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SYNTHESIS AND HYDROLYSIS STUDIES OF APS MODIFIED IMOGOLITE

By

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ABSTRACT

SYNTHESIS AND HYDROLYSIS STUDIES OF APS MODIFIED IMOGOLITE

by

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The silylation of the tubular aluminosilicate imogolite, was undertaken in an attempt to synthesize a new phase transfer catalyst. The Al-OH outer surface of imogolite may be rendered more hydrophobic through treatment with the organosilane gamma-aminopropyltriethoxysilane (APS). The solubility properties of the tubular particles are modified without altering their desirable characteristics, such as a large surface area and the capability of accommodating small ions in the inner cavity of the tube. Synthesis of APS modified imogolite was accomplished, but the material was found to be unstable toward hydrolysis. A time dependent dialysis experiment was conducted to compare the rate of hydrolysis of APS from the surface of imogolite with that of the hydrolysis rate from gamma-alumina, an amorphous material possessing planar surface Al-OH sites. The results showed that APS modified imogolite was more stable toward hydrolysis than APS modified gamma-alumina. Future work will utilize surfactants for the surface modification of imogolite.

To my family and Phil

ACKNOWLEDGMENTS

I am deeply grateful for the guidance and support of Dr. T.J. Pinnavaia in the pursuance of this work. Through his insightful direction, he shaped the results that were obtained and helped me to follow the path that became the focus of this thesis. May he continue to broaden my perspective in science throughout work on my dissertation. In addition to his contagious optimism and invaluable insight, the financial support which he was able to provide was greatly appreciated.

My fiance, Philip Lyman, who has endured untold hardships as a result of my decision to undertake this endeavor, has nonetheless assisted me unfailingly in the technical aspects of developing this thesis into its final form. In addition to his technical assistance, I would like to express my sincere gratitude for his support and undying faith in me.

Tribute must also be given to Dr. Ahmad Moini. Through his efforts, many potential crises were thwarted and many seemingly unsolvable problems were surmounted. I would like to express my thanks for those efforts and for the many words of wisdom that enabled me to successfully "deal with" the situations at hand.

I would also like to thank my friends and family for their patience and encouragement. The Chemistry department staff, especially Kermit Johnson for his assistance with the NMR and the library personnel, are greatly appreciated for their efforts.

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INTRODUCTION

A. Research Objectives

The family of aluminosilicate minerals is comprised of a wide variety of structurally dissimilar materials. A three dimensional porous network system is adopted in zeolites. Clay minerals generally take the form of layered compounds containing accessible space between the layers. Halloysite is composed of a single sheet which has been wound into a roll. Hollow spherical particles constitute the structure of allophane. Imogolite, as a member of this diverse group also possesses its own fundamental features. Its structure is that of a hollow tube.

The outer surface of imogolite consists of an aluminum hydroxide layer and silanols are exposed on the inner surface. These unique structural characteristics give rise to the particular behavior exhibited by imogolite in solution. The multitude of surface hydroxyls provide a wealth of potential reactive sites. These hydroxyls also give imogolite a small but significant cation exchange capacity (CEC). Because of the nature of the CEC, its magnitude varies with the type of cation and the pH of the solution. The tubular structure is also responsible for imogolite's unusually high surface area.

The combination of its shape, CEC, accessible cavity within the tube, high surface area and water solubility characteristics make imogolite an attractive candidate for applications in catalysis and other areas of materials chemistry. The purpose of the present investigation is both to improve the reliability of the synthesis of imogolite and to modify the surface of imogolite. Surface modification of these inorganic tubes may prove to be useful in various catalytic applications. Toward this end, the first goal is to find a way to render the surface hydrophobic. This was to be accomplished by attaching long chain hydrocarbon moieties to the outside surface of the tubes through the use of organosilane coupling agents. In this way, an inorganic compound could be made to behave very much like an organic compound. The imogolite would subsequently be extractable by organic solvents.

If the functionalized imogolite retains a significant affinity for water on its inner surfaces, a phase transfer catalyst with very unique activity in an organic-aqueous system would be expected. The long chain organic functionalities will be too large to fit into the cavity and thus interact with the silanols on the inside of the tubes. Therefore the inner surface of the tube can be used to adsorb small organic or inorganic cations, making the imogolite a sort of "ion shuttle" between the organic and inorganic phases of a phase transfer system.

Imogolite also has an extensive surface area on which a reaction may occur. This leads to another possible application for the successfully surface modified tubes. Chelating agents coupled to reactive silane functionalities are readily available. Affixing compounds of this nature to the imogolite surface would allow metal cations to be complexed by the chelating functionality. A system complexed with a specific metal may be useful catalytically, or the system may be used to concentrate metal ions from solutions for subsequent quantitative analysis of their composition.

In order to synthesize functionalized imogolite, a reproducible synthesis and suitable purification techniques must be found. To accomplish this, concentration and pH limits were explored, and purification techniques were developed. Thus, a method for reliably obtaining well dispersed, well-formed imogolite tubes was documented.

Surface modification efforts centered around the coupling agent gamma-aminopropyltriethoxysilane (APS). APS was chosen because of the large quantity of information available documenting its reactivity and application to a wide variety of surfaces. It is also readily hydrolyzable and well behaved in solution. Developing an understanding of this system would provide the groundwork necessary for the pursuit of more poorly understood coupling agents that might impart the desired characteristics to imogolite for use in the aforementioned applications.

Preliminary experiments to achieve coupling of APS to imogolite proved inconclusive. Through further study, it was determined that under the silylation conditions utilized, bonding is achieved between APS and imogolite. It was also found that the Si-O-Al bond is hydrolytically unstable. In fact, all of the coupling agent can be removed from imogolite by dialyzing the solution for two to three days. Although this discovery was a temporary setback to the goal of surface modification, it also revealed a way in which the relative stabilities of the Si-O-Al bond could be compared in different systems. A time dependent dialysis experiment was conducted to compare the stability of APS on imogolite with that of APS on alumina. The relative stabilities of the two systems were easily determined from the data collected in this experiment.

Further efforts continue to focus on the modification of the imogolite surface in a less reversible manner. Preliminary success has resulted from the treatment of imogolite with the surfactant sodium lauryl sulfate. Future studies will be directed toward understanding and controlling the interaction between imogolite and sodium lauryl sulfate and the behavior of this new system.

B. Imogolite

The empirical formula for the tubular aluminosilicate imogolite is $(HO)_3Al_2O_3SiOH$. The formula is written so that

it corresponds to the ordering of atoms along a path from the outside to the inside of the tube. The inner wall of the tube is made up of orthosilicate units which have been condensed to one side of a single gibbsite sheet which defines the outer wall. (See figure 1).[1] The strain introduced by the coupling of tetrahedrally coordinated silicate units to the octahedrally coordinated aluminum hydroxide sheet gives rise to curvature, allowing the edges to be conjoined, resulting in tube formation. Evidence for the strain is provided by the shortening of the O-O distance around the vacant site in the gibbsite sheet to which the SiO_4 tetrahedron is condensed. This shortening of oxygen contacts reduces the repeat distance along the tube to 8.4Å compared with the gibbsite repeat distance of 8.6Å. Electron diffraction patterns of non-oriented tube samples give reflections at 1.4, 2.1, 2.3 (broad), 3.3 (broad), 3.7, 4.1, 5.7 (broad), 7.8 (broad), 11.8 (broad) and 21-23Å.[2] The 11.8, 7.8 and 5.7Å reflections indicate the 8.4Å repeat unit along the tube unit axis. The 4.1, 3.7, 3.3, 3.1 and 2.3Å reflections arise from the lateral arrangement of the tube unit with interaxial separations of 21 to 23Å.[3] Other supporting evidence for this structure include transmission electron microscopy, which shows the tubular morphology, infrared spectroscopy, which indicates the presence of orthosilicate units (peaks at $930cm^{-1}$ and $995cm^{-1}$), x-ray diffraction patterns, which corroborate the electron

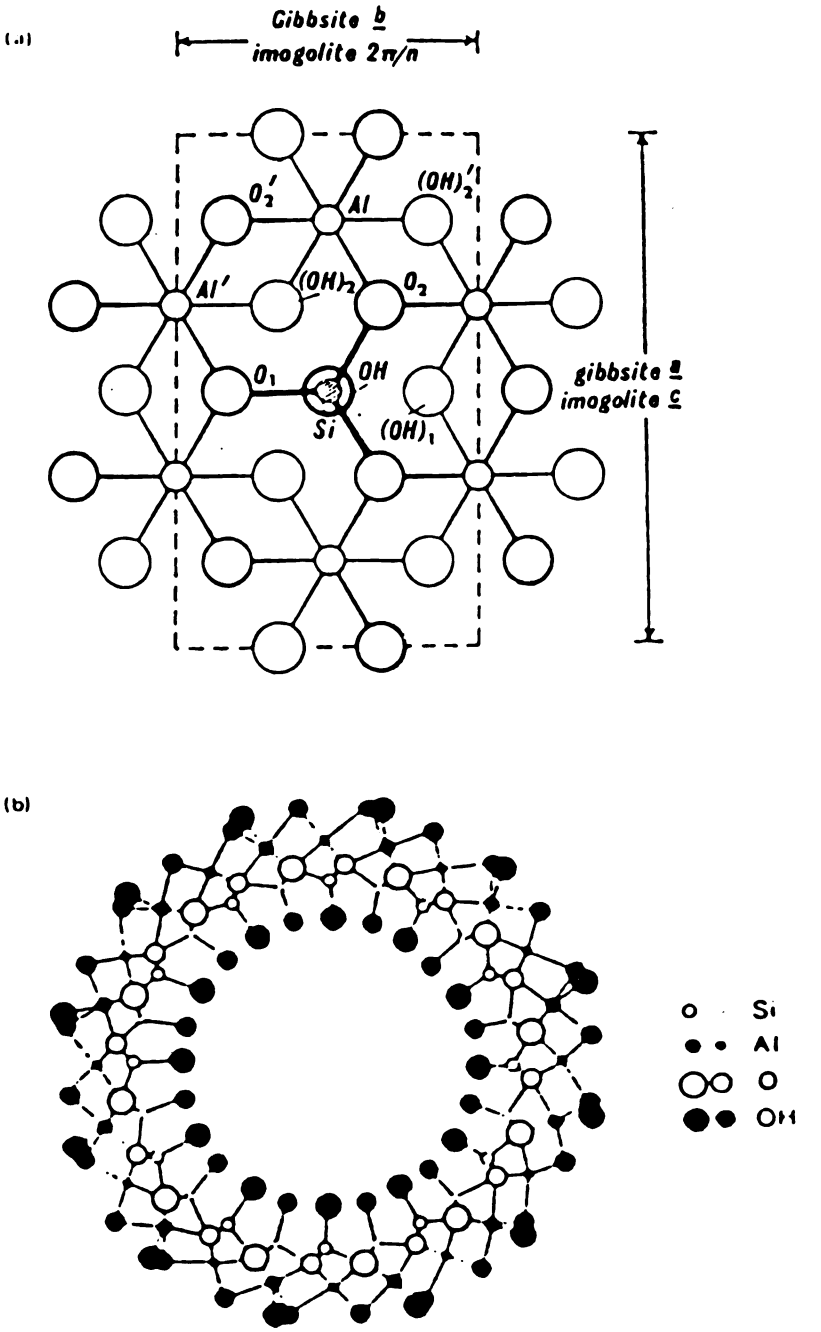
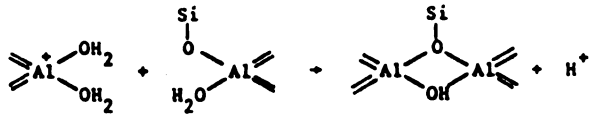


Figure 1 Structure of Imogolite (a) Mode in which the orthosilicate group is attached to the face of a gibbsite sheet. (b) Cross sectional view of the imogolite structure.

diffraction patterns, and thermal analysis, which shows the loss of water associated with the tubes.

Natural imogolite can be found as a component of weathered volcanic ash and pumice beds. It was first identified in soil samples of this type by Yoshinaga and Aomine[4] in 1962. Structural determination was slow because of difficulties encountered in the separation of imogolite from the spherically shaped, amorphous aluminosilicate allophane, with which it is found. An unequivocal structure of imogolite was presented in 1972 by Cradwick[3] et al. using electron and x-ray diffraction data. In addition, a chemical procedure for differentiating between silicate anions of different degrees of polymerization was applied to imogolite. This procedure involves converting the silicate anion present in the sample to its corresponding trimethylsilyl ether and identifying the ether or ethers by gas chromatography.[5,6] For imogolite, it was found that 95% of the silicate anions are derived from orthosilicate units and only 5% are from pyrosilicate units. The ratio of ortho to pyrosilicate obtained for imogolite was higher than that obtained for other orthosilicates by this method. These results required that the structure of imogolite contain only orthosilicate units. The chain structure proposed by Wada and Yoshinaga[2] in 1969 was no longer acceptable because of its 2.80Å repeat distance and the fact that it contained linked SiO_4 tetrahedra.

Once the structure of imogolite was known, a synthetic route to its synthesis could be sought. The preparation of imogolite was described by Farmer[7] et al. in 1977. Imogolite was synthesized through the growth of a proto-imogolite structure, made by the reaction of orthosilicic acid and hydroxyaluminium ions in aqueous solution. Once the product imogolite begins to form, a decrease in pH is observed. This is believed to be due to the release of H^+ during imogolite formation according to the following scheme:[8]



When the proper conditions have not been met, nucleation and growth is inhibited and the pH of the solution either stays the same or increases slightly.

A comparison of synthetic and natural imogolite reveals some fundamental differences. Natural imogolite has an outer diameter of 20Å, whereas the outer diameter of synthetic imogolite is 23Å. The internal diameter is 9-11Å. This requires that natural imogolite form tubes with 12 gibbsite unit cells and synthetic imogolite form tubes with 14 units. The lengths of the tubes vary from hundreds of angstroms to several microns in both natural and synthetic materials[9]. Natural imogolite gives several higher order reflections that are unobtainable in electron diffraction patterns of the

synthetic material. This is due to the fact that naturally formed tubes tend toward more regular packing in the solid state than the synthetic imogolite, which arrange themselves in a more disordered fashion.

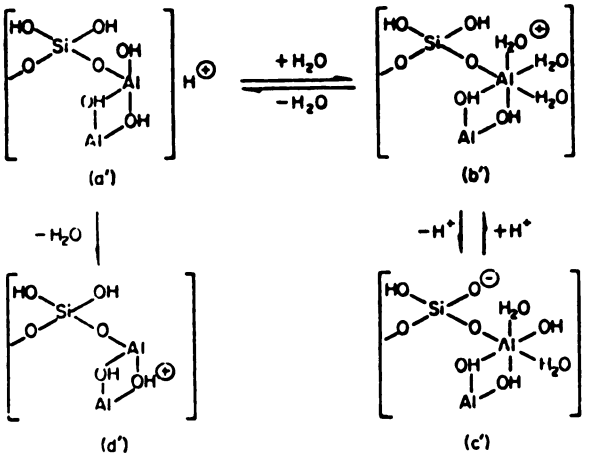
Natural and synthetic imogolite, being formed in aqueous solution, have very distinct colloid behavior depending upon the pH and imogolite concentration. At very low concentrations, 30mM Al or less, in acidic aqueous solution imogolite is completely soluble and forms a crystal clear solution. At a pH of about 7, aggregation of the tubes begins, turning the solution slightly cloudy. As the pH continues to increase, gelation begins. This behavior can be attributed to the change in surface charge on the imogolite tubes with changing pH. Below pH 5.5 the surface aluminum hydroxides are all protonated, according to a study by Inoue and Wada.[10] The study was based on the premise that the titration of imogolite gave a near neutral reaction at the equivalence point. The like charged tubes remain separated by their electrostatic repulsions. Above pH 8 the surface aluminum hydroxides are completely deprotonated and the inner silicon hydroxide sites begin to deprotonate. In the absence of electrostatic repulsions, the tubes are able to interact and therefore flocculation begins. Aggregation of the tubes begins to occur at pH 7, so the aggregation process itself can be expected to interfere with the ability to determine the state of ionization on the surface at these pH values.

Electrophoretic mobility measurements on imogolite were measured in 0.001M NaCl by Horikawa.[11] These measurements determine that the pH at which the surface of imogolite becomes neutral is about 9. It is best to view the results involving basic solutions as guidelines to flocculation behavior, rather than absolute descriptions of the imogolite surface charge. The other factor influencing the degree of aggregation is imogolite concentration. Imogolite suspensions corresponding to aluminum concentrations greater than 30mM, will begin to flocculate, even in acidic solution. As more and more water is removed from the solution, a gel begins to form. Aggregation of imogolite particles by either means (by pH or by concentration variation) is never completely reversible. Aggregated tubes may be partially redispersed by sonification in acidic aqueous solution. The most effective redispersion is achieved when freeze dried imogolite is used. Even then, a cloudy mixture is obtained.

In addition to the unique solution and flocculation behavior of imogolite, its tubular nature lends itself to several distinct physical properties. One of these is microporosity. Microporosity was first invoked to explain the discrepancy in density measurements between two methods used by Wada and Yoshinaga.[2] One set of density measurements on imogolite was collected with a pycnometer using water as the displacement liquid. A second data set was obtained using a float-sink test involving incremental addition of

acetylene tetrabromide ($C_2H_2Br_4$) to a sample. The results from the liquid displacement method gave values of 2.53-2.70 g/cm^3. Those from the float-sink method gave consistently lower values of 1.70-1.97g/cm^3. This discrepancy cannot be explained simply by the fact that water may be adsorbing onto the imogolite surface in the liquid displacement method. The different results are obtained because water molecules can penetrate into the small micropores in imogolite, but the larger $C_2H_2Br_4$ molecules cannot. The porosity in imogolite is due to both the spaces inside the tubes and to those formed between the tubes in their solid state packing arrangement. The porosity was estimated at 55% of the total volume of air-dried imogolite. As might be expected from its porous nature, imogolite has been found to have a very large surface area, from 1100-1200m^2/g.[12] These values were obtained using the EGME (ethylene glycol monoethylether) method, the lower value being a sample dried over P_2O_5 in a vacuum, the higher value being an air dried sample. It is believed that drying under vacuum may cause the tubes to collapse, reducing their surface area. The properties of the imogolite surface are determined in part by the presence of hydroxyl groups. The availability of these surface hydroxyls gives rise to surface acidity. This acidity has been measured by observing the color change of Hammett indicators of known pKa adsorbed on the surface.[13] Each indicator pKa is matched with the weight percent of sulfuric acid necessary

to establish the pH at its equivalence point for reference. The acidity of imogolite was measured for samples equilibrated in atmospheres at different relative humidities. It was found that under very dry conditions, <5% relative humidity, imogolite is very acidic, corresponding to the acidity of 71% H_2SO_4. Below 20% relative humidity its acidity is reduced to that of $2X10^{-2}$% H_2SO_4. Above 20% relative humidity the acidity is reduced to an equivalent H_2SO_4 concentration of $8X10^{-8}$%. This latter value is comparable to that of gibbsite at any moisture level. A representation of the structure of the acid sites under changes in relative humidity is as follows:[13]



In the presence of water, weak acidity is explained by proton donation from SiOH and $AlOH_2^+$ groups, such as are shown from species b′ to species c′. In the absence of water the acid strength increases as the above scheme is followed in reverse from b′ to a′ and then from a′ to d′. The same explanation

applies for the decrease in pH as the material is heated. Species a′ represents a strong Bronsted acid site and species d′ represents a strong Lewis acid site.

As a result of the surface charge, there is a CEC and an AEC associated with imogolite. The CEC was determined to be 30meq/100g[13] for an oven-dried sample by determining Na retention from 0.05N $NaCH_3COO$ at pH 7. The AEC, measured from adsorption of Cl from 0.05M NaCl, was found to be 15meq/100g at pH 7. The CEC and AEC values are both highly pH dependent. They also depend on the particular cation or anion being measured. The AEC values increase in the order $NO_3^- < Cl^- < CH_3COO^- << SO_4^{2-}$. The CEC values increase as $Na^+ < K^+ < Mg^{2+} < Ba^{2+}$. This trend is due to the net charge and the size of the hydration sphere of each ion. When imogolite is titrated with n-butylamine, the amounts of n-butylamine absorbed are nearly equal to the CEC. This suggests that the acid sites may also be the cation-exchange sites. This conclusion would be erroneous if the n-butylamine were able to adsorb onto the anion exchange sites as well as the acid sites. The CEC of imogolite is found to increase 30-50% upon heating to 105°C. It may be recalled that the acidity of imogolite increases in this manner also. The CEC also shows a dependence on background salt concentration. The exchangeable cations adsorbed on imogolite are readily hydrolyzed during dialysis against deionized water.

The stability of imogolite can also be understood through the examination of its structure. Upon heating, imogolite first undergoes dehydration at temperatures between 50 and 150°C. At 250-400°C dehydroxylation occurs and above 900°C mullite or gamma-alumina can be detected in samples.[14] The surface area and CEC decreases with dry grinding.[15] Changes in the IR and alteration of morphology as seen in transmission electron micrographs offer direct evidence of the low stability of imogolite under dehydrated conditions. Low levels of phosphate perturb nucleation, growth and formation of imogolite by retarding the polymerization of proto-imogolite during synthesis.[16] Imogolite exhibits excellent stability in acidic environments, but it begins to dissolve above pH 12.[15]

C. Coupling Agents

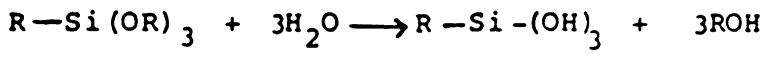
Coupling agents are compounds used in the modification of inorganic surfaces, typically oxides and glasses.[17,18] These materials often have desirable bulk properties but their surface properties may be undesirable. The use of coupling agents can create a surface with hydrophobic characteristics. For example, a flat meniscus and the complete transferability of liquids from a pipet can be achieved by coating the glass surface with a silane coupling agent. A coupling agent may also provide a suitable interphase region between two components in a composite to

enable it to perform as a single bulk material. One such application is in the use of glass fibers to reinforce organic polymers. Coating the fibers with a coupling agent increases the flexural properties of the material and prevents fracture between the fibers.

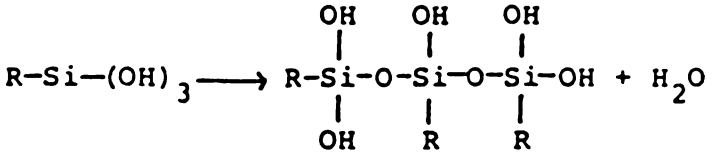
Organofunctional silanes of the form $R_nSiX_{(4-n)}$ are typically used in these types of applications. The R group is alkyl in nature but it commonly contains different functionalities. The X group is usually a halogen, alkoxy, acyloxy or amine. This group undergoes hydrolysis early in the coupling reaction. Hydrolysis occurs fastest when X is a halogen. When the hydrolyzable group is an alkoxy group, the rate of hydrolysis decreases as the number of carbons in the alkoxy and the value of n increase. The alkoxy silanes are more convenient to work with than the halogen forms, although hydrolysis occurs more slowly, because they do not form acids as hydrolysis products. Trialkoxy coupling agents are better than the disubstituted or monosubstituted compounds because they are able to provide more effective coverage of the surface, making them better able to alter the characteristics of inorganic surfaces.

Different silanes are applied as coupling agents in much the same manner. The steps involved in the coupling reaction are shown in figure 2.[19] First, there is a prehydrolysis step, taking up to one hour, to transform the hydrolyzable groups to hydroxyl groups. Water for hydrolysis may be

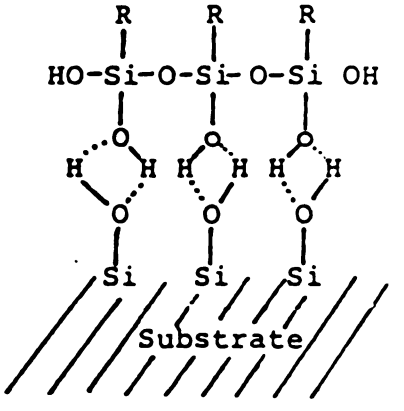
HYDROLYSIS



CONDENSATION



H-BONDING TO SUBSTRATE



COVALENT BOND FORMATION

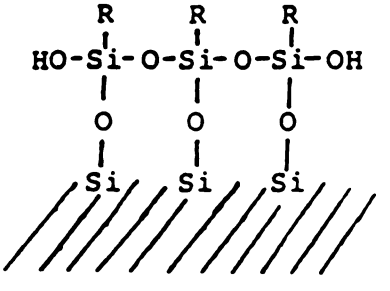
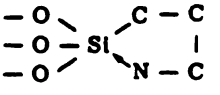


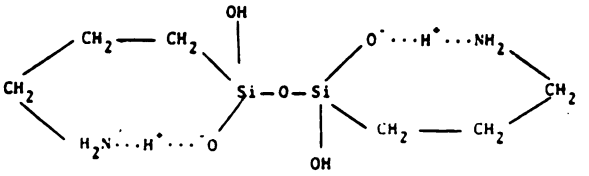
Figure 2 Sequence of events leading to a coupling reaction.

derived from the atmosphere, substrate or generated in the course of the reaction for some preparations. Next is the condensation step in which the trisilanols begin the react to form oligomeric siloxanes. These siloxane oligomers then hydrogen bond to the hydroxyl groups present on the inorganic surface whereupon they condense to form Si-O-M bonds. Here, M is the metal or semimetal belonging to the inorganic oxide of interest. The degree of coverage obtained can be monolayer or multilayer depending upon the amount of silane and the number of free hydroxyls present on the surface. Because the extent of oligomerization is difficult to control, surface coverages are often irreproducible. Condensation generally takes only a matter of minutes at room temperature even for multilayer coverages. The final step is the drying or curing process. Air-drying is often sufficient, but heating can also give desirable results. Heating may, however, lead to increased crosslinking of the alkyl siloxane on the surface weakening its interaction with the substrate. The surface modifications actually obtained will be a function of the substrate, actual method of application, quantity and type of silane used. Several different methods have been used to study the interactions at the silane-surface interface including Fourier Transform and Diffuse Reflectance Infrared Spectroscopy, Raman Spectroscopy, X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy and Secondary Ion Mass Spectrometry.[20]

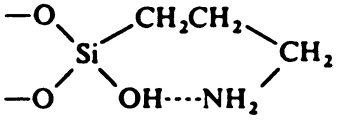
One of the most extensively studied coupling agents is gamma-aminopropyltriethoxysilane (APS). Although its behavior is similar to other coupling agents, it is in many ways unique. Hydrolysis, for example, is much faster than is typical of triethoxysilanes. This is because the amino functionality acts as a catalyst for the hydrolysis reaction. Another anomaly exhibited by this alkoxysilane is its ability to remain in monomeric form when acidified prior to hydrolysis at low concentrations (5% by weight).[21] When the pH is not adjusted, a 0.15% concentration is necessary in order to get a large number of monomeric silanetriols. In neutral solutions, hydrolysis is slowed and micelles form. The natural pH of this silane in solution is 10.0. The stability of the silane in solution is also unique. No precipitation is seen even in fairly concentrated solutions after aging. The reason for this stability has been the center of much discussion in the literature. All of the researchers agree that the explanation must involve an interaction centered around the aminofunctional group, but there are several different ways in which the interaction has been described. Plueddemann[22] first suggested that the silane may cyclize and form a five membered ring through association between the silicon and the nitrogen atoms as follows:



He has also proposed the existence of an internal zwitterion structure under acidic conditions.[23] Boerio[24] et al. have studied the structure of APS, not in solution, but deposited on polished iron mirrors. They believe that the five membered ring may exist for thick films several hundred angstroms thick by virtue of an infrared band at 1575cm^{-1}. Thin films, however, gave a 1510cm^{-1} band which was assigned to a symmetric NH_3^+ deformation of a cyclic internal zwitterion structure. Further studies were performed, centered around the analysis of spectra obtained under both dry and moist dehydrating conditions. This led them to propose a new structure[24] consisting of a hydrolyzed oligomer with amino groups hydrogen bonded to silanol groups:

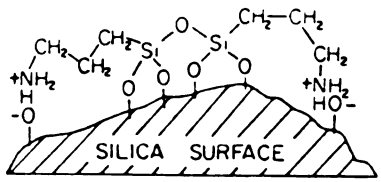


Also at that time, Chiang[25] proposed a similar but monomeric structure for the silane in solution:

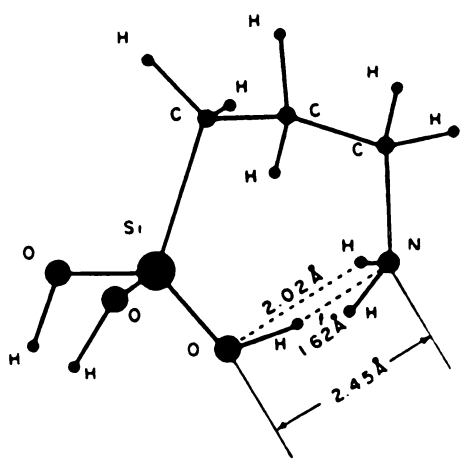


This structure was similar to the one proposed by Moses[26] et al. for APS bonded to the surfaces of SnO_2 electrodes. The Chiang structure was suggested on the basis of changes in the NH_2 deformation stretch in the IR under various heat treatments. Chiang[25] proposes that the dimeric siloxane is

condensed to the surface of the silica, but rather than associated with the silanols, the amino group is associated with other surface hydroxyls as follows:



Plueddemann[27] later agreed that the monomeric structure for APS in solution was consistent with the chemical reactivity of the silanols, but that a structure of that nature would exist as a seven membered ring:



The latest structure for APS deposited on a surface was proposed by Boerio[28] et al. and supported by experimental evidence collected by Naviroj[29] et al. The structure is that of an amine bicarbonate salt which appears to be formed when APS is deposited onto a substrate at natural pH and dried in air. This hypothesis was supported by infrared spectra taken

of the samples dried in nitrogen, carbon dioxide and air. Also in support of this, heating of the surface resulted in detectable loss of CO_2.

In summary, it appears that in acidic solutions, the unusual stability of APS arises from the fact that it takes on a six or seven membered cyclic structure which involves the internal hydrogen bonding of the amino group with one of the silanols. This structure is also responsible for the fact that APS exists chiefly in monomeric form at low concentrations. On the surface of a substrate, APS condenses as a siloxane dimer. Depending upon the drying conditions and substrate, its structure may be that of an amine bicarbonate salt, a cyclic structure with the amine associated with the APS silanols, or one with the amine associated with the surface hydroxyl groups.

Chapter 2

EXPERIMENTAL METHODS

A. Imogolite Synthesis

Imogolite was synthesized according to the method described by Farmer and Fraser.[8] Aluminum tri-sec butoxide (Aldrich) was hydrolyzed in a mixture of 0.10M perchloric acid and deionized water sufficient to give an initial aluminum concentration of 33mM. The amount of perchloric acid used was equal to half the number of moles of aluminum being hydrolyzed. The hydrolysis required from 2 to 6 hours to complete. At this point the solution changed from cloudy to clear in appearance. Deionized water was then added to bring the overall aluminum concentration to 10-30mM. Tetraethylorthosilicate (Aldrich) was added to the hydrolyzed aluminum solution in an amount equal to half the number of moles of aluminum. The mixture was then adjusted to pH 5.0 with 1M sodium hydroxide and immediately acidified to pH 4.0 using 1M acetic acid. The concentration of acetic acid did not exceed the concentration of silicon. The mixture was heated for 2 to 3 days at a temperature of 90-100^{o}C. The final solution was water-clear after heating. Occasionally, a cloudy appearance was observed due to the formation of insoluble products such as gibbsite. These insoluble products were not easily separated from the imogolite. An aliquot removed from the clear reaction product gave a gel

upon addition of 1M ammonium hydroxide, which was indicative of the presence of imogolite. Soluble by-products of the reaction were easily removed by dialyzing the solution for one week in cellulose dialysis tubing (Spectrapor-Spectrum Medical Industries) molecular weight cutoff 12,000-14,000. This treatment yielded suitably pure imogolite for use in subsequent reactions.

B. APS-imogolite Synthesis

A 2% solution of gamma-aminopropyltriethoxysilane (Petrarch Systems) in deionized water was hydrolyzed for half an hour in the presence of enough 1M acetic acid to achieve a pH of 3.5 to 3.7. The solution was water clear. The silane solution was added to a solution of imogolite and the mixture was allowed to stir overnight. The amount of silane added was equal to the aluminum concentration used in the synthesis of the imogolite. Since some soluble by-products were always formed in the imogolite synthesis, the silane was in excess of the amount needed for monolayer coverage.

C. APS-alumina Synthesis

Gamma-aminopropyltriethoxysilane was hydrolyzed as described above. A 0.3% suspension of gamma-alumina, surface area 280m^2/g, (Catapal B, Vista) was adjusted to pH 4.2 with

1M acetic acid. The two solutions were combined and allowed to stir overnight. The amount of silane added was equal to the amount of hydroxyls on the surface of the gamma alumina. The surface hydroxyl group concentration was assumed to be 16.6 OH/100Å^2.

D. Sodium Lauryl Sulfate-imogolite Synthesis

A 0.20% solution of sodium lauryl sulfate (Fisher) in deionized water (below the critical micelle concentration of 8.34 X 10^{-3} mole/l) was prepared and the pH was adjusted to 4.3 by the addition of 1M acetic acid (a few drops). This was added to a solution of imogolite prepared as outlined above. The number of moles of sodium lauryl sulfate added equaled the number of moles of aluminum used in the original imogolite synthesis. Since imogolite was not formed in 100% yield, the amount of sodium lauryl sulfate was in excess of that needed to form a monolayer. The solution was stirred overnight and then dialyzed for one week to remove excess sodium lauryl sulfate. The imogolite was then present as a flocculated mass.

E. Fourier Transform Infrared Spectroscopy

The FTIR instrument used to obtain vibrational spectra was an IBM model IR 40S with an IBM AT workstation equipped with IR44 software. All IR specimens were KBr pellets containing 2 weight percent of the air-dried samples. The

KBr (Mallinkrodt) was spectroscopic grade. The 13mm pellets were made by pressing 0.04g of powder under 20,000psi for ten seconds.

F. MAS ^{29}Si NMR

The instrument used to obtain solid state NMR spectra was a Bruker WH-180 equipped with Nicolet NTCFT-1180 computer software and Doty solid state probe spinning at the magic angle of $55^{o}44'$. Air-dried samples were packed into sapphire rotors and spun at a rate of 3.5-4.2kHz. Chemical shifts were obtained by setting a talc peak equal to the literature value of -78.1ppm with respect to TMS. Pulse width (P2) is set equal to 6.0 usec and relaxation delay (D5) is set equal to 2.0 sec for each sample.

G. Time Dependent Dialysis Experiment

Aqueous suspensions of silylated imogolite, silylated gamma-alumina and hydrolyzed gamma-aminopropyltriethoxysilane were prepared as described above. Each mixture contained the same amount of silane. Thirteen dialysis membranes were made for each of the three systems studied, each membrane containing 25mls of solution. The membranes were placed in 5-liter buckets of deionized water. A membrane was removed every two hours for the first eighteen hours, and at longer intervals thereafter. Each time a sample was removed, the deionized water was replaced. The samples were removed from

the membranes and air-dried. Samples of the initial solutions (25ml) were also air-dried. Infrared spectra were obtained for each of the samples collected, except for the pure silane. The weights of each of the air-dried silane samples collected were determined by difference.

H. Elemental Analysis

Carbon and hydrogen analysis was done by Galbraith Laboratories in Nashville, Tennessee. Silicon and aluminum analysis was done at the inorganic chemistry laboratory of the Department of Toxicology at Michigan State University. The analysis was done on a Jarrell-Ash 955 Atom-Comp instrument. J.T. Baker instra-analyzed grade standards were used. NBS plastic clay 98a served as a clay reference. Samples were prepared by mixing 0.025g of sample with 0.150g lithium borate (Aldrich, Gold Label) in a carbon crucible and heating to 1000^{o}C for 12 minutes. The resulting melt was immediately transferred to a mixture of 20mls 6% hydrochloric acid and 20mls 6% nitric acid and stirred for fifteen minutes. This solution was diluted to 100mls and submitted for analysis.

Chapter 3

RESULTS AND DISCUSSION

A. Imogolite Synthesis

Prior to this investigation, imogolite was regularly synthesized by a method similar to the one reported in the experimental section of this thesis, but the success rate was extremely low. Some somewhat subtle, but important changes have since been made to render the current synthesis method quite reliable. The most important of these changes was a reduction of the concentration of Al in the final solution from 60mM to 30mM. Because the synthesis of imogolite is the result of a nucleation process, the overall concentration of reactants in solution play an important role in determining what products will be formed. Higher reactant concentrations lead to the formation of insoluble products in addition to the desired product imogolite, as evidenced by the cloudy appearance of the reaction mixture after refluxing. As may be expected, the concentrations of other ions in solution also have a marked effect upon the imogolite nucleation process. Perchlorate ion, from the perchloric acid used to hydrolyze the aluminum tri-sec-butoxide will inhibit imogolite formation if present in concentrations greater than that of silicon. The presence of dissolved salts and phosphate ion[30] have also been found to decrease the yield of imogolite, as determined by the height of the gel formed when

NH_4OH is added to a volume of imogolite solution in a test tube and centrifuged. Acetate ion, on the other hand, in quantities no greater than that of the silicon concentration seems to be necessary for the formation of imogolite under laboratory conditions. The final determining factor for successful imogolite synthesis is pH. Allowing the pH to increase beyond 5.0 will promote the formation of insoluble products. Successful imogolite synthesis results in a drop in pH during the reflux step. Even under ideal conditions, some soluble products are formed along with the imogolite. These soluble products can easily be removed through dialysis of the contents of the entire reaction vessel against deionized water for approximately one week. These products have a much lower molecular weight than the imogolite and pass easily through the pores in the tubing. After dialysis, what remains is pure imogolite in solution. The imogolite remains stable over long periods, but after nine to twelve months precipitation can be seen to occur even in dilute samples.

B. Characterization of Imogolite

Once the synthetic procedure has been carried out, the first step is to determine whether a portion of the product gels upon addition of 1M NH_4OH. Gelation is indicative of

the presence of imogolite. The next step is to dialyze the solution. Further characterization includes MAS ^{29}Si NMR, electron microscopy and FTIR.

FTIR is the fastest and easiest method of characterization. Representative spectra of both dialyzed and non-dialyzed samples are shown in figure 3. Both spectra have prominent water peaks at around 3500cm^{-1} due to the OH stretch and 1630cm^{-1} from the HOH bending vibration. Substantial differences appear in the lower wavenumber region of the two spectra. The dialyzed sample contains the two peaks characteristic of the Si-O-Al vibrations in imogolite, one at 995cm^{-1} and the other at 940cm^{-1}. These peaks are consistent with the presence of isolated orthosilicate units in imogolite. That same region in the non-dialyzed sample however, shows a peak at 943cm^{-1} and two large peaks at 1143cm^{-1} and 1090cm^{-1}. The small peak is due to imogolite, but the absorbances at wavenumbers greater than 1000cm^{-1} are due to Si-O-Si vibrations. It is easy to identify these peaks with impurities because there are no Si-O-Si bonds in the imogolite structure. There is only one additional peak that differs widely between the two spectra. This one is sharp and falls at 630cm^{-1}. This peak is attributed to the COO^- vibration of the acetic acid that is added during synthesis. From this analysis it becomes clear that dialysis is essential in order to obtain imogolite in absence of soluble impurities. The FTIR spectrum of imogolite seems

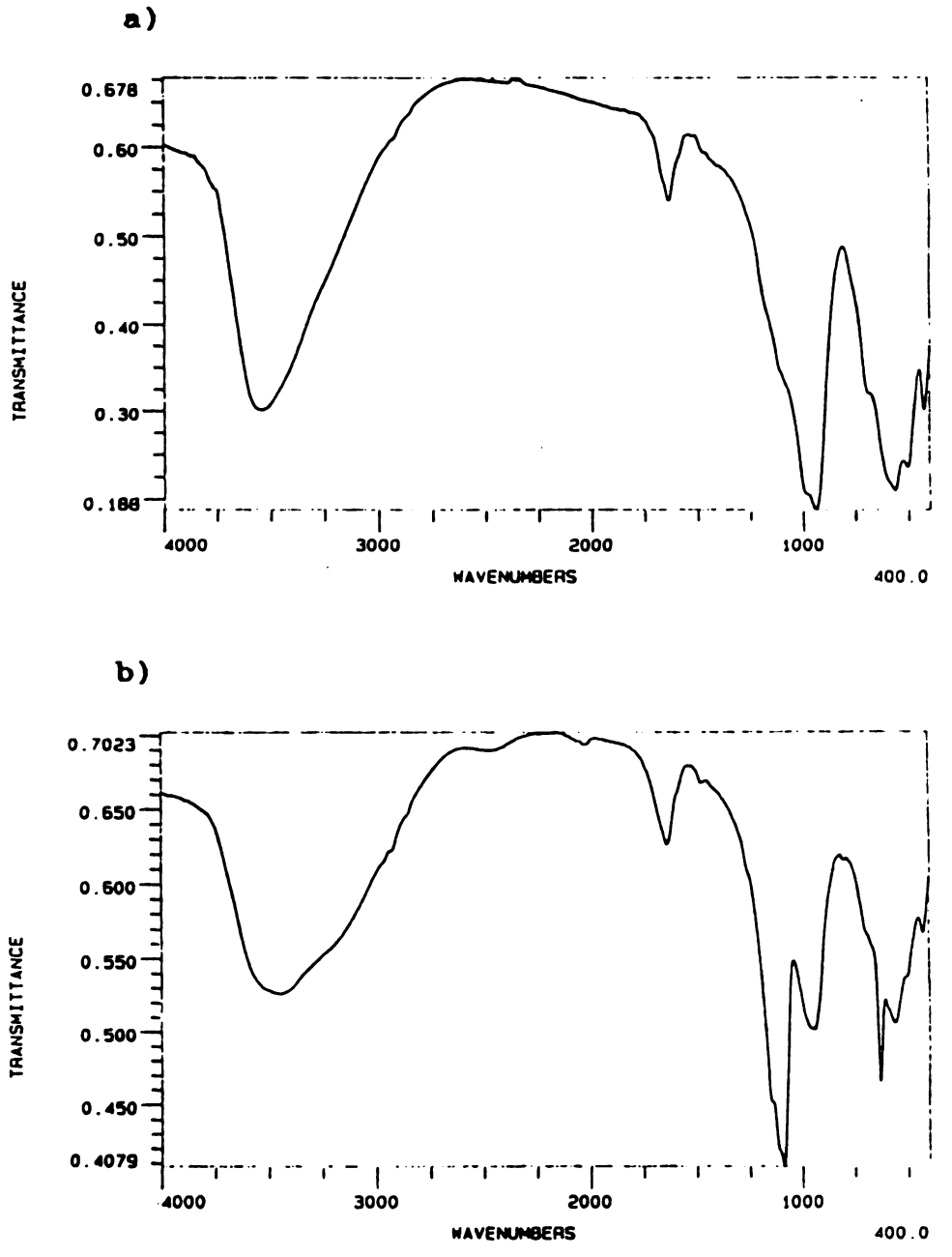


Figure 3 IR spectra of a) Dialyzed imogolite. b) Non-dialyzed imogolite.

almost too simple to satisfactorily identify imogolite. But in the region from 900-1000cm^{-1}, the ability to detect two separate peaks is unique to imogolite. For example, in allophane, another aluminosilicate found with imogolite in nature, there is only one broad peak observable in that region. In fact, the degree of definition achieved between the two peaks is an indirect measure of how well-formed the tubes are in the sample. Another peak, not shown in these spectra, can be found at 348cm^{-1}. This medium intensity band is convenient for differentiating between allophane and imogolite because it is absent in allophane. It is present in other ordered aluminosilicates such as montmorillonite, however.

Another useful means of imogolite characterization is MAS ^{29}Si NMR. This is somewhat less convenient both because large amounts of sample and large blocks of time on the instrument are needed as a result of the low silicon content of imogolite. The spectrum is a singlet at -79 ppm with respect to TMS. The singlet is due to the isolated orthosilicate units which correspond to a Q^{o} site.

C. APS-imogolite Synthesis

Retaining imogolite in its non-agglomerated state in solution during this reaction was desired. As has been mentioned previously in this thesis, imogolite begins to flocculate above pH 7, so acidic pH synthesis conditions were

necessary. APS exhibits a pH of 10.0 in aqueous solution so acidification was necessary during the prehydrolysis step in the coupling reaction. The acidic conditions proved to be beneficial in two additional ways. Hydrolysis of the ethoxy groups is accelerated in acidic environments and the aminofunctional group is protonated. Since the silanol groups have an isoelectric point at pH 2-3, it is likely that a negative charge is associated with the silanol. The amino functionality is expected to be positively charged in the pH range 3-6.[27] Therefore, at pH 4 the positive external charge on the imogolite tubes will assist in preferentially orienting the silane on its surface by repelling the positively charged amino group and attracting the negatively charged silanols. Acetic acid was chosen to adjust the pH because of its use in imogolite synthesis. The tubes can tolerate exposure to it without any adverse effects.

The quantity of coupling agent needed in the reaction proved to be difficult to determine. As was indicated previously, only indirect methods of determining imogolite yield are possible. A useful indirect method involves the measurement of the height of a gel formed by raising the pH of a standard volume of solution. This method fails to allow subsequent calculation of the amount of coupling agent needed in the reaction. The procedure adopted to circumvent this problem was to use the concentration of aluminum from the imogolite synthesis for the calculation of the amount of

coupling agent needed in the silylation reaction. Because the yield of imogolite is never 100%, this method results in the use of excess coupling agent. There are 1.5 hydroxyls available for each aluminum on the external surface of imogolite and three silanols for every mole of APS. Thus for an aluminum to APS ratio made equal to one, there is a two-fold excess of coupling agent. This ratio should provide sufficient APS for monolayer coverage where every surface hydroxyl is condensed with a coupling agent silanol.

Once the reaction has been completed, a new problem arises. How can unreacted silane, present as a result of the addition of excess coupling agent, be separated from the silylated imogolite? Filtration is not possible because the tubes are too small. Dialysis was the obvious choice because of its utility in the purification of imogolite from soluble synthetic byproducts. After dialysis of the reaction mixture for several days, no trace of coupling agent could be found in the FTIR! This revelation lead to the subsequent quantitative study of the hydrolysis reaction of the silylated imogolite and in attempts at stabilizing the product.

D. Characterization of APS-imogolite

Silylated imogolite has been characterized by MAS ^{29}Si NMR, elemental analysis and FTIR.

The FTIR spectra of APS polymerized by air-drying on a glass slide is shown in figure 4(a). Table 1 lists some typical IR stretches and the frequencies at which the vibrations occur. The peak at 3370cm^{-1} is due to the N-H stretch, the one at 2932cm^{-1} is the CH_2 stretch. The peak at 1580cm^{-1} is due to NH_2, at 1484cm^{-1} due to NH_3^+, 1336cm^{-1} a CH_2 bend, 1131cm^{-1} and 1028cm^{-1} are due to Si-O-Si stretches, and 930cm^{-1} is attributed to Si-OH. The weak band at 2150cm^{-1} has been assigned to an NH_3^+ combination band vibration.

When an IR is takcn of a sample consisting of APS reacted with imogolite as described in the experimental section of this thesis, several things can be noted. Figure 6(a) is a spectrum of a two to one ratio of APS to aluminum in imogolite calculated in the usual way. There are two peaks present just above 1000cm^{-1}. One peak is at 1127cm^{-1} and the other occurs at 1033cm^{-1}. Identification of these two peaks indicates the presence of a network of highly polymerized silane covering the imogolite tubes. A monolayer of individual silanols and dimers would have been represented by a single peak near 1016cm^{-1}.[25] The polymerization of the silane on the surface is controlled in part by the conformation of the APS on the surface. Polymerization of the silane on the surface is prohibited in the same way as it is prevented in solution, that is, through hydrogen bonding between the NH_2 functionality on the silane and a hydrogen,

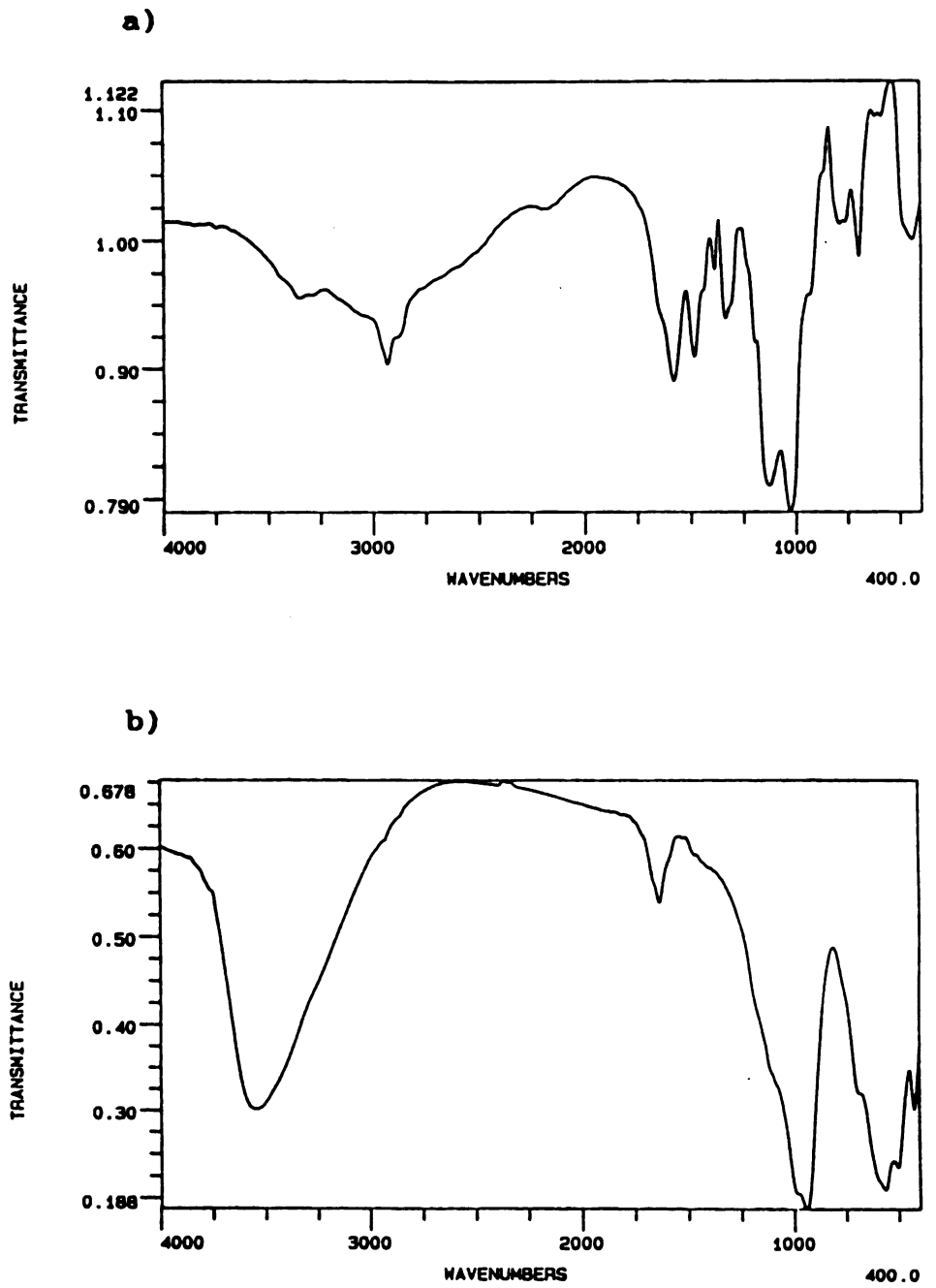


Figure 4 IR spectra of a) Air dried APS. b) Air dried imogolite.

Table 1. IR active vibrations and their frequencies

Functional Group	Frequency (cm^{-1})
N-H stretch	3370 to 3390
CH_2 stretch	2928 to 2932
HCO_3^-	1630 and 1332
NH_2 bend	1550 to 1600
NH_3^+	1470 to 1492
Si-CH_2 bend	1410 to 1412
Si-O-Si stretch	1000 to 1130
Si-O-Al	990 and 940
Si-OH	930
COO^-	630

either on the surface or on one of the silanols. The presence of strong IR bands at 1480cm^{-1} and 1550cm^{-1} to 1575cm^{-1} (NH_3^+) signify the presence of such bonding, although the exact nature of these bands is still the subject of current debate in the literature. These assignments are based upon studies of thin films of APS on polished iron mirrors[24] in dry atmosphere and of APS deposited on high surface area silica gel.[25] The silane on the silica gel is actually stabilized by hydrogen bonding to the anionic surface hydroxyls characteristic of that surface. The silane on the iron mirrors is believed to contain intramolecular hydrogen bonds between NH_2 and a silanol hydrogen. This hydrogen bonding is extremely sensitive to exposure to atmospheric moisture. It is believed that the slightly acidic effect of water vapor in the presence of carbon dioxide causes disruption of this hydrogen bonding. This is indicated by the IR spectra of samples aged under atmospheric conditions. The 1480cm^{-1} peak disappears and the 1550cm^{-1} peak increases to 1585cm^{-1} (which approaches the 1585cm^{-1} peak observed for the free NH_2 vibration in polymerized APS.) Deposition of silane under basic conditions (pH 12) results in a subsequent decrease in the intensity of the 1480cm^{-1} band after prolonged atmospheric exposure. In addition, those films deposited at lower pH (9.1) or exposed to the atmosphere for long periods of time showed a shift of the Si-O-Si stretch to higher wavenumbers, from 1105cm^{-1} to

1130cm^{-1}, indicating that in the absence of hydrogen bonding the APS films were more highly polymerized. Both of these results were attributed to the weakening of the hydrogen bonding between the NH_2 and the silanol protons. Elsewhere, aminosilanes have been shown to form an amine bicarbonate salt when exposed to moisture and CO_2.[20] Salt formation would also explain the higher degree of polymerization because the NH_2 is no longer associated with the silanol.

Because the APS-imogolite system is adjusted to a pH of 4 through the addition of acetic acid, it is expected that the protonated aminofunctionality will have little affinity for the protonated imogolite surface hydroxyls. Under these conditions, it is very likely that the amine remains fully protonated after condensation of the silanols to the imogolite surface. Silane deposition onto the iron mirrors and the high surface area silica, to which the results obtained here are being compared, is performed at pH 9-12. The surface coverage obtained in these experiments is also much lower than the surface coverage obtained in this study. Both pH and degree of surface coverage severely effect the conformation adopted by the silane on the surface. It is not surprising, then, that there are both similarities and differences in the infrared spectra obtained here and in these other studies. In the 1600cm^{-1} to 1400cm^{-1} region in particular, the spectral bands obtained in all three cases are similar in number and relative intensity. The difference

arises in the frequency at which the bands occur. A shift in the 1580cm^{-1} band to lower wavenumbers is associated with the presence of hydrogen bonding between the amine and surface hydroxyl or silanol hydrogens. Weakening hydrogen bonding of this type in the iron mirrors as described above, was accompanied by a weakening or disappearance of the band at 1480cm^{-1}. In the APS-imogolite system, the band at 1580cm^{-1} is shifted between 1564cm^{-1} and 1572cm^{-1}. The 1480cm^{-1} band, however is shifted between 1410cm^{-1} and 1414cm^{-1}! The Si-O-Si region contains stretches at 1127cm^{-1} and 1033cm^{-1} suggesting a large degree of polymerization on the surface. Combination of the above data provides evidence for the presence of an amine salt on the surface of imogolite under air-dried conditions. Acetate is the probable anion for the protonated amine. The presence of a sharp band at 650cm^{-1} is analogous to the band detected in the non-dialyzed imogolite sample at 630cm^{-1}. The sharp band present in the IR of the original polymerized APS spectra is also present in the APS-imogolite sample at 680cm^{-1}, so the 650cm^{-1} band is not characteristic of pure APS. The large degree of polymerization is due to the lack of protection of the silanols by amine hydrogen bonding as a result of the NH_3^+ being associated with the acetate anion. The decrease in the frequency of the NH_3^+ band may be due to the presence of fully protonated amine species.

These observations collectively support the assumption that there is a direct interaction between imogolite and APS. But because these IR spectra are taken of samples dried from the reaction vessel, it is desirable to show that there is an interaction between the APS and imogolite, and to dispel the possibility that the spectra obtained may be the same as if the residue from the reaction were just a mixture of APS and imogolite powders. This was done through the analysis of spectra obtained by digitally subtracting the imogolite spectrum from each of four spectra. The four spectra represent the patterns obtained from reaction mixtures of four different mole ratios of APS to Al: 0.5 to 1.0, 1.0 to 1.0, figure 5, and 2.0 to 1.0, 2.5 to 1.0, figure 6, calculated in the usual way. The resultant spectra after the subtraction process are shown in figures 7 and 8.

Shifts in the placement of the bands can be seen in the unprocessed spectra in the 1200cm^{-1} to 1400cm^{-1} range by noting that a band, initially a shoulder on the Si-O-Si peak, becomes isolated and then becomes a shoulder on the 1410cm^{-1} peak as the concentration of APS increases. At low concentrations of APS a higher value is obtained in the 1570cm^{-1} range. The region of interest in the subtracted spectra is around 1140cm^{-1}. This peak is the Si-O-Si stretch arising from the self condensation of hydrolyzed APS units. Recall that there are no Si-O-Si bonds present in the imogolite structure. In each of the four resultant spectra

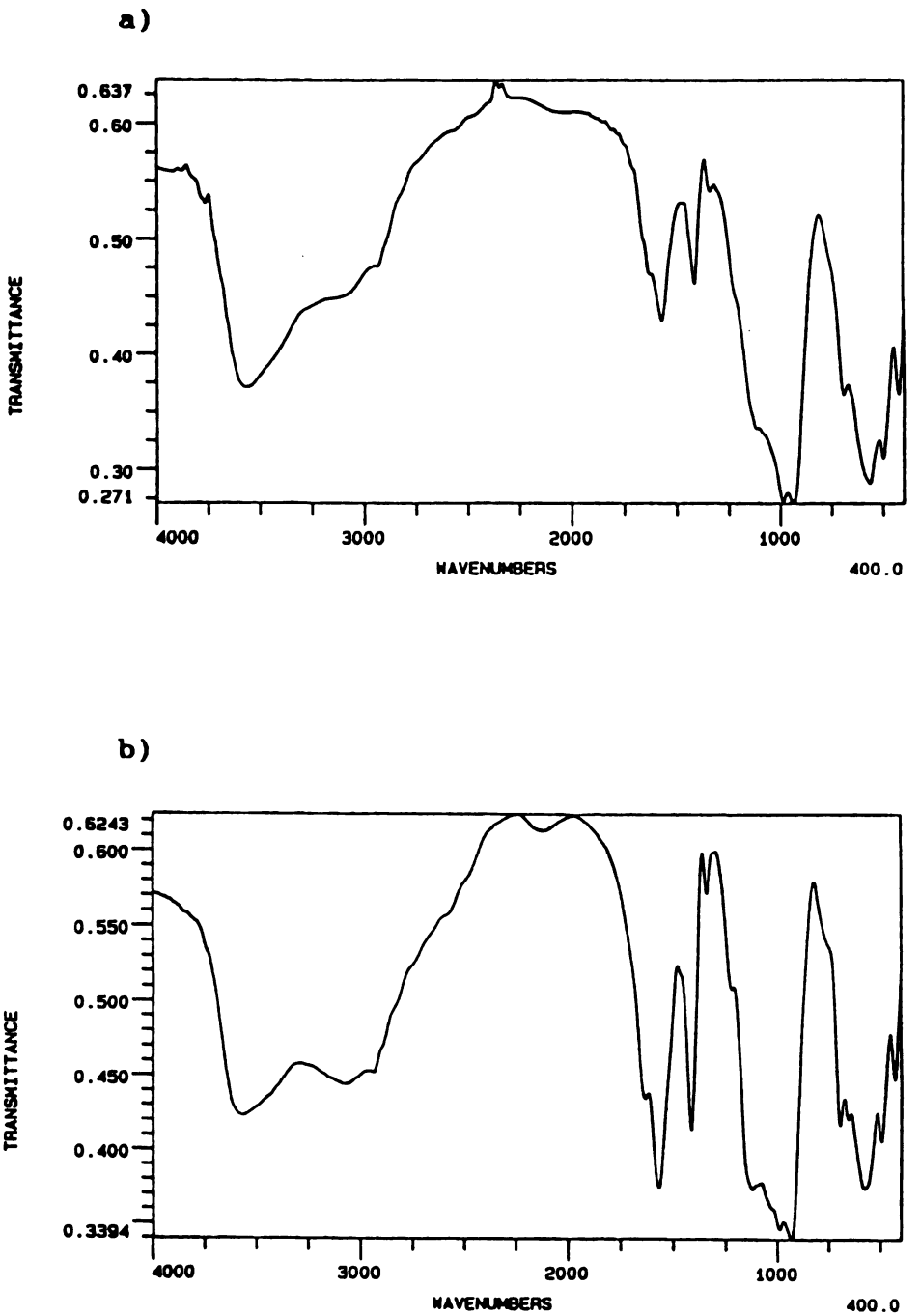


Figure 5 IR spectra of APS-imogolite samples containing the following APS to Al mole ratios: a) 0.5 to 1.0 b) 1.0 to 1.0.

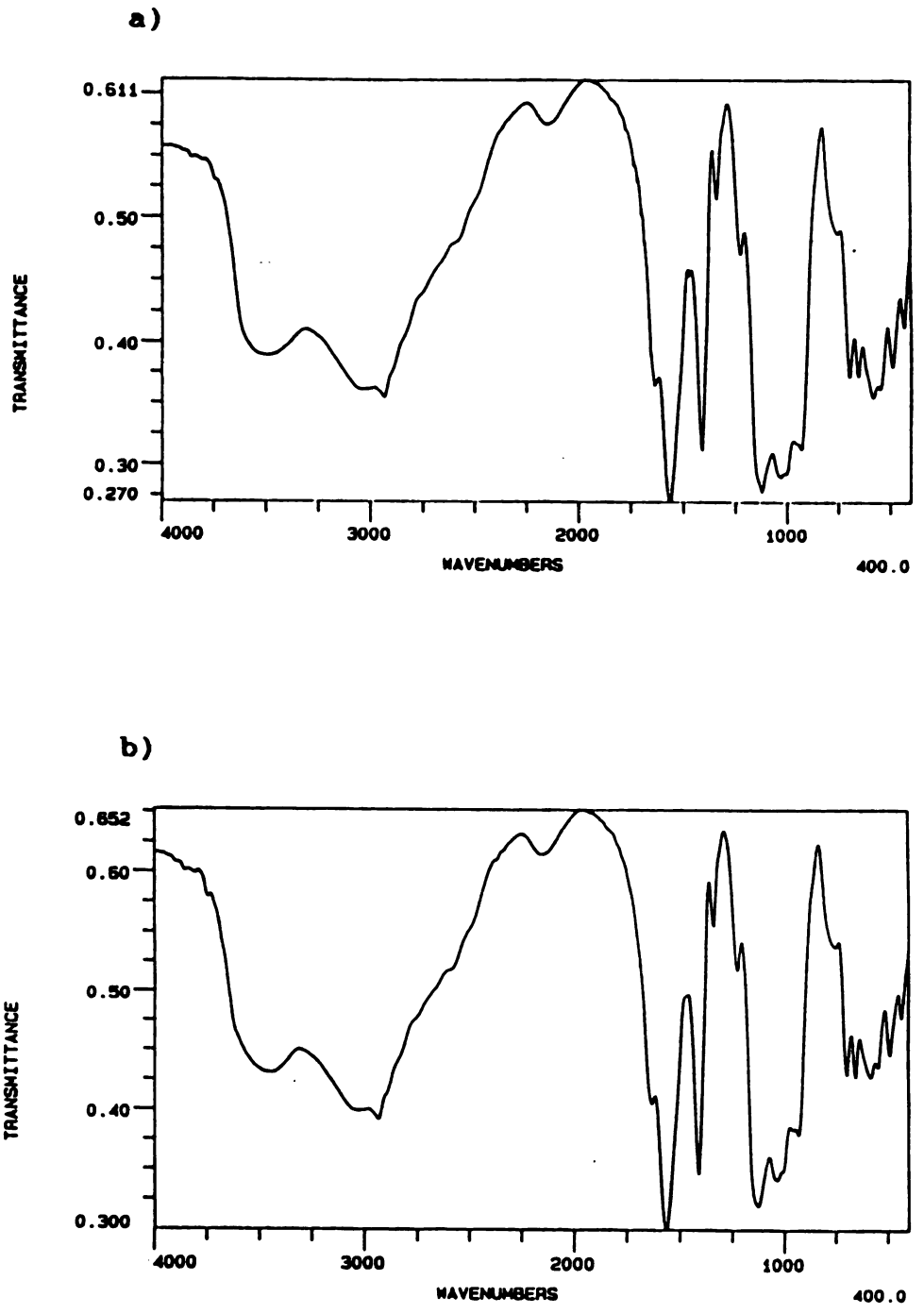


Figure 6 IR spectra of APS-imogolite samples containing the following APS to Al mole ratios: a) 2.0 to 1.0 b) 2.5 to 1.0.

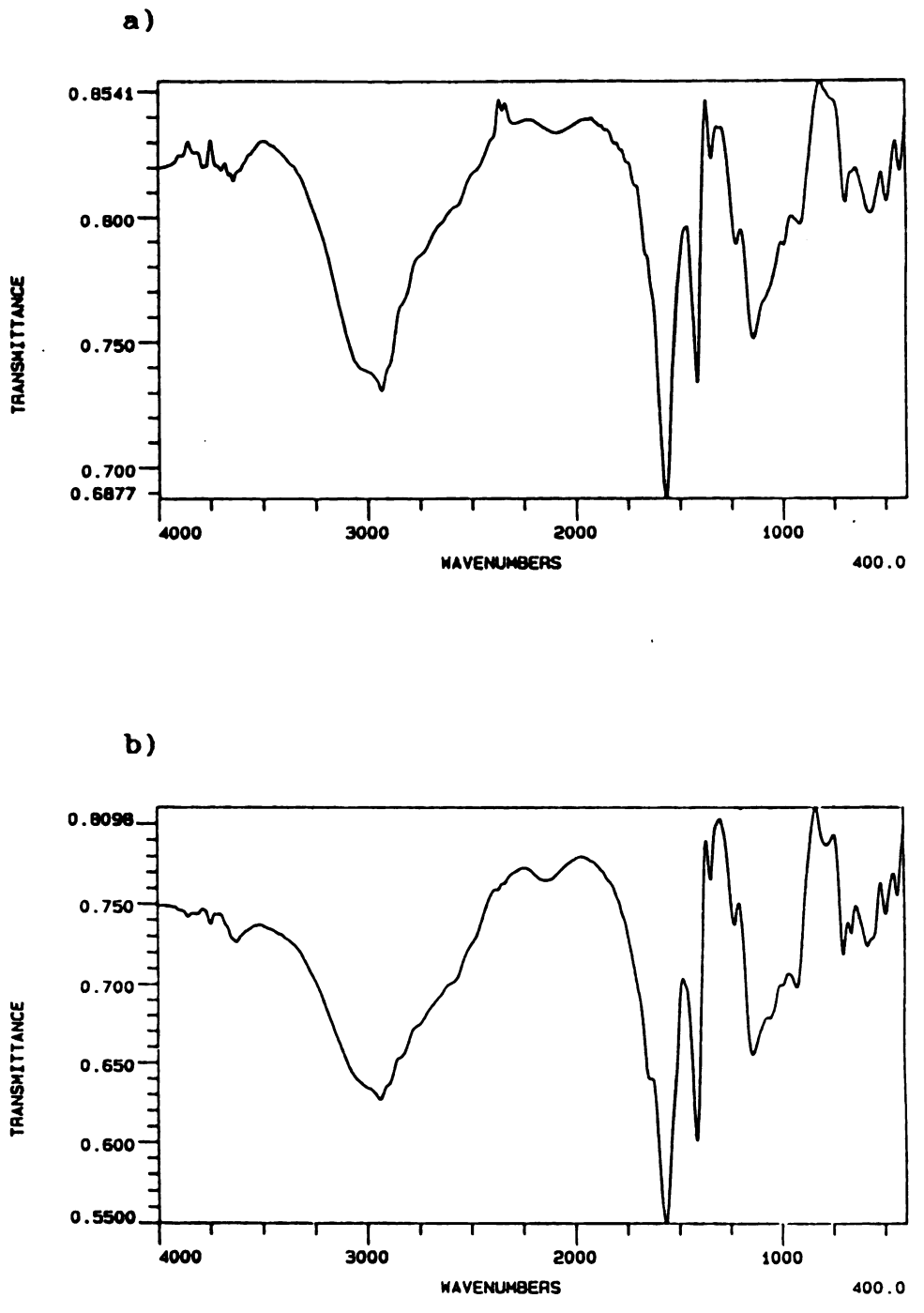


Figure 7 IR spectra resulting from the subtraction of a pure imogolite spectrum from the spectra in figure 5. APS to Al mole ratios a) 0.5 to 1.0 b) 1.0 to 1.0.

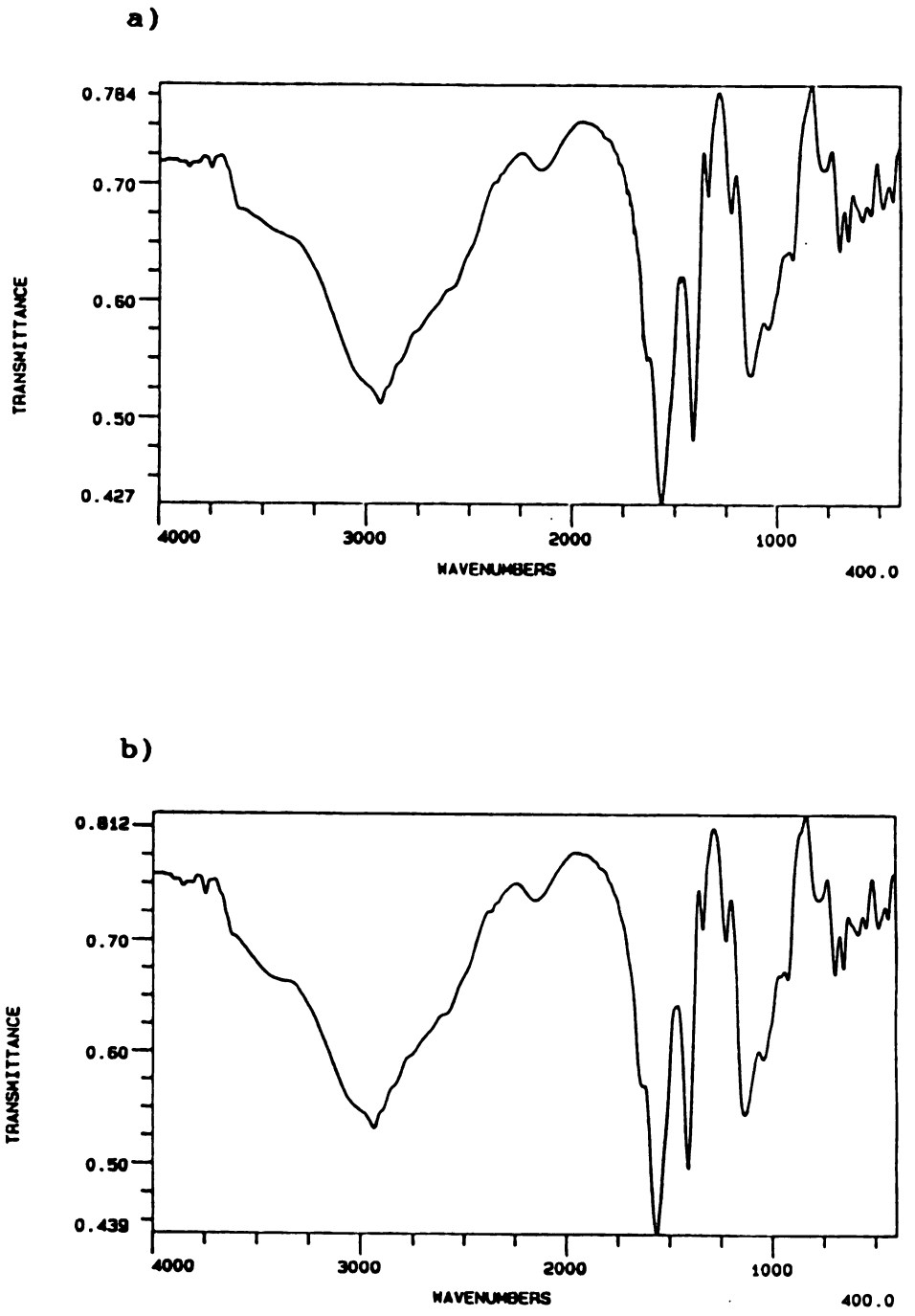


Figure 8 IR spectra resulting from the subtraction of a pure imogolite spectrum from the spectra in figure 6. APS to Al mole ratios a) 2.0 to 1.0 b) 2.5 to 1.0.

this Si-O-Si band is shifted to lower wavenumber with increasing concentration of APS. Table 2 gives a list of concentration ratios versus the wavenumber observed for the Si-O-Si stretch. The value for pure polymerized APS is also included. The $12cm^{-1}$ shift from $1131cm^{-1}$ in the pure polysilane to $1143cm^{-1}$ in the 0.5:1.0 mole ratio APS to Al sample is expected to be significant on a FTIR with a resolution of $2.00cm^{-1}$. A measure of the consistence achieved on the instrument for the CH_2 stretch at $2929cm^{-1}$ to

Table 2. Si-O-Si stretching frequency vs. APS concentration

MOLE RATIO APS:AL	FREQUENCY (cm^{-1}) Si-O-Si Stretch	FREQUENCY (cm^{-1}) CH_2 Stretch
pure APS	1131.4	2932
2.5 to 1.0	1137.2	2929
2.0 to 1.0	1137.0	2932
1.0 to 1.0	1141.0	2932
0.5 to 1.0	1143.0	2929

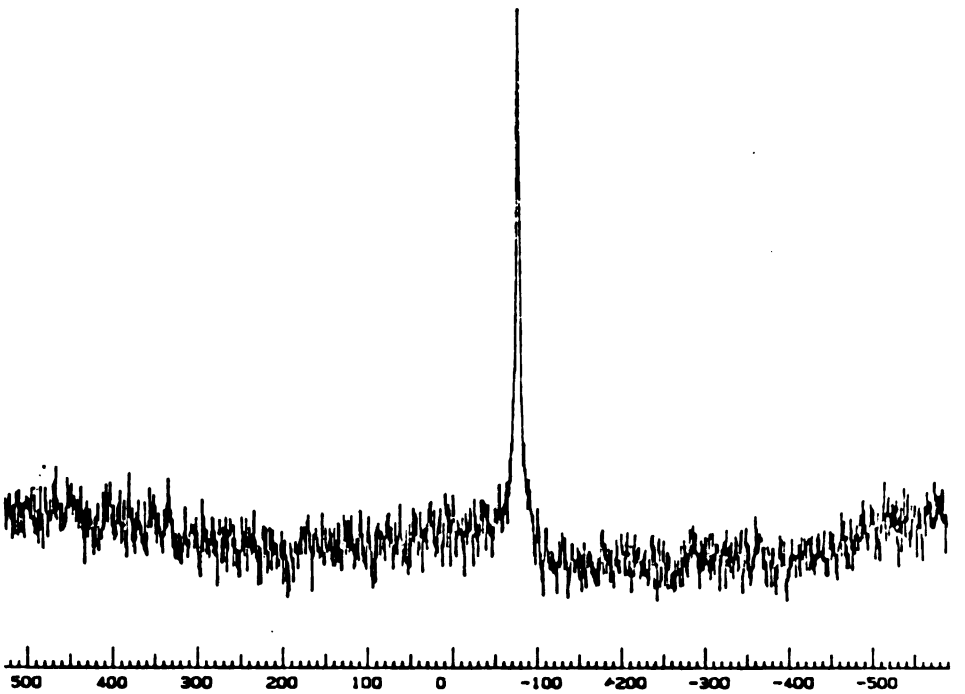
$2932cm^{-1}$ is included in the table. The shift in the Si-O-Si peak to lower wavenumber with increasing concentration of APS requires explanation. It is believed that the shift in the Si-O-Si stretch is being caused by the increasing amount of Si-O-Al character nearby as a result of the partial condensation of the polymerized APS to the Al-OH sites on the surface of imogolite. At high concentrations of APS, the bulk Si-O-Si signal will show essentially polysilane

character because all of the imogolite surface sites will be occupied by silane and the remaining silane will be forced to polymerize with the APS already on the surface. The APS far from the surface of the imogolite will be essentially identical to the pure polysilane. The Si-O-Si band due to APS close to and bonded to the imogolite surface, however, will be strongly affected by the presence of the nearby Si-O-Al bonds and, therefore, at lower concentrations of silane a larger shift in the band resulting from the Si-O-Si vibration would be expected. Unfortunately, the IR pattern of imogolite consists largely of Si-O-Al bands, so simply looking for the presence of peaks in the Si-O-Al portion of the spectrum is not a viable test for imogolite-coupling agent interaction. Even with spectral subtraction capabilities it is difficult to remove the substrate signals completely because of concentration differences between the two spectra being subtracted. The direction of the shift is also consistent with this model. The frequency (v) of a vibration in the IR $v \propto \sqrt{k/u}$, where k is the force constant and u is the reduced mass. When Si-O-Al begins to enter into the Si-O-Si vibration the reduced mass is lowered, increasing the frequency of the vibration. Since frequency is directly proportional to wavenumber, the wavenumber of the observed vibration should also increase. As the concentration of APS

decreases, the Si-O-Si peak increases in wavenumber, as predicted by an increase in aluminum character due to nearby Si-O-Al bonds.

Further evidence for interaction has been obtained through MAS ^{29}Si NMR spectroscopy. Figure 9(a) shows the ^{29}Si NMR spectrum of pure imogolite. It consists of a single peak located at -79.3ppm with respect to TMS corresponding to a Q^0 site. The next spectra, figure 9(b) is that of air-dried APS. This consists of three peaks, Q^1 at -50.9ppm, Q^2 at -60.3ppm and Q^3 at -68.6ppm with respect to TMS. Typical structural representations of each of these sites are shown in figure 10. The last spectra, figure 11, is that of a mole ratio 0.5:1.0 APS to Al mixture of APS and imogolite. Three peaks are observed here. The peak at -79.7ppm corresponds to imogolite. The two peaks at -69.7ppm and -61.0ppm are due to the silane. The difference between the individual APS and imogolite spectra and that of the APS-imogolite system lies in the absence of the -50.9ppm peak in the mixture. The presence of imogolite seems to cause the Q^1 sites, those corresponding to end groups in the polymer chain, to disappear. The continuous nature of the tubular imogolite surface may allow for a more continuous polymer network to form in the presence of imogolite. The conformation of the APS on the surface of imogolite may also promote crosslinking, leaving fewer oxygen sites uncondensed, transforming Q^1 sites to Q^2 and Q^3 sites.

a)



b)

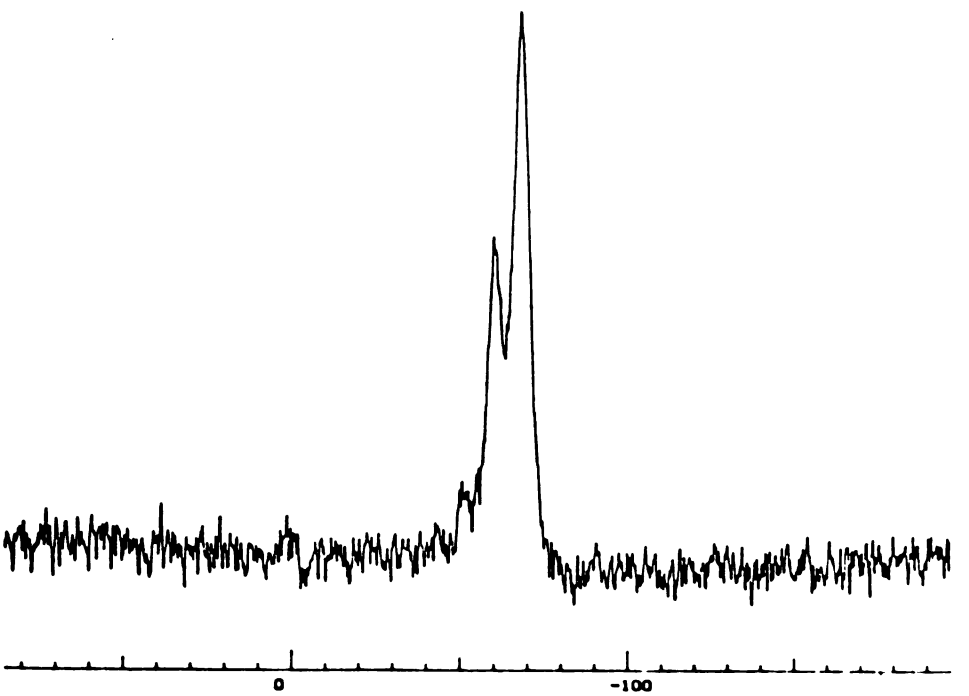


Figure 9 **^{29}Si MAS NMR of a) Air-dried dialyzed imogolite and b) air-dried APS, with chemical shifts reported with respect to TMS.**

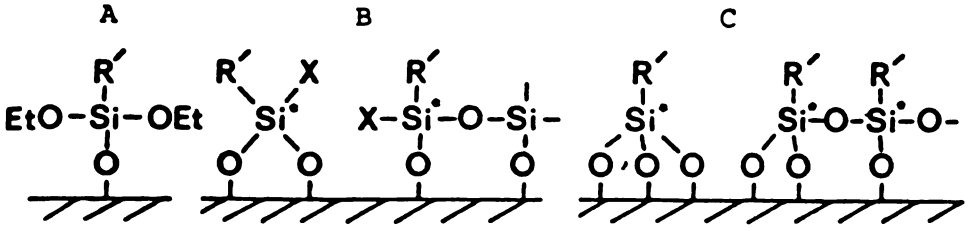


Figure 10 Structural models illustrating the molecular bonding at the silane/silica interface. a) Q^1 site b) Q^2 site c) Q^3 site.

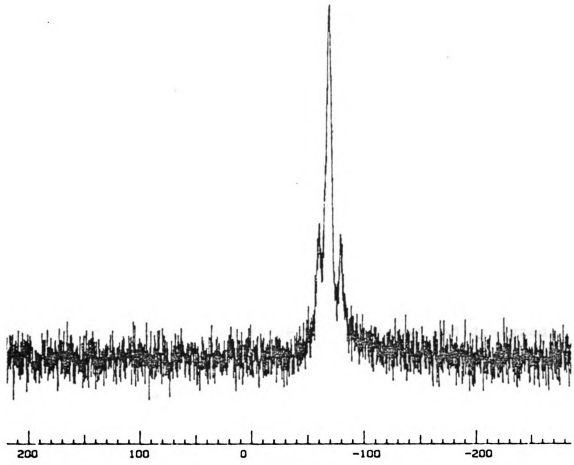


Figure 11 ^{29}**Si MAS NMR of air dried APS-imogolite with mole ratio 0.5APS to 1.0Al.**

The combined results from the IR and MAS ^{29}Si NMR studies support the conclusion that APS is bonded to the surface of imogolite. The fact that the APS can be completely removed by dialysis of the aqueous solution of APS and imogolite suggests that the resulting bond is hydrolytically unstable.

Attempts at forming a more stable bond by altering synthetic procedures proved to be unsuccessful. The mixture was air-dried, to allow maximum APS-imogolite contact, then resuspended in deionized water and dialyzed. The APS completely disappeared. The mixture was air dried, heated to 120^{o}C for twenty four hours to drive out water adsorbed on the surface, resuspended in deionized water and dialyzed. This treatment appeared to prolong the process of APS removal, but the APS was still reversibly bonded. The APS-imogolite solution was heated at various temperatures overnight with no change in the resulting IR spectra.

This additional data coupled with several reports from the literature by Borisov[31] of acid catalyzed hydrolysis, suggest strongly that hydrolysis is the cause of the instability of the APS modified imogolite. Although Si-O-Al hydrolysis was responsible for the degradation of the APS-imogolite system, it can be used to study the hydrolysis rate.

E. Time Dependent Dialysis Experiment

Once it had been determined that the Si-O-Al bond between imogolite and APS was hydrolytically unstable, it became apparent that this system was ideally suited for a semi-quantitative study of the siloxy alumane hydrolysis rate. An experiment was subsequently designed to compare the rate of hydrolysis of the alumasiloxane bond of the APS-imogolite system to that of the APS-gamma alumina system. The bonding in both systems occurs between APS and surface aluminum hydroxyls. The major difference between alumina and imogolite are the surface area, (280 vs. 900 m^2/g), respectively and the number of hydroxyls per $Å^2$ (16 vs. 18 $OH/100Å^2$), respectively. There is also the fact that the imogolite surface is curved while the gamma-alumina surface is planar. In addition, the crystallinity of gamma-alumina is less than that of imogolite.

The experiment entails dialysis of three different systems for a period of 50 hours: APS-imogolite, APS-alumina and APS in aqueous solution. IR spectra of the imogolite and alumina substrates are shown on figure 12. Details can be found in the experimental section of this thesis. Samples of APS-imogolite and APS-alumina were taken at various intervals during the dialysis, dried and analyzed by Fourier Transform Infrared Spectroscopy. Since the APS passes readily through the dialysis tubing, the rate of diffusion of APS from solution was monitored by weighing the amount of APS

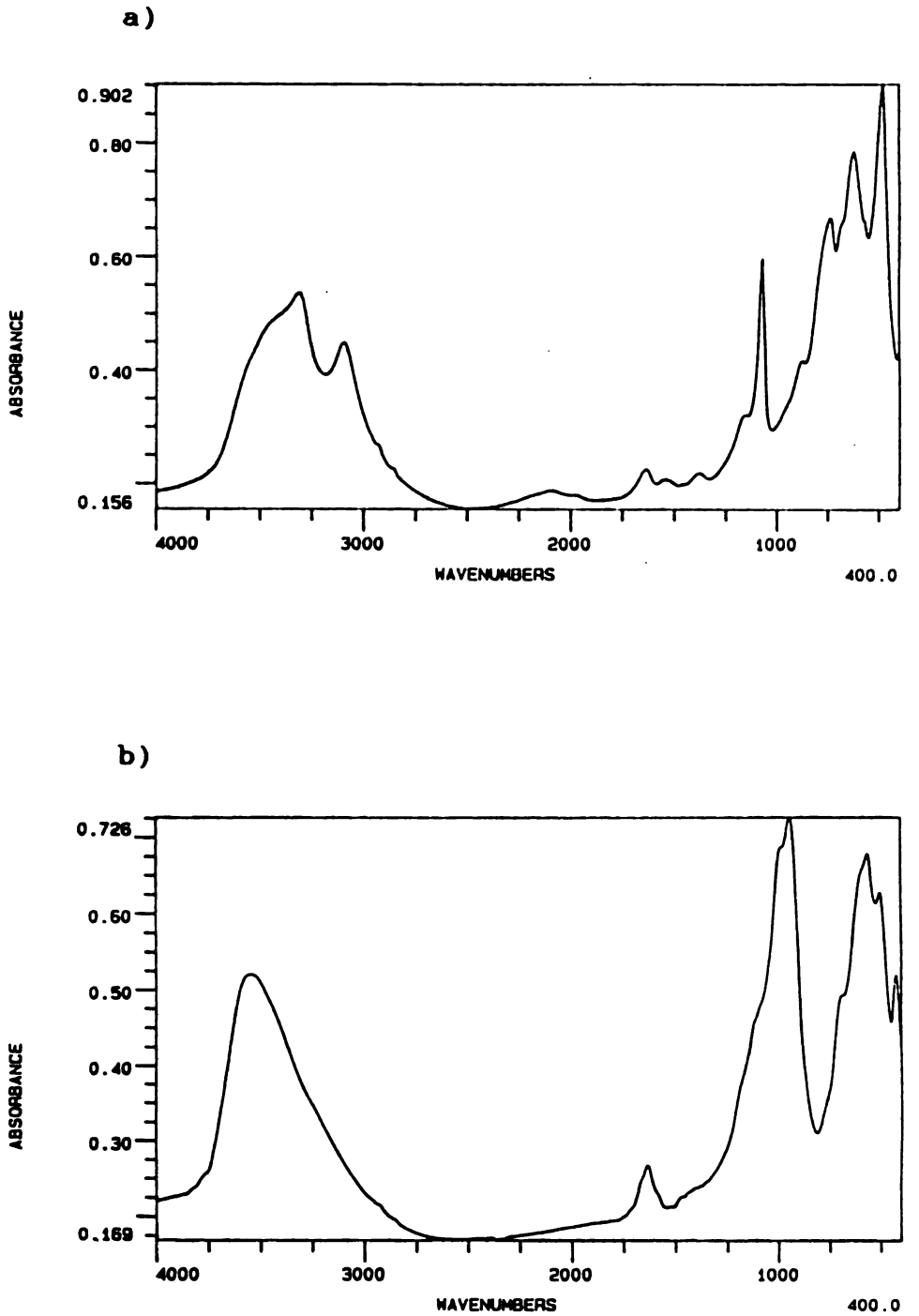


Figure 12 IR Spectra of a) Gamma-alumina b) air-dried imogolite.

recovered as a solid at each sampling. The individual weights were converted to percent APS values by setting equal to 100% the number of grams of solid obtained by air drying the first sample.

For the APS-alumina and APS-imogolite, the conversion from absorbance to percent APS was more complex. Absolute solution absorbances were unacceptable measures of concentration because of the irreproducibility of the KBr pellets. Solution state spectra were not useful because of difficulties in keeping the gamma-alumina particles suspended and because of the low concentrations of APS being used. Imperfect mixing of components and different pellet thicknesses were the major factors attributing to the poor reproducibility of the pellets. To overcome this problem, ratios of the absorbances of spectral bands due specifically to the substrate and to APS were used to determine the concentration of APS in each of the samples. IR spectra of the initial APS-alumina and APS-imogolite samples are shown in figure 13. In the APS-imogolite system the APS peak at approximately $1570cm^{-1}$ and the imogolite peak at $954cm^{-1}$ were chosen, in an attempt to avoid regions in the spectra which overlap. In the APS-alumina system, the same APS absorbance at $1570cm^{-1}$ and the alumina absorbance at $1070cm^{-1}$ were used. IR spectra of APS-alumina and APS-imogolite after twelve hours of dialysis are shown in figure 14. IR spectra of the final sample of APS-alumina and APS imogolite are shown in

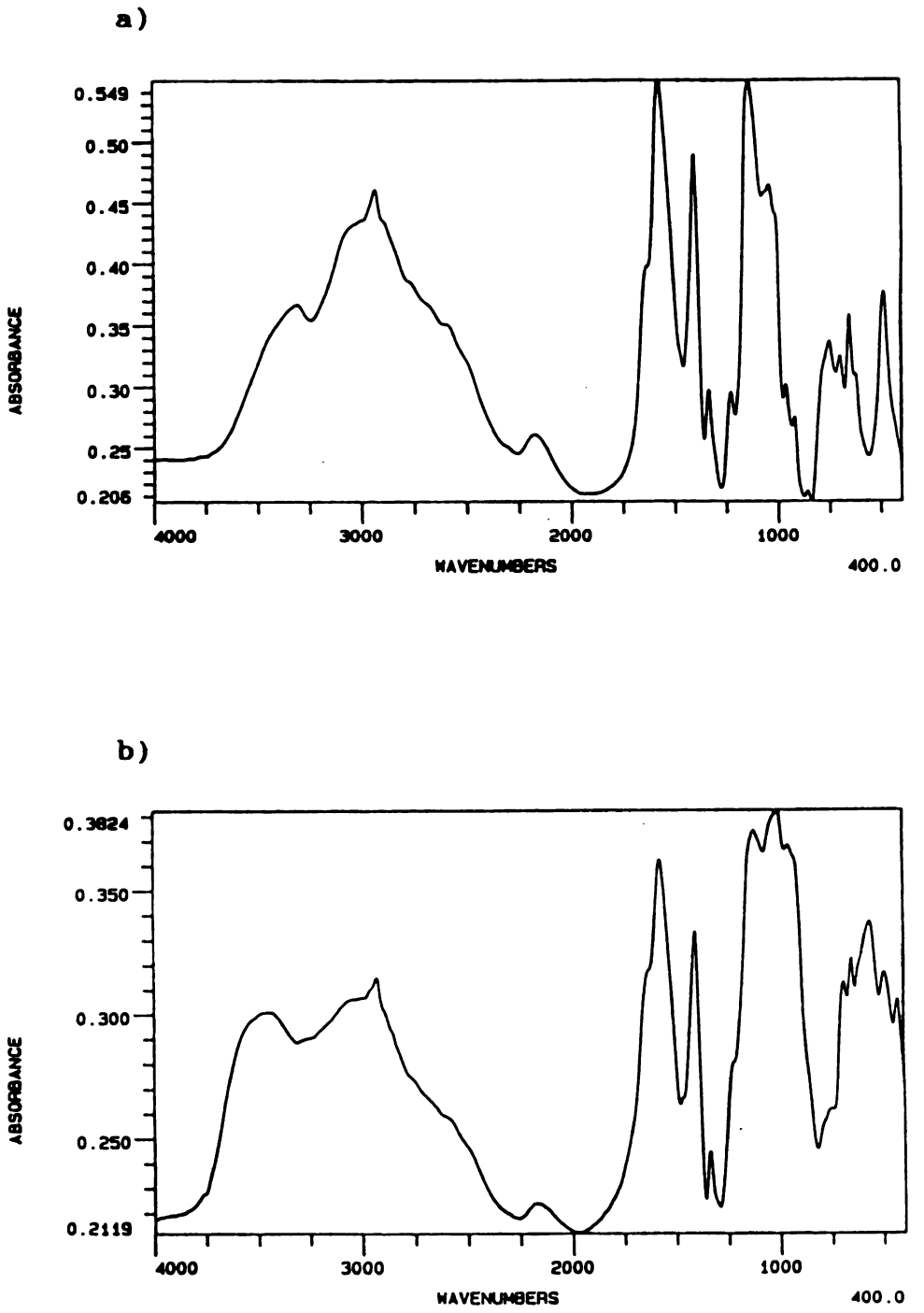


Figure 13 IR spectra of initial Time Dependent Dialysis Experiment samples, 1.0 to 1.0 mole ratio APS to Al, a) APS-alumina b) APS-imogolite.

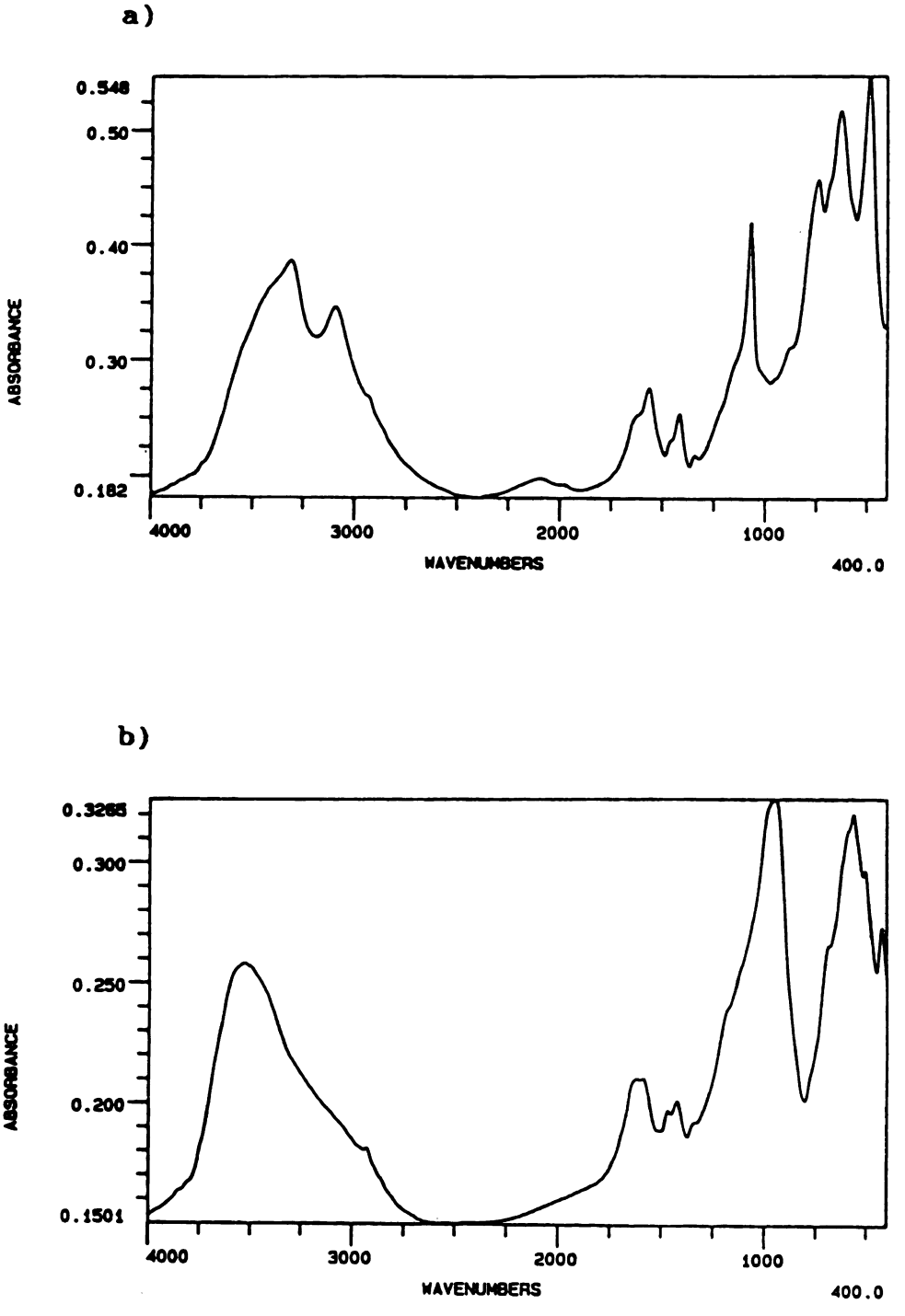


Figure 14 IR spectra of Time Dependent Dialysis Experiment samples after twelve hours, a) APS-alumina b) APS-imogolite.

figure 15. After the absorbance ratios were determined, they were converted to %APS by assigning the value calculated for the initial conditions to the absorbance ratio obtained for the initial samples collected, and zero to the absorbance ratio obtained when a spectra of the substrate alone is taken.

A plot of the percent APS versus time was made to compare the rate of loss of APS for the three systems. The curves for the three systems studied, are superimposed on the plot shown in figure 16. The pure APS drops to nearly zero within four hours of dialysis at which point a more gradual rate of disappearance begins. It takes approximately fourteen hours before the mixed systems begin to show a reduction in the rate of change in APS concentration. This is due to the fact that the APS is initially associated with the substrates, which are unable to diffuse through the dialysis tubing. Another important observation is that the concentration of APS at the point of the change in slope of the APS-imogolite and APS-alumina samples are markedly different. The APS-alumina curve levels off close to zero percent APS. The APS-imogolite curve, on the other hand, levels off near 25% APS.

Elemental analysis of the weight percent carbon in the APS-imogolite sample taken after fourteen hours of dialysis gave a mole ratio of APS to imogolite of 0.28, assuming the water content of the air dried imogolite to be 22%. Ideal

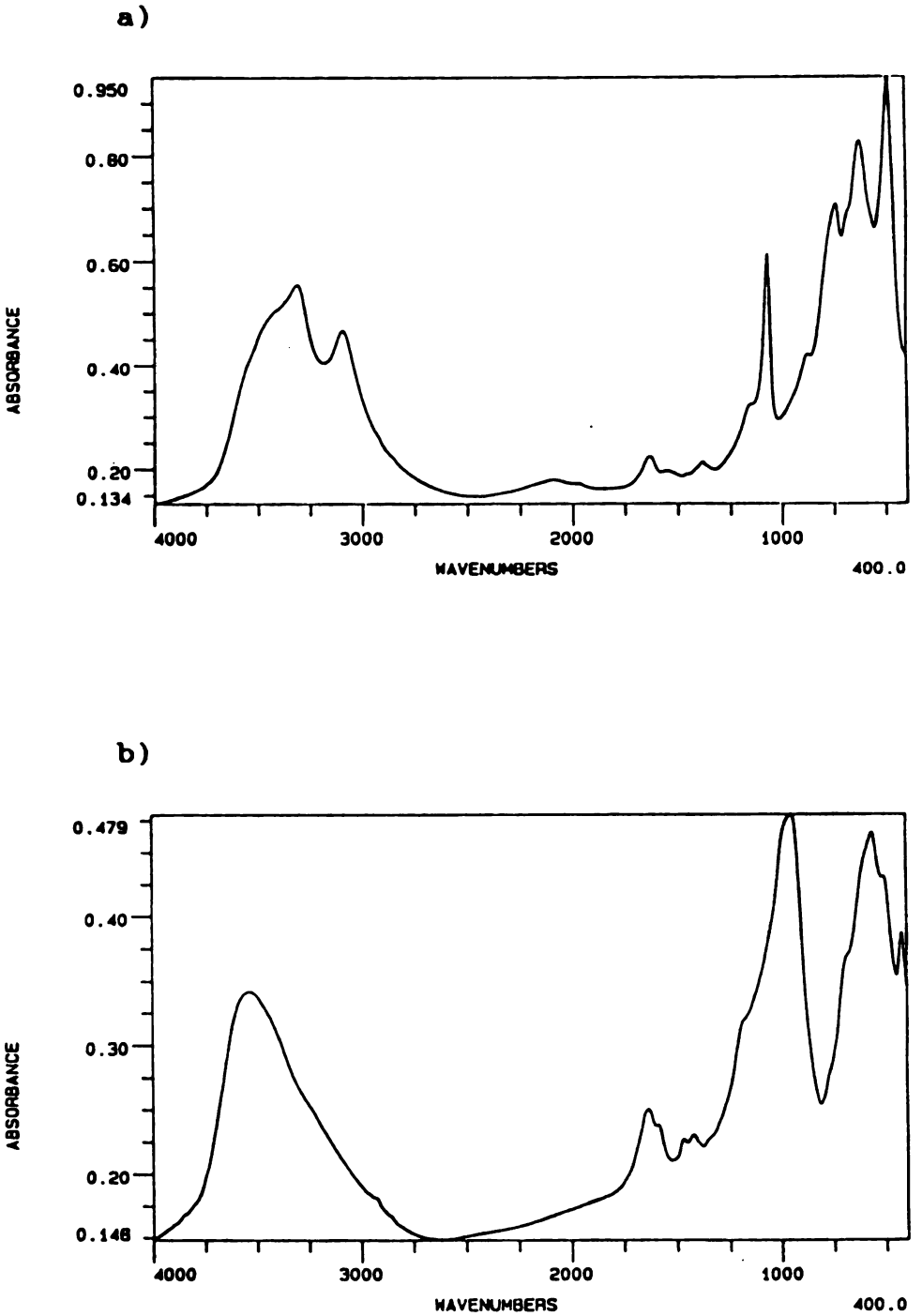


Figure 15 IR spectra of Time Dependent Dialysis Experiment samples after fifty hours, a) APS-alumina b) APS-imogolite.

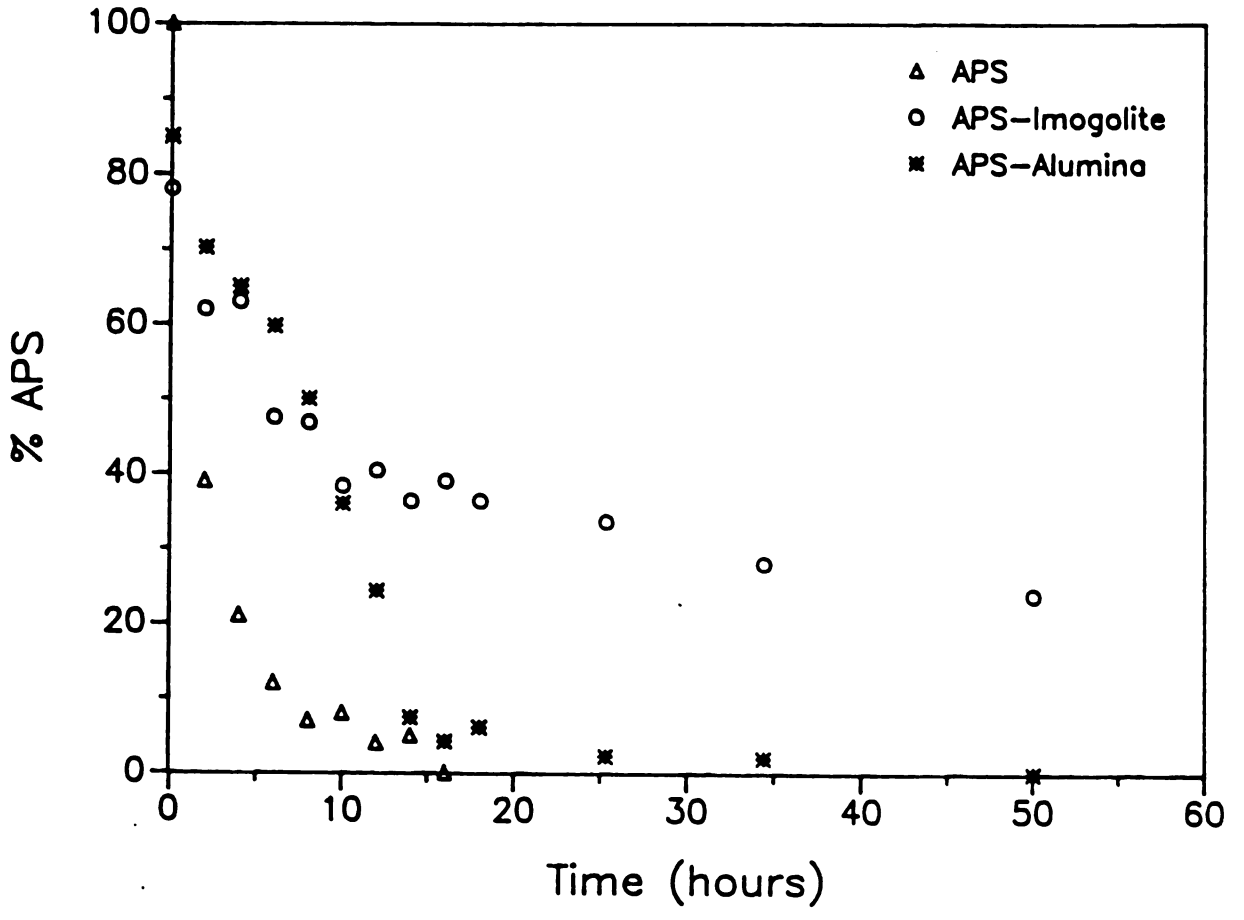


Figure 16 Plot of percent APS versus dialysis time.

monolayer coverage results in each available silanol condensing to a surface aluminum hydroxide. This leads to a one to one mole ratio of APS to imogolite. When the fact that APS tends to condense to surfaces in the form of a dimer is taken into account, there are only 2 hydroxyls per mole APS. This leads to a more realistic monolayer of 0.67 mole APS per mole imogolite. The true mole ratio for monolayer coverage is probably lower still, due to the presence of uncondensed silanol hydroxyls and inaccessible surface aluminum hydroxyls which have been rendered unreactive by the close proximity of an alkyl ammonium chain. As a result, the group of samples dialyzed for fourteen hours or longer, can be expected to have near monolayer to below monolayer silane surface coverage. This information allows for the explanation of the data when they are plotted on a semilog plot.

On the plot of the logarithm of the percent APS versus time, figure 17, the APS-imogolite data can be treated as two different sets of linear points, each with a different slope. The slope of the first six data points is greater than that of the slope of a line drawn through the last seven data points. Both slopes are much smaller than the aqueous APS slope. When only the first six data points in the APS-alumina data set are considered, a line of very nearly the same slope as was obtained for the APS-imogolite data can be drawn. The subsequent data points for longer times,

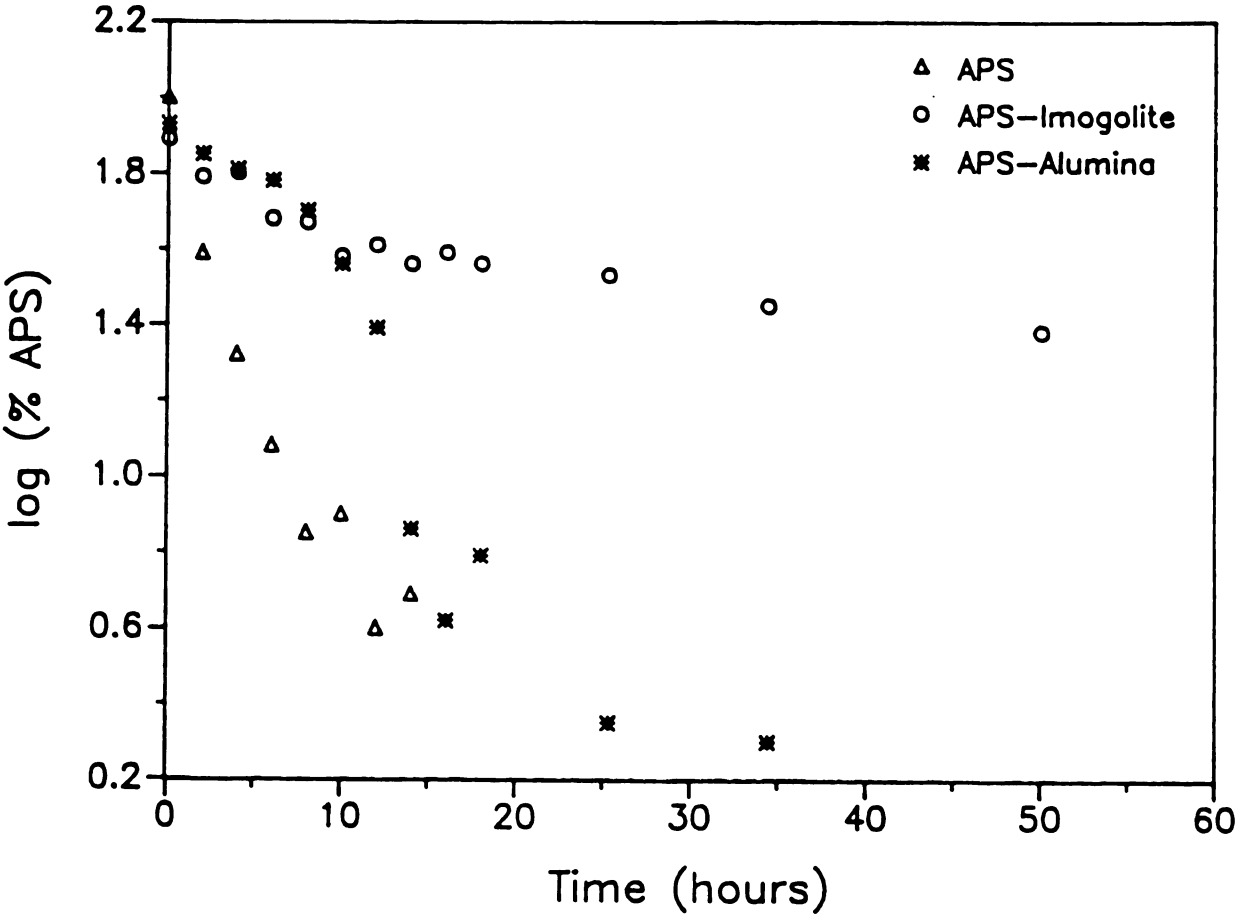


Figure 17 Plot of the log(%APS) versus dialysis time.

however aren't nearly as well behaved, but seem to approach the behavior of the aqueous APS system. The data points for the aqueous APS seem to lose their linearity at low percent silane also. This suggests that the nonlinearity of the APS-alumina data may be a result of the error involved in measuring such low levels of APS. The average error in the value determined for percent APS was calculated by averaging the values obtained from the spectra of several different KBr pellets of the same sample. The average error was found to be 2%, with the individual errors ranging from less than half a percent to 5%. As the concentration of APS in the sample decreases, the error arising from the method of measurement becomes more and more significant. The linearity of sections of the data in a logarithmic plot at long dialysis times suggest that the hydrolysis rate is pseudo first order. The hydrolysis rate depends upon both the concentration of APS and the concentration of water, but since water is present in large excess, the rate becomes independent of its concentration. This means the slopes of the lines drawn through the second seven data points will be directly proportional to the rate constant for the hydrolysis. The slopes were calculated by the least squares method using the first six data points for the APS-alumina and the APS-imogolite system. The values -0.033 and -0.029 were obtained, respectively. The slope was also obtained in the same manner for the last seven points for the

APS-imogolite system. The value obtained for this slope was -0.006. From these slopes, the initial rate appears to be equivalent for the APS-imogolite and the APS-alumina system. The rate at long dialysis times decreases dramatically for the APS-imogolite system.

Recall the fact that both of these systems were synthesized in the presence of APS in excess of that needed to form a monolayer. A plausible explanation of this data is that there is a bimodal distribution of silane coverage. The first type of APS removed is due to the solubilization and removal of excess silane polymerized on the surface of the silylated substrate due to the change in the conformation of the silane in the presence of the substrate. This APS does not have the opportunity to interact directly with the substrate. The second rate is actually a measure of the rate of hydrolysis of the Si-O-Al bond due to the remaining APS close to the surface of the substrate. At short times, the rate of disappearance of APS is expected to be approximately independent of the nature of the substrate. At longer times the rate is expected to depend highly on the substrate. The stability of the Si-O-Al bond toward hydrolysis determines the resulting slope. A steep slope indicates the bond is readily hydrolyzable and conversely a small value for a slope indicates a low propensity for hydrolysis of the alumosiloxane bond. This analysis for the APS-alumina system leads to the conclusion that APS is much more stable with

respect to hydrolysis when bonded to imogolite than when bonded to alumina. Although it is not possible to draw a meaningful line through the latter points plotted for the APS-alumina system, it is clear that the rate of disappearance of APS is much faster in the APS-alumina system than in the APS-imogolite system. Further studies must be done to determine the reason for the significant difference in APS hydrolysis rates for imogolite and alumina surfaces.

F. Conclusions

The success rate of imogolite synthesis has been improved dramatically through the adjustment of several of the synthetic variables. Dialysis of the reaction mixture facilitates separation of imogolite from other reaction products formed. An imogolite-APS complex was formed, as determined by FTIR and MAS ^{29}Si NMR studies, but found to be hydrolytically unstable. The hydrolysis rate was measured by a time dependent dialysis experiment, where the amount of silane present at various dialysis times was determined by FTIR. The rate of APS hydrolysis was measured using this method for the substrates imogolite and gamma alumina. It was found that the APS-imogolite system was more stable toward hydrolysis than the APS-alumina system.

Chapter 4

FUTURE STUDIES

A. Imogolite Synthesis

Much progress has already been made to improve the success rate of the imogolite synthesis. More experiments need to be done, however, to try to understand the process of tube formation itself. The key to this is the understanding of the step which involves the subsequent raising and lowering of the solution pH. Is the pH adjustment critical or is the addition of acetic acid to the mixture the true purpose of that step? This could be tested by adding equivalent amounts of acetic acid and sodium hydroxide to otherwise identical reaction mixtures. To one, the acid and base would be added together, not allowing the pH of the solution to change. To the other, the acid and base would be added separately as is done at present, allowing the pH of the solution to adjust. Another aspect of the synthesis that requires further study is the yield with respect to both reflux time and overall concentration. The yield could be monitored by the gel test, FTIR spectroscopy and electron microscopy. The present method of synthesis involves low concentrations and a long reflux time, which make imogolite less attractive for potential industrial applications.

B. APS-imogolite Synthesis

Although silylated imogolite is too unstable in aqueous solution for use in a mixed organic-aqueous system such as phase transfer catalysis, it should be stable in purely organic systems where the amount of water present is quite low. The current methods being developed for applying silane coupling agents[17] involves depositing them from non-aqueous solvent, and either adding stoichiometric amounts of water or taking advantage of water already adsorbed on the surface to achieve hydrolysis of the coupling agent. This method has been shown to allow more control of the amount of coupling agent bound to the surface. A resulting enhancement of stability, surface properties and reproducibility has been observed. It is possible, and even desirable to modify surfaces with silane from purely organic solution. Successful surface modification of imogolite may be accomplished in this way.

C. SLS-imogolite Synthesis and Catalysis

A recent preliminary reaction between the surfactant sodium lauryl sulfate (SLS) and imogolite has produced promising results. The reaction was carried out as described in the experimental section of this thesis. A suitable interaction was anticipated at low pH between the positively charged imogolite and the anionic surfactant SLS. The result of the combination was flocculation of the imogolite tubes.

Sodium lauryl sulfate had successfully transformed the imogolite from hydrophilic to hydrophobic in nature. When the mixture was placed into a dialysis membrane for one week, the concentration initially decreased according to the IR, but eventually remained constant. Dialysis successfully removed the excess SLS and the rest remained firmly associated with the imogolite tubes.

The ability of the particles to remain flocculated under agitation such as that applied during sonification must be determined and the surface coverage of the imogolite analyzed. The solubility of the flocculated mixture should be determined by attempting to extract it with organic solvents. The synthetic conditions should be varied to see how they affect the product. Other surfactants should be used to try to build the most desirable characteristics into the complex. The phase transfer catalytic properties of the resulting complexes should then be studied.

D. Analytical Techniques

The extensive use of MAS NMR and FTIR has been made throughout this thesis. Many methods for elucidating the nature of surface phenomenon, in particular, have permeated the recent literature. As a result of this, it will be necessary to understand and, where possible, apply these new techniques to the systems being developed. A list of some of these techniques includes Electron Microscopy, Diffuse

Reflectance IR Spectroscopy, X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy.

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