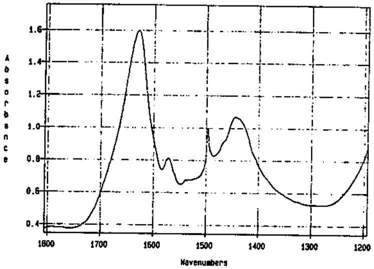


Figure A24. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 6 hours, 1200-1800cm^{-1}.

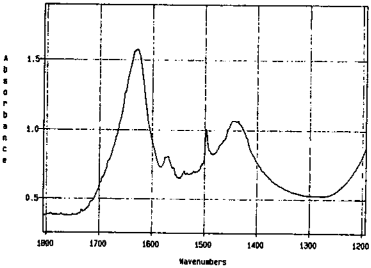


Figure A25. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 7 hours, 1200-1800cm^{-1}.

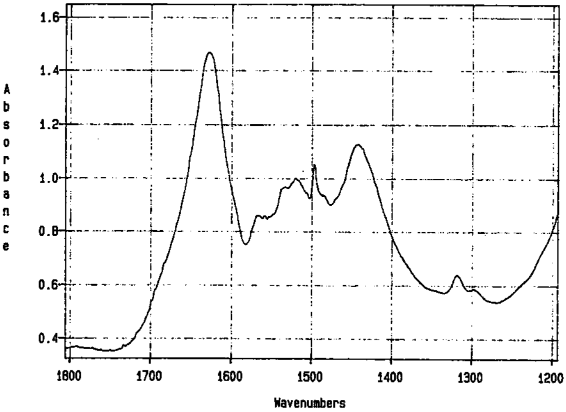


Figure A26. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 2 weeks, 1200-1800cm^{-1}.

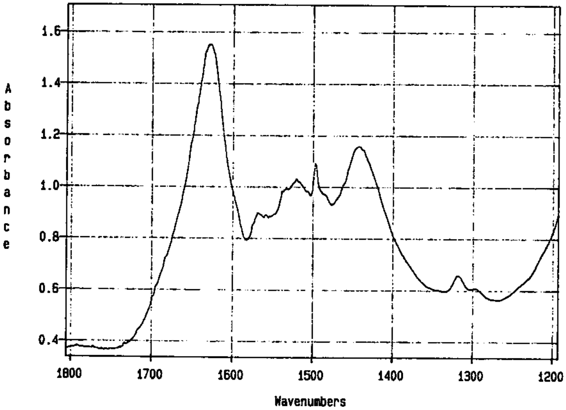


Figure A27. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 3 weeks, 1200-1800cm^{-1}.

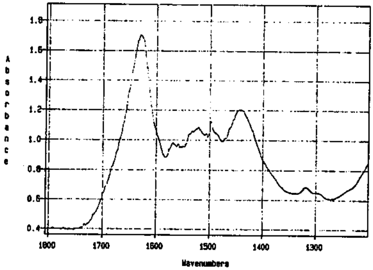


Figure A28. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 3 weeks and under ambient conditions 3 weeks, 1200-1800cm^{-1}.

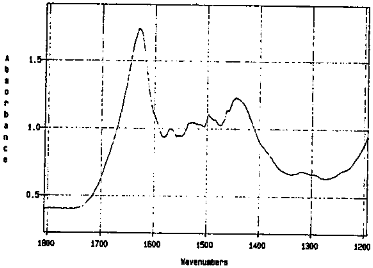


Figure A29. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 3 weeks and under ambient conditions 11 weeks, 1200-1800cm^{-1}.

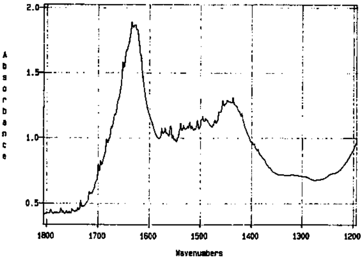


Figure A30. Infrared absorbance spectrum of same Copper(II) Hectorite film exposed to Aniline 3 weeks and under ambient conditions 17 weeks, 1200-1800cm^{-1}.

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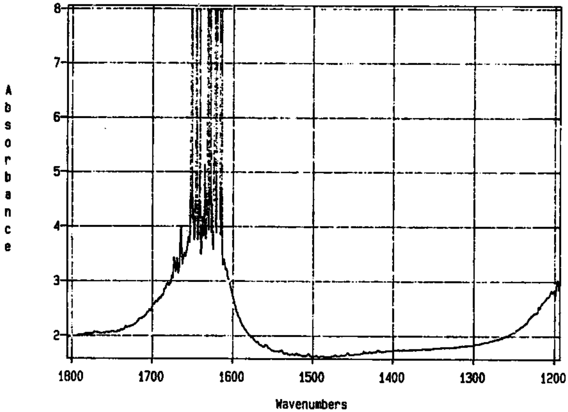

Figure A31. Infrared spectrum of Vanadyl(II) Hectorite Film, 1200-1800cm^{-1}.

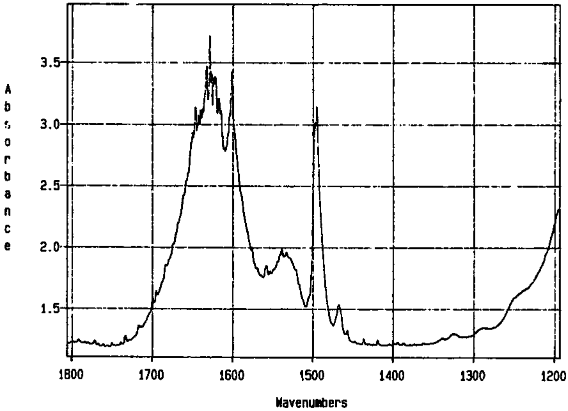

Figure A32. Infrared spectrum of Vanadyl(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

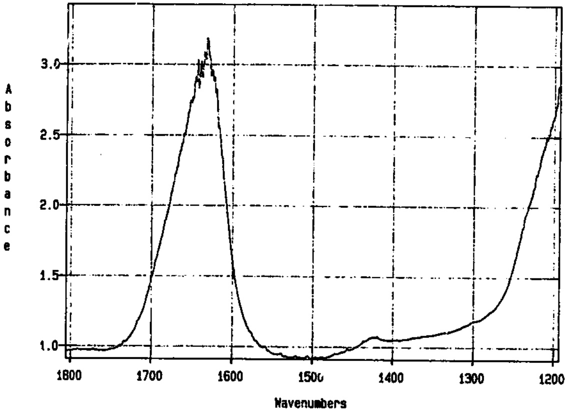

Figure A33. Infrared spectrum of Vanadyl(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

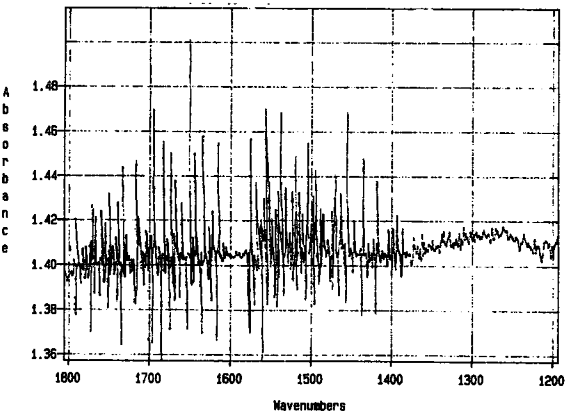

Figure A34. Infrared spectrum of Vanadyl(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

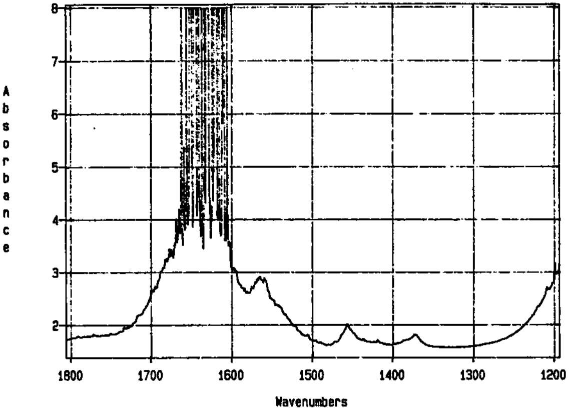

Figure A35. Infrared spectrum of Chromium(III) Hectorite Film, 1200-1800cm^{-1}.

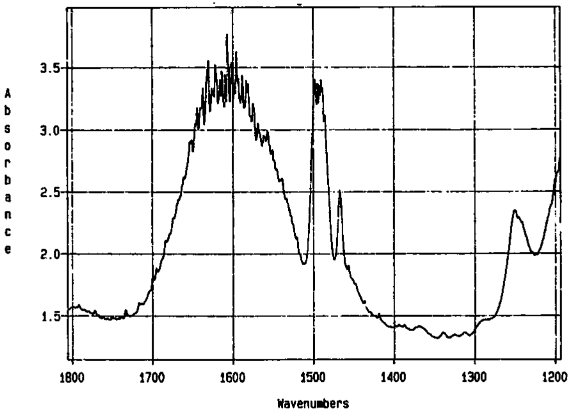

Figure A36. Infrared spectrum of Chromium(III) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

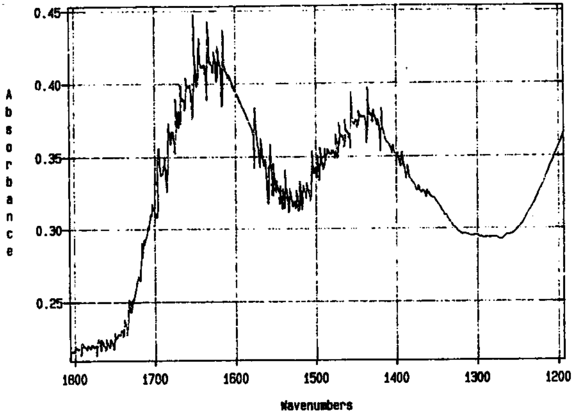

Figure A37. Infrared spectrum of Chromium(III) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

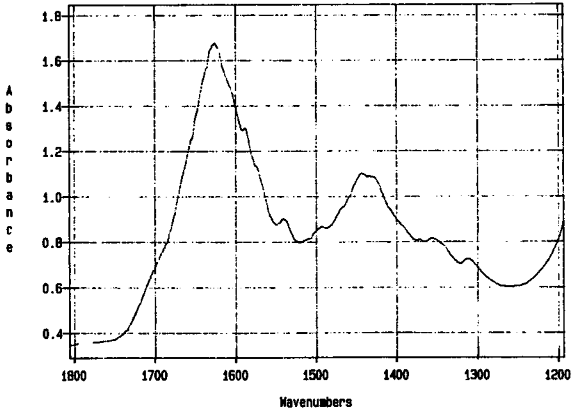

Figure A38. Infrared spectrum of Chromium(III) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

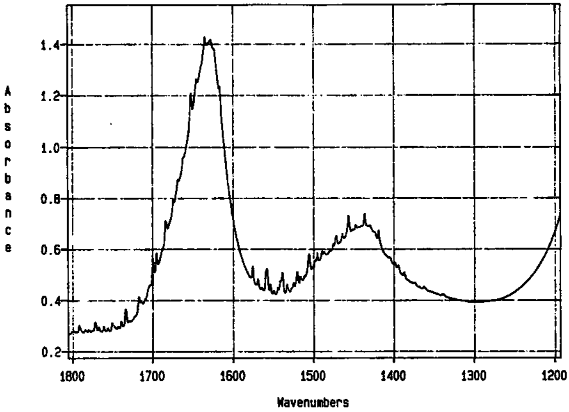

Figure A39. Infrared spectrum of Manganese(II) Hectorite Film, 1200-1800cm^{-1}.

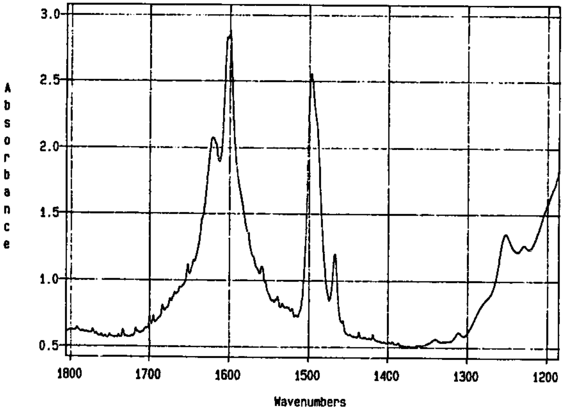

Figure A40. Infrared spectrum of Manganese(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

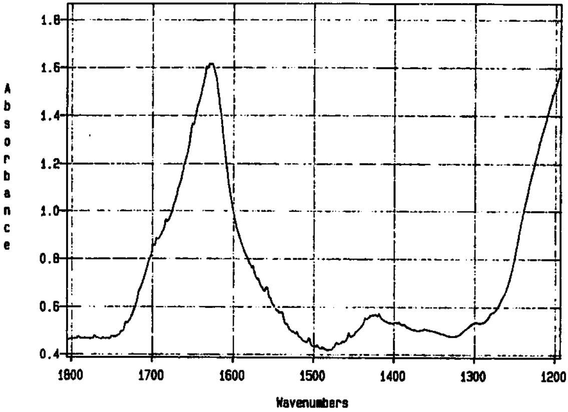

Figure A41. Infrared spectrum of Manganese(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

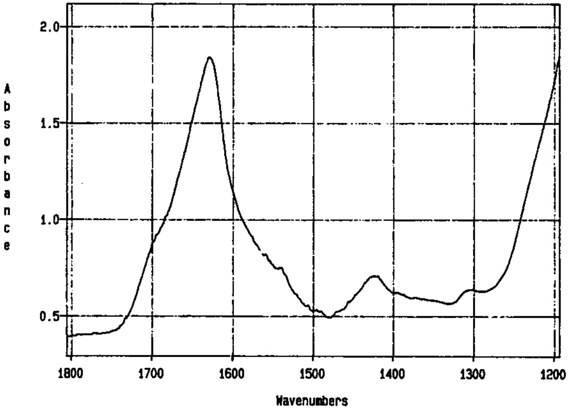

Figure A42. Infrared spectrum of Manganese(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

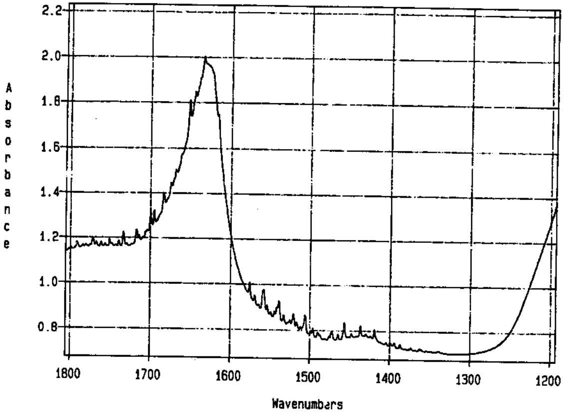

Figure A43. Infrared spectrum of Iron(III) Hectorite Film, 1200-1800cm^{-1}.

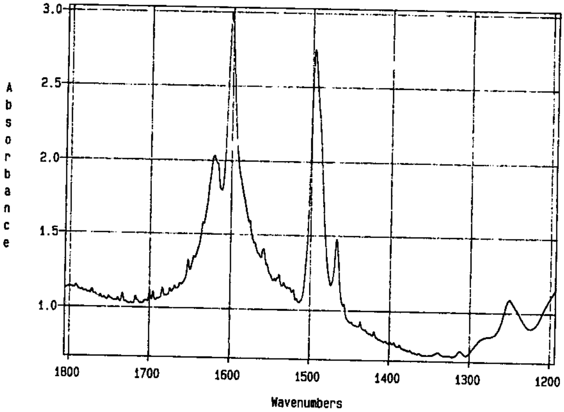

Figure A44. Infrared spectrum of Iron(III) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

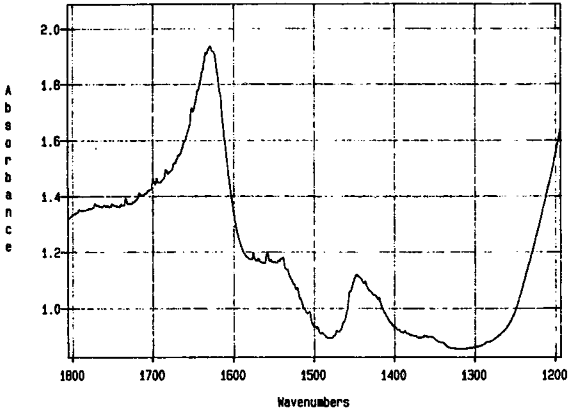

Figure A45. Infrared spectrum of Iron(III) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

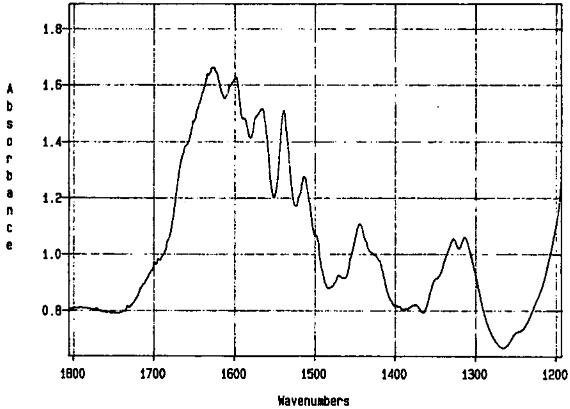

Figure A46. Infrared spectrum of Iron(III) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

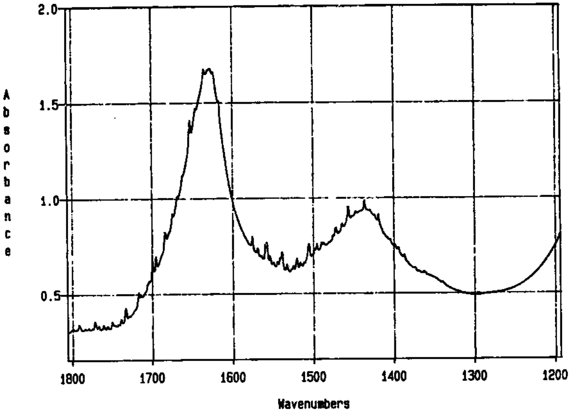

Figure A47. Infrared spectrum of Cobalt(II) Hectorite Film, 1200-1800cm^{-1}.

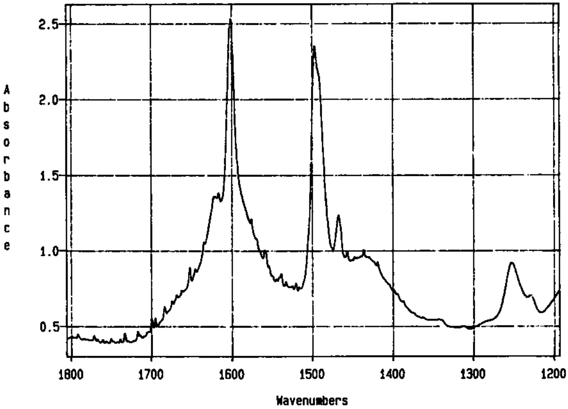

Figure A48. Infrared spectrum of Cobalt(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

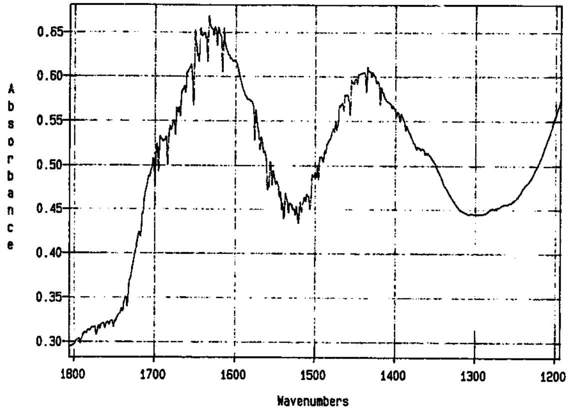

Figure A49. Infrared spectrum of Cobalt(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

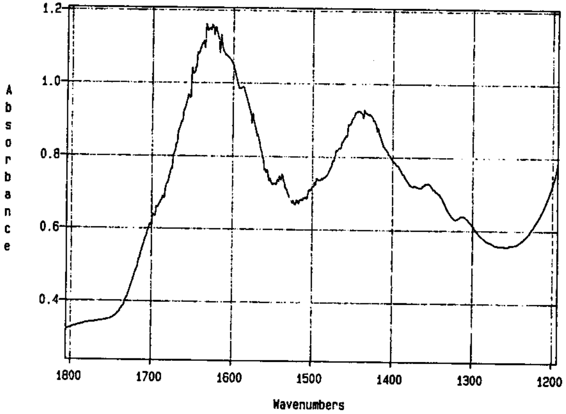

Figure A50. Infrared spectrum of Cobalt(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

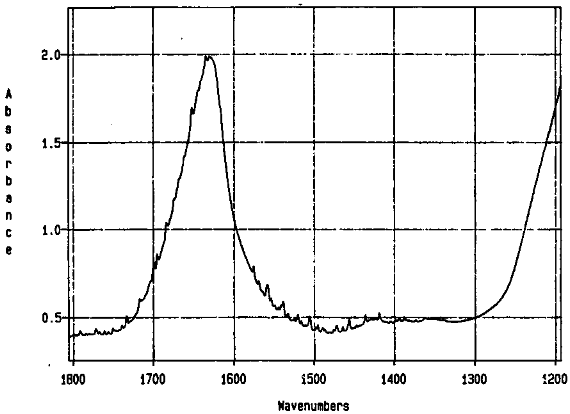

Figure A51. Infrared spectrum of Nickel(II) Hectorite Film, 1200-1800cm^{-1}.

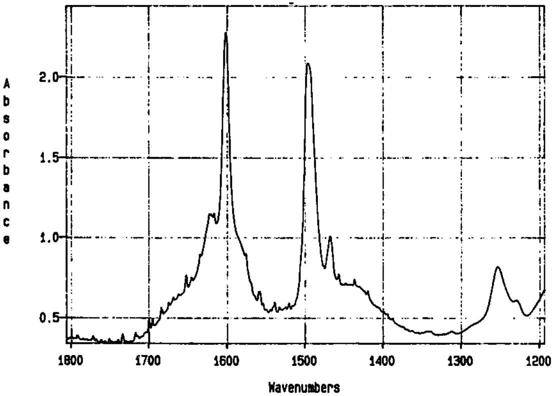

Figure A52. Infrared spectrum of Nickel(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

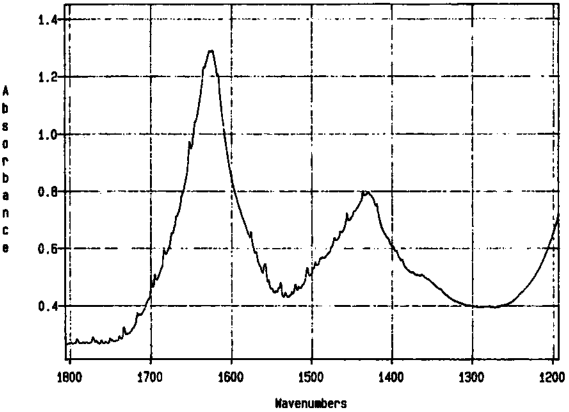

Figure A53. Infrared spectrum of Nickel(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

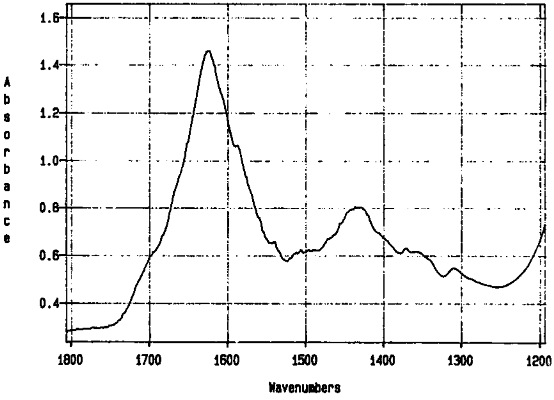

Figure A54. Infrared spectrum of Nickel(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

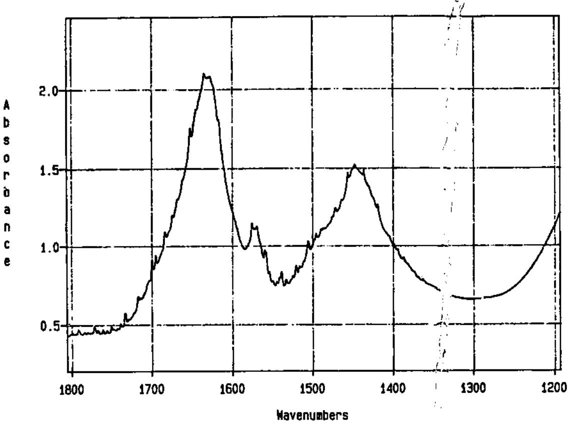

Figure A55. Infrared spectrum of Copper(II) Hectorite Film, 1200-1800cm^{-1}.

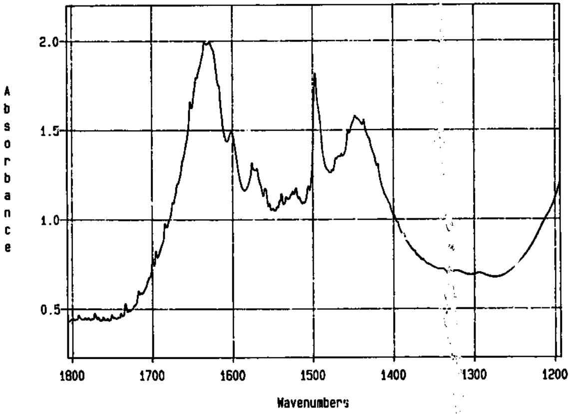

Figure A56. Infrared spectrum of Copper(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

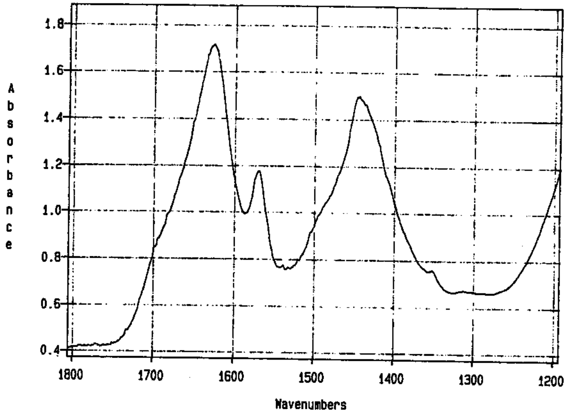

Figure A57. Infrared spectrum of Copper(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

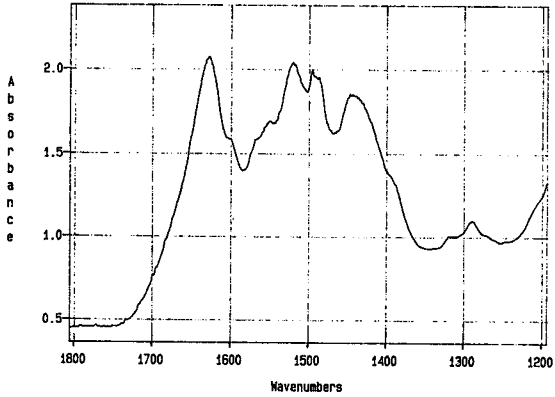

Figure A58. Infrared spectrum of Copper(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

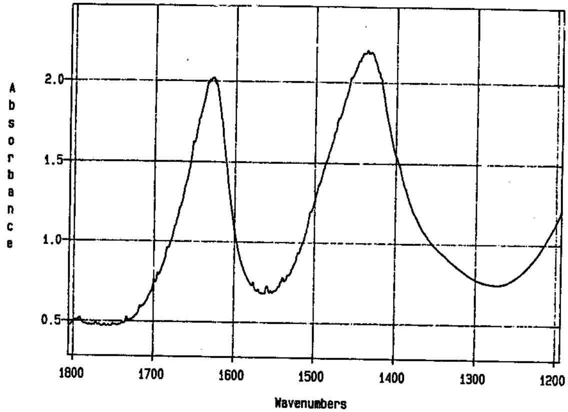

Figure A59. Infrared spectrum of Zinc(II) Hectorite Film, 1200-1800cm^{-1}.

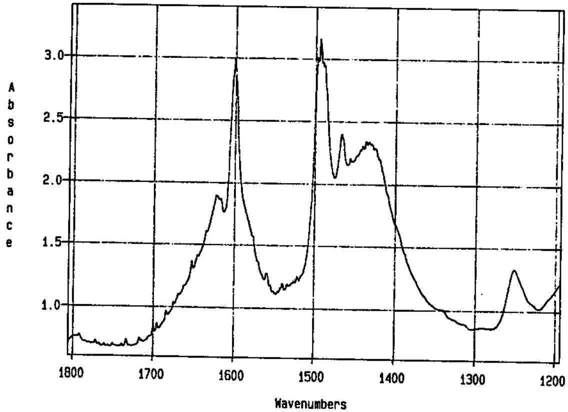

Figure A60. Infrared spectrum of Zinc(II) Hectorite Film exposed to Aniline 24 hours, 1200-1800cm^{-1}.

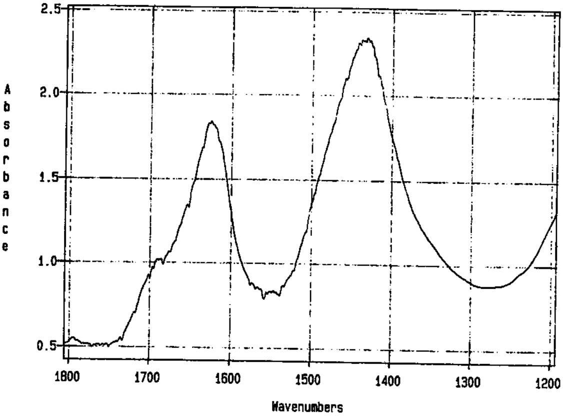

Figure A61. Infrared spectrum of Zinc(II) Hectorite Film after 6 months ambient conditions, 1200-1800cm^{-1}.

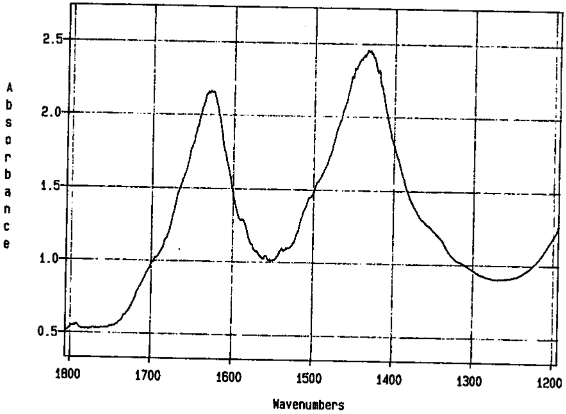

Figure A62. Infrared spectrum of Zinc(II) Hectorite Film exposed to Aniline 24 hours and ambient conditions 5 months, 1200-1800cm^{-1}.

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