

Adsorption of γ -Aminopropyltriethoxysilane Onto Bulk Iron from Aqueous Solutions

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Synopsis

The adsorption of γ -aminopropyltriethoxysilane (γ -APS) onto mechanically polished iron coupons from 1% aqueous solutions has been investigated using reflection-absorption infrared spectroscopy. Thick films were formed on the coupons during 1-hr exposures to the γ -APS solutions. The outermost portion of these films consisted of highly hydrolyzed polysiloxanes that were weakly bound and easily desorbed by cold water. This fraction of the films was characterized by an infrared band near 1575 cm^{-1} that was tentatively assigned to the NH_2 deformation of acceptor amine groups in strong hydrogen bonds or to coordination of the amino nitrogen atoms to silicon atoms. Removal of the weakly bound outermost portion of the films with water revealed an incompletely hydrolyzed, strongly bound film approximately 60 \AA in thickness characterized by a band near 1510 cm^{-1} that was assigned to NH_3^+ groups. Formation of NH_3^+ groups indicated that γ -APS may have been adsorbed initially as cyclic, internal zwitterions.

INTRODUCTION

The adsorption of γ -aminopropyltriethoxysilane (γ -APS) from solution onto bulk glasses and metals has been studied extensively to determine the mechanisms by which this material enhances the adhesion of organic polymers to such substrates. Tutas¹ used ellipsometry to investigate the structure of films formed by γ -APS adsorbed onto glass and chromium from aqueous solutions. Films formed on glass varied in thickness according to the concentration of the solution but were at least 60 \AA thick. Films formed on chromium from a 1% solution were about 10 \AA in thickness. No tendency for the films to thicken with time was observed. Sterman and Bradley² studied the adsorption of γ -APS onto glass cloth from aqueous solutions using electron microscopy and found that γ -APS was deposited on the surface as polymerized particles rather than as a smooth, continuous film. Schrader³ studied the adsorption of ^{14}C -labeled γ -APS onto glass blocks from benzene solution and separated the adsorbed material into three fractions according to the ease of extraction from the blocks. The first fraction, about 97% of the adsorbed material, was extracted by water at room temperature. The second fraction was extracted by boiling water, but the third fraction was firmly bound to the substrate and survived extraction in boiling water for 100 min. Electron microscopy revealed particles of adsorbed γ -APS in fraction 2, similar to those observed by Sterman and Bradley. Fraction 3 could not be observed in the electron microscope, but radioisotope counting of the apparently bare surface indicated that the equivalent of approximately a monolayer still remained. These observations led Schrader to suggest that γ -APS was adsorbed as both a smooth, continuous film and as agglomerated particles.

Johannson⁴ has studied the adsorption of ¹⁴C-labeled γ -APS onto E-glass fibers from aqueous solutions. Examination of the fibers in the electron microscopy revealed smooth, continuous films on the surfaces. Adsorption of the γ -APS onto E-glass cloth resulted in both continuous films and particulate deposits apparently formed during evaporation of solution trapped in the glass cloth. Extraction of treated E-glass fibers with toluene failed to remove any coupling agent, but extraction with boiling water quickly removed much of the adsorbed γ -APS. It was suggested that removal of the silane from the glass surface occurred by attack on the glass itself. Lee⁵ studied the wettability of films formed by γ -APS adsorbed onto heat-cleaned microscope slides from methanol-water mixed solvents. The critical surface tension of the films was found to be 35 dynes/cm, and it was suggested that such a nonpolar surface would require the γ -APS to be adsorbed with the electron pair on the nitrogen atom oriented toward, or parallel to, the glass surface.

These results indicate that γ -APS adsorbed on bulk glass surface forms smooth, continuous films along with particulate deposits depending on the substrate and the method of preparation. The surfaces of these films are rather nonpolar, indicating some preferred orientation of the adsorbed molecules. However, very little is known about the structure of these films on the molecular level. Bascom,⁶ however, did obtain ATR infrared spectra of γ -APS adsorbed onto germanium from cyclohexane and water. Spectra of films formed in these solvents were identical, indicating that the structures of the films were similar. Spectra obtained from films adsorbed from cyclohexane were, however, somewhat more intense, indicating that these films were thicker than those adsorbed from water. Bascom suggested that a broad band near 3000 cm^{-1} in the spectra of the adsorbed films was the result of hydrogen bonding of the amine groups which normally absorb near 3350 cm^{-1} . Little other information concerning the molecular structure of γ -APS adsorbed on bulk surfaces is available.

The purpose of this paper is to describe the use of reflection-absorption infrared spectroscopy to determine the structure of the films formed by γ -APS adsorbed onto bulk iron from aqueous solutions. Adsorption of γ -APS onto iron coupons from organic solvents will be described in a subsequent publication.

REFLECTION-ABSORPTION INFRARED SPECTROSCOPY

Infrared spectroscopy has been used successfully for some time to study adsorption on high surface area powders, and it has long been known that this type of spectroscopy could, in principle, be used to investigate thin, organic films formed on bulk metal substrates if the necessarily weak infrared absorption of such films could be suitably enhanced and detected. In the past, efforts have been made to do so by increasing the geometric path length of the infrared rays in the film by making multiple reflections of the incident radiation at near-normal incidence from opposing samples, as shown in Figure 1. However, when light is incident on a highly reflecting metallic surface at near-normal incidence, the incident and reflected waves combine to form a standing wave having a node very near the surface of the metal.⁷ Accordingly, the electric field has zero amplitude near the surface of the metal, and it cannot interact with molecules adsorbed on the surface. As a result, the sampling arrangement shown in Figure 1 is not expected to be effective for small values of θ .

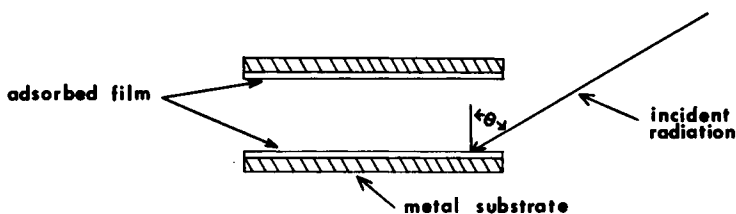


Fig. 1. Sample arrangement for obtaining multiple reflections at an angle θ from opposed coated mirrors.

Recently, however, Francis and Ellison⁸ and Greenler⁷ have reconsidered the problem of obtaining the infrared spectra of organic films formed on metallic surfaces. Their results have shown that only for radiation polarized parallel to the plane of incidence and making an angle of incidence that is only a few degrees less than 90° will the incident and reflected rays combine to establish a standing wave with appreciable amplitude at the surface of the metal that is capable of interacting with adsorbed molecules. This prediction of high absorption intensity for parallel polarized radiation and high angles of incidence is not based on the geometric path length of the infrared radiation in the organic film. Accordingly, this type of infrared spectroscopy is considerably different from conventional infrared spectroscopy, and Greenler and associates⁹ have suggested that it be called reflection-absorption (R-A) spectroscopy.

Francis and Ellison⁸ have shown that ΔR , the fractional change in reflectivity due to the presence of a film on a reflecting substrate, is given approximately, for radiation polarized parallel to the plane of incidence, by

$$\begin{aligned} \Delta R &= 1 - \frac{R}{R_0} \\ &= \frac{16\pi d \cos \theta}{\lambda} \\ &\left\{ \frac{n_1 k_1 [k_4^2 \sin^2 \theta (k_4^2 \cos^2 \theta + 1) + n_1^4 (k_4^2 \cos^2 \theta + 1)] - n_4 k_4 (n_1^4 - n_1^2 \sin^2 \theta - n_1^6 \cos^2 \theta)}{n_1^4 [k_4^2 \cos^2 \theta (k_4^2 \cos^2 \theta + 2) + 1]} \right\} \end{aligned} \quad (1)$$

where R and R_0 are the reflectivity of the metal with and without the film, n_1 and k_1 are the refractive index and absorption constant of the film, n_4 and k_4 are the refractive indices and absorption constant of the metal, θ is the angle of incidence, λ is the wavelength, and d is the thickness of the film.

Equation (1) is obviously a complex function of θ , but it has been shown that ΔR has a maximum value at some particular value of θ that is obviously the optimum angle of incidence. The optimum angle of incidence varies somewhat with wavelength and with the optical constants n_1 , k_1 , n_4 , and k_4 , but generally lies near 88° .

ΔR is the fractional change in reflectivity for one reflection. Generally speaking, the change in reflectivity can be enhanced by making multiple reflections so long as the total energy reaching the detector does not fall below $1/e$, or about 37% of its initial value.¹⁰ Thus, N_{opt} , the optimum number of reflections, may be obtained from

$$R_0^{N_{\text{opt}}} = \frac{1}{e} \quad (2)$$

or, equivalently,

$$Nc_{\text{opt}} = \frac{-1}{\ln R_0} \quad (3)$$

For all metals, R_0 is a function of angle of incidence and of wavelength, making N_{opt} a function of the same variables. For good reflectors such as copper, gold, and silver, R_0 actually changes little over the range of wavelengths of interest (2.5 μ to 20.0 μ), and the optimum number of reflections is determined mainly by the angle of incidence. For relatively poor reflectors, such as iron, R_0 and N_{opt} are strongly dependent on both wavelength and angle of incidence.

For angles of incidence less than about 80°, the second term on the right side of eq. (1) is negligible and ΔR can be approximated⁸ as

$$\Delta R = \frac{16\pi dk_1 \sin^2 \theta}{\lambda n_1^3 \cos \theta} \quad (4)$$

Since

$$\frac{k_1}{\lambda} = \frac{\alpha}{4\pi} = \frac{2.303\epsilon c}{4\pi} \quad (5)$$

where α is the absorption coefficient, ϵ is the molar extinction coefficient, and c is the concentration of absorbing species, ΔR may be written, for $0^\circ \leq \theta \leq 80^\circ$, as

$$\Delta R = \frac{\epsilon cd}{n_1^3} \left(\frac{9.212 \sin^2 \theta}{\cos \theta} \right) \quad (6)$$

EXPERIMENTAL

Samples for studying the adsorption of γ -APS onto iron by reflection-adsorption infrared spectroscopy were prepared as follows. Coupons of Armco ingot iron (2 cm \times 4 cm) were mechanically polished (final polishing was with 0.05 micron γ -alumina), repeatedly washed with distilled water, and then dried with a stream of nitrogen. Coupons prepared in this way were initially hydrophilic. However, after a short exposure to the laboratory atmosphere, the coupons became hydrophobic, apparently as a result of the adsorption of organic compounds. Analysis of polished coupons by Auger spectroscopy confirmed the presence of adsorbed organic compounds as well as adsorbed oxygen and nitrogen. No evidence for retention of the alumina polishing compound on the surface was found. Auger analysis also indicated the presence of an oxide layer approximately 30 Å thick.

In order to minimize contamination of the samples, coupons polished, washed, and dried as described above were immediately immersed in freshly prepared solutions of γ -APS. After removal from the solutions, the coupons were usually air dried and then mounted in a multiple reflection accessory as shown in Figure 2. The accessory was then placed in the sample beam of a Perkin-Elmer 180 infrared spectrometer. Uncoated, but otherwise identical, coupons were mounted in a second reflection accessory which was then placed in the reference beam of the spectrometer, enabling all spectra to be recorded differentially. A AgBr wire grid polarizer, oriented to transmit only radiation polarized parallel

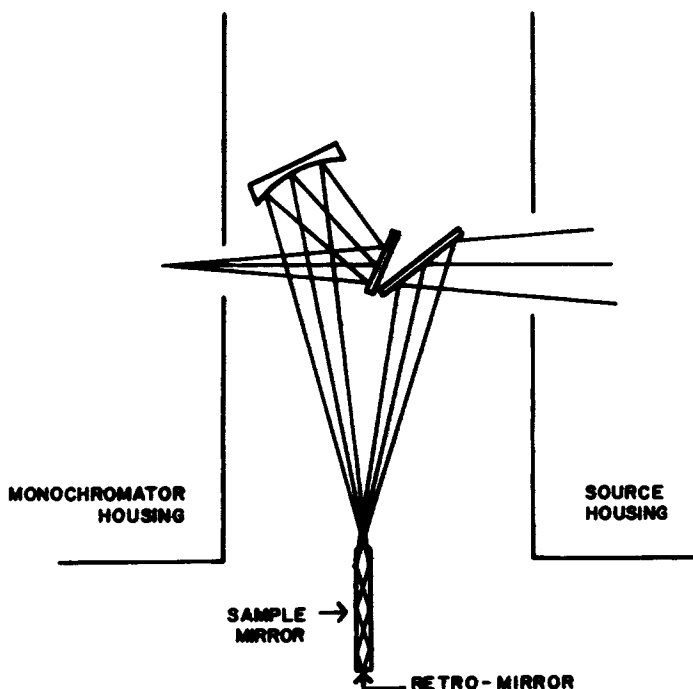


Fig. 2. Sampling arrangement for reflection-absorption spectroscopy using multiple reflections from sample mirrors.

to the plane of incidence, was placed in front of the entrance slit of the monochromator. The instrument was continuously purged with dried air to eliminate interfering absorption by atmospheric water vapor.

Since the coupons were dried following removal from the γ -APS solutions, it is likely that the films obtained were formed by deposition from evaporating solvent as well as by adsorption. This must be borne in mind when the results are interpreted.

RESULTS AND DISCUSSION

The spectrum shown in Figure 3 was obtained from coupons exposed to an argon-purged 1% solution of γ -APS in water at room temperature for 1 hr and then air dried. This spectrum was obtained using two reflections at 78° and $5\times$ scale expansion. Very intense bands are observed near 2920 , 2870 , 1575 , 1490 , and 1105 cm^{-1} . Weaker bands are found near 1440 , 1380 , 1330 , 1300 , 1040 (shoulder), and 925 cm^{-1} . The intensity of the observed bands indicates that this film, which is typical of those adsorbed from aqueous solutions at room temperature and then air dried, is probably several hundred angstroms in thickness.

Some details of the structure of these thick films may be obtained by comparing the spectrum in Figure 3 with spectra of γ -APS monomer shown in Figure 4 and with the spectrum of the polymer formed by hydrolysis and condensation of γ -APS shown in Figure 5. The spectrum of the monomer is dominated by three very strong absorptions, near 960 , 1080 , and 1105 cm^{-1} , that are charac-

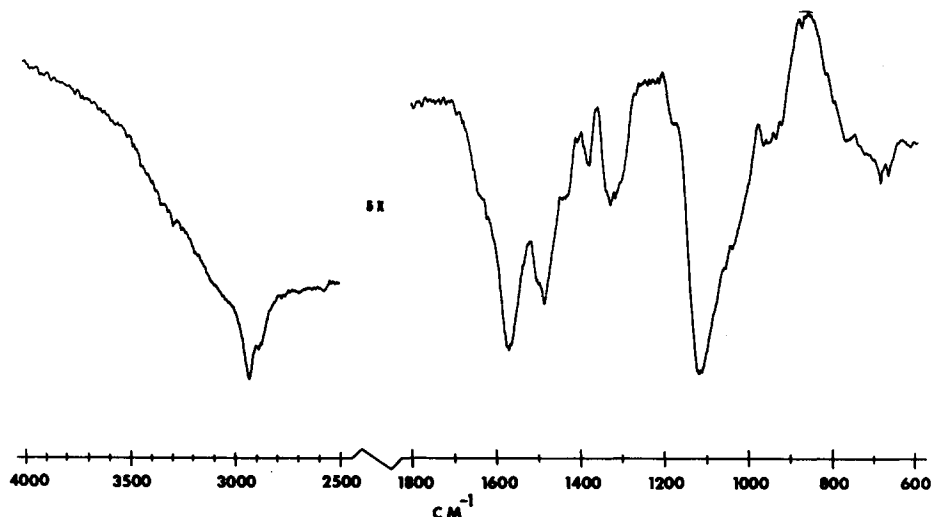


Fig. 3. Reflection-absorption infrared spectrum of iron mirrors exposed to argon-purged 1% aqueous solution of γ -APS at room temperature and then dried; 2 reflections at 78° , $5\times$ scale expansion.

teristic of Si—O bonds in Si—O—CH₂CH₃ groups.¹¹ The polymer has strong bands near 1130 and 1040 cm^{-1} that are characteristic of Si—O—Si groups in polysiloxanes¹² and a band near 930 cm^{-1} that is probably related to Si—O bonds in hydrogen-bonded SiOH groups.¹³ Observation of the bands near 1040 and 925 cm^{-1} in the spectra shown in Figure 3 indicates that adsorption of γ -APS on iron from aqueous solutions involves hydrolysis and condensation to form a polysiloxane. Further evidence of this is provided by an analysis of the absorption bands near 3000 cm^{-1} . In the monomer, bands are observed near 2970, 2920, 2880, and 2855 (shoulder) cm^{-1} . The band near 2970 cm^{-1} arises mainly from the —CH₂CH₃ groups present in the monomer^{11,12} and should, therefore,

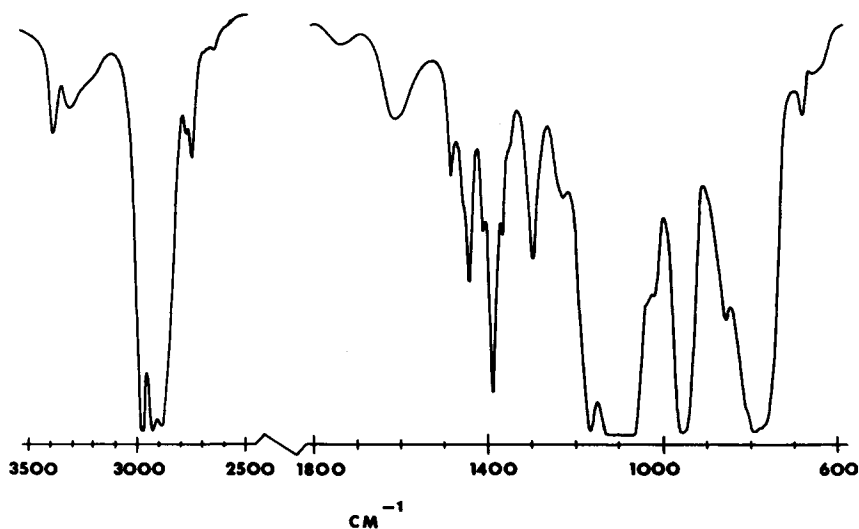
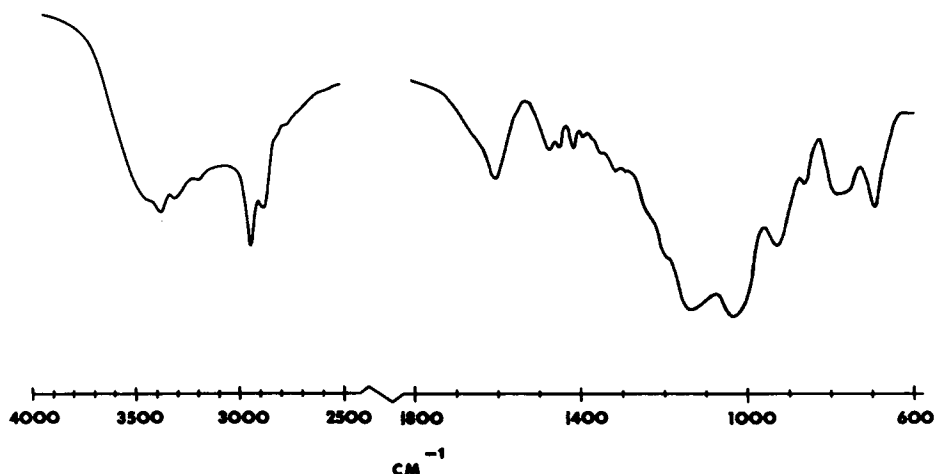


Fig. 4. Infrared spectrum of γ -APS monomer.

Fig. 5. Infrared spectrum of γ -APS polymer.

be absent following hydrolysis and condensation. This band is, indeed, absent from spectra of the polymer (Fig. 5) and from spectra of the films formed on iron (Fig. 3). The bands near 2920 and 2850 cm^{-1} in spectra of the monomer, polymer, and films formed on iron may be assigned to the CH_2 groups in the propylamine group attached to the silicon atom in γ -APS.¹¹

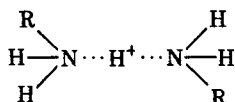
While these observations undoubtedly indicate polymerization of γ -APS on the surface of the coupons, the presence of the strong band near 1575 cm^{-1} for films formed on iron and its absence in spectra of the polymer indicate that there are some differences in structure between the adsorbed film and the polymer obtained by hydrolysis and condensation. The band near 1575 cm^{-1} undoubtedly corresponds to the NH_2 deformation vibration found near 1610 cm^{-1} in spectra of the monomer and the polymer. There are several possible explanations for the observed shift in frequency from 1610 cm^{-1} to 1575 cm^{-1} . The band at 1575 cm^{-1} could be assigned to the asymmetric deformation of an NH_3^+ group formed by protonation of the amine. However, vibrations of this type are usually found at considerably higher frequencies. Fripiat¹⁴ has assigned this mode to bands near 1613 cm^{-1} in propylamine hydrochloride and in butylamine hydrochloride, and its assignment at 1575 cm^{-1} in γ -APS seem unlikely.

An alternative is to attribute the shift of the NH_2 deformation from 1610 cm^{-1} to 1575 cm^{-1} to hydrogen bonding. $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding could be expected in γ -APS and would result in a small increase in the NH_2 deformation frequency of the donor amine and a small decrease in the corresponding mode of the acceptor NH_2 group.¹⁵ However, while there is a small shoulder on the high-frequency side of the band near 1575 cm^{-1} that might be assigned to the NH_2 deformation of the donor, there is little reason to believe that this type of hydrogen bonding could explain the lowering of the NH_2 deformation vibration of the acceptor to 1575 cm^{-1} .

Only relatively strong hydrogen bonding could explain a perturbation of the NH_2 deformation of the magnitude observed here. Strong hydrogen bonding of the $\text{O}-\text{H}\cdots\text{N}$ type could also be expected for hydrolyzed γ -APS. The silanol group is rather strongly acidic and might be expected to form strong hydrogen bonds with the strongly basic amino group. However, little information is

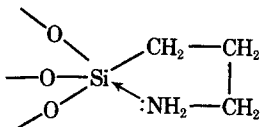
available in the literature describing the effects of such bonding on the deformation mode of the acceptor amine, and it is not known if these bonds would be strong enough to produce the observed shift from 1610 cm^{-1} to 1575 cm^{-1} .

The spectrum shown in Figure 3 is remarkably similar to spectra of ethylamine adsorbed on ethylammonium montmorillonite reported by Farmer and Mortland.¹⁶ Ethylammonium montmorillonite has absorptions near 1617 cm^{-1} and 1510 cm^{-1} corresponding to the asymmetric and symmetric deformation modes of the NH_3^+ group. When ethylamine is adsorbed on ethylammonium montmorillonite, these absorptions are replaced by an absorption near 1590 cm^{-1} . This perturbation of the NH_3^+ deformation modes of the ethylammonium ion was attributed to strong hydrogen bonding between ethylamine and ethylammonium as shown below:

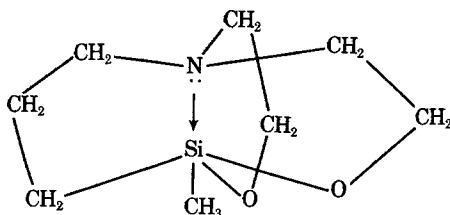


Hydrogen bonding of this type could also be obtained for γ -APS and might explain the occurrence of the NH_2 deformation mode near 1575 cm^{-1} .

The spectrum shown in Figure 3 is also similar to spectra of coordinated primary amines. The NH_2 deformation mode in *n*-propylamine complexes with $\text{Cu}(\text{I})\text{Cl}$ is found near 1585 cm^{-1} , a downward shift in frequency of some 30 cm^{-1} from its position in the free amine.¹⁷ Similar results have been reported for methylamine adsorbed on γ -alumina,¹⁸ and Farmer and Mortland¹⁶ have shown that ethylamine coordinated to copper montmorillonite absorbs strongly near 1590 cm^{-1} . It may thus be possible to assign the band near 1575 cm^{-1} in γ -APS adsorbed on iron to the deformation mode of amine groups coordinated to the silicon to form cyclic, inner complexes as suggested by Plueddemann:¹⁹



While complexes of silicon with nitrogen are not particularly common, several have been prepared and characterized, principally by x-ray diffraction.^{20,21} An example is methyl-(2,2',3-nitrilodiethoxypropyl)silane having the structure²⁰



The coupons used to obtain the spectrum shown in Figure 3 were subsequently soaked in toluene and then in ethyl acetate. It was expected that these solvents would dissolve monomer and low molecular weight polymer from the coupons. Spectra obtained from the coupons following this treatment were virtually

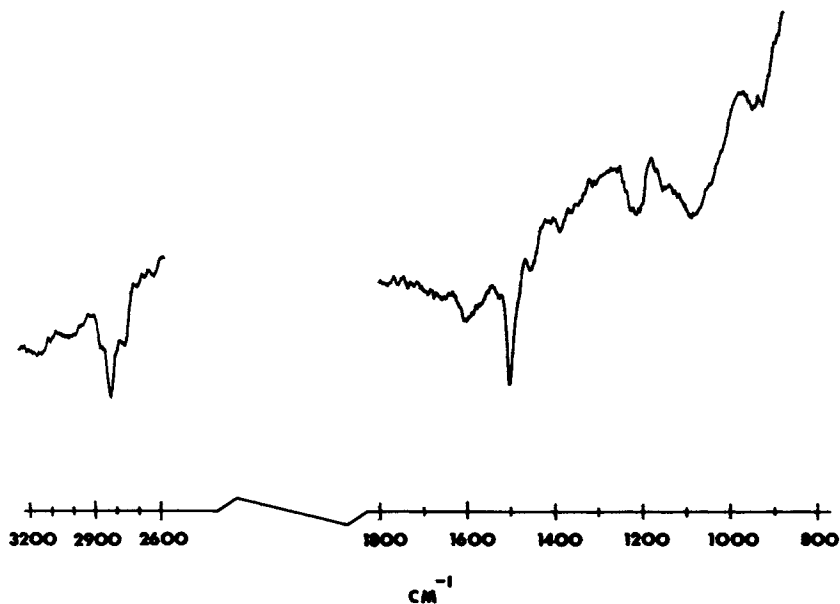
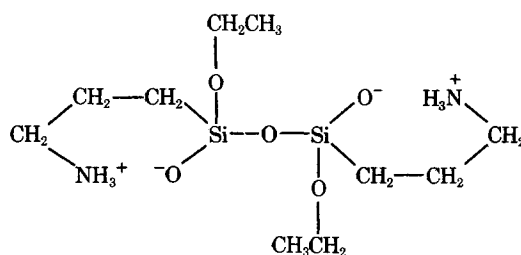


Fig. 6. Spectrum obtained after iron coupons used to obtain Fig. 3 were washed for 15 min in water at room temperature; two reflections at 78° ; $20\times$.

identical to that shown in Figure 3, indicating again that γ -APS is adsorbed from aqueous solution onto iron as a polysiloxane.

The same coupons were then washed in water at room temperature for 15 min and their spectra were again recorded as shown in Figure 6. These spectra were obtained using two reflections at 78° and $20\times$ scale expansion. It may be observed that water has extracted most of the polysiloxane from the surface of the coupons, leaving only a thin film. Bands are observed near 2970 (shoulder), 2920, 2850, 1600, 1510, 1235, 1090, and 930 cm^{-1} . Observation of the band near 2970 cm^{-1} , assigned to $\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$ groups, indicates that the γ -APS initially adsorbed on the coupons was only partially hydrolyzed. The band near 1090 cm^{-1} may be assigned to $\text{Si}-\text{O}-\text{Si}$ linkages, indicating that the partially hydrolyzed γ -APS has condensed to form polysiloxanes.

The bands near 1510 cm^{-1} and 1600 cm^{-1} are assigned to the symmetric and asymmetric deformation modes of NH_3^+ groups. As indicated earlier, the corresponding modes for ethylammonium ions in ethylammonium montmorillonite are found¹⁶ near 1617 cm^{-1} and 1510 cm^{-1} , and Fripiat has assigned bands near 1613 cm^{-1} and 1510 cm^{-1} to NH_3^+ deformation modes in *n*-propylamine adsorbed on montmorillonite.¹⁴ These results indicate that initially γ -APS may have been adsorbed as low molecular weight (mainly dimers) internal zwitterions as suggested by Plueddemann and Erickson:²²



The weakness of the asymmetrical NH_3^+ deformation mode near 1600 cm^{-1} relative to the symmetric deformation near 1510 cm^{-1} is thought to arise from an orientation effect. The spectra shown in Figure 6 were, of course, obtained using radiation polarized parallel to the plane of incidence. As shown by Francis and Ellison,⁸ only the component of the dipole moment perpendicular to the surface will produce appreciable absorption in this case. For an isotropic film, this is of no particular consequence. However, for an anisotropic film, vibrations having transition moments parallel to the surface appear only weakly while those having perpendicular transition moments appear with enhanced intensity. The intensity of the band near 1510 cm^{-1} , relative to that near 1600 cm^{-1} , indicates that the NH_3^+ group is oriented toward the surface, perhaps as the result of chelation with the iron surface. Fripiat¹⁴ has observed similar orientation effects in spectra of *n*-propylamine adsorbed on acid montmorillonite.

In principle the thickness of the films whose spectra are shown in Figure 6 may be calculated from eq. (6) provided ϵ , c , and n_1 are known. Unfortunately, these quantities are not easily determined for an adsorbed film. Nevertheless, it is desirable to estimate the thickness of these films, and that may be done as follows. Sandorfy and Jones²³ have suggested that the extinction coefficient for a chain of CH_2 groups is 75 l./mole-cm per CH_2 group. Thus, for the propylamine group, $\epsilon \approx 225$ l./mole-cm. The density of γ -APS is about 0.95 g/cm^3 ; and for a molecular weight of 221 g/mole, the density of propylamine groups is found to be $c = 4.3$ mole/l. The refractive index for the adsorbed film can be approximated by the value for γ -APS monomer, $n_1 = 1.421$. Assuming $R_0 = 0.65$, ΔR is found, from Figure 6, to equal 0.0089. The thickness d was found to equal about 60 Å. This indicates that the films remaining on the coupons after washing in water at room temperature are only a few molecular layers in thickness.

The band near 1235 cm^{-1} in Figure 6 can probably be assigned to $\text{Si}-\text{CH}_2$ bonds in the propylamine substituents.¹² This band is usually obscured by the intense $\text{Si}-\text{O}$ vibrations near 1150 cm^{-1} and is rather weak in spectra of the monomer (Fig. 4) and the polymer (Fig. 5).

The results obtained here indicate that reflection-absorption infrared spectroscopy is an extremely effective technique for studying adsorption of organic compounds onto bulk metals and can provide information about the structure of adsorbed films that is not easily obtained by any other means. The results reported here for the adsorption of γ -APS onto bulk iron from aqueous solutions are in excellent agreement with those obtained by Schrader³ for adsorption of γ -APS onto glass blocks from benzene solutions. The thick, loosely held, highly hydrolyzed films characterized by the infrared band near 1575 cm^{-1} undoubtedly correspond to Schrader's "first fraction" and may have been formed by deposition rather than adsorption. The strongly bound, incompletely hydrolyzed films characterized by the infrared band near 1510 cm^{-1} correspond to the "second fraction" observed by Schrader and were undoubtedly formed by chemisorption. The "first fraction" is undoubtedly several hundred angstroms thick. The thickness of the "second fraction" has been estimated at approximately 60 Å.

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