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Structure and Adsorption Characteristics of Silane Coupling Agents on Silica and E-glass Fiber; Dependence on pH

by

S. Naviroj, S. Culler, J.L. Koenig, and H. Ishida

Department of Macromolecular Science

Case Western Reserve University

Cleveland, Ohio 44106

ABSTRACT

Fourier transform infrared spectroscopy was used to study the adsorption of silane coupling agents on silica and E-glass fiber surfaces. The structures of the adsorbed species of γ-aminopropyltriethoxysilane (γ-APS) coupling agent under various preparation conditions are postulated based on an interpretation of the NH deformation and SiOH stretching modes. The amount of γ-APS deposited on high-surface-area silica depends on the pH of the treating solution. On the contrary, the amounts of adsorption of γ-methacryloxypropyltrimethoxysilane (γ-MPS) and vinyltriethoxysilane (VS) coupling agents are independent of pH. The number of adsorbed molecules of γ-MPS and VS is comparable to that of γ-APS only at its acidic pH. The unique adsorption of γ-APS on the silica surface is partly due to the structure of the γ-APS itself in the treating solution. When E-glass fiber is used as the substrate, the amount of γ-APS adsorption is affected by pH but less than observed with silica powder. The structure of γ-APS is affected by the presence of carbon dioxide when the pH range of the silane solution is between 6 and 12.

INTRODUCTION

The surface treatment of glass fibers with silane coupling agents has enhanced the performance of the fiber reinforced plastics [1,2]. The interaction of the silane coupling agent with the glass surface may vary depending on the composition of the glass surface and the type of silane coupling agent. Many theories have been proposed to explain the function of silane coupling agents treated on glass fibers [3-10]. There is some evidence to support each of these theories but none of the theories is conclusive enough to explain all the data. The mechanism by which silane coupling agents function in composites remains undetermined.

When glass fibers are treated with coupling agent, the mechanical performance of composite materials is significantly improved under humid environments. The resistance to water may be explained by either the formation of hydrogen bonds to the surface, electrostatic bonding by the attraction of oppositely charged ions, or covalent bonding to the substrate surface. Surfaces of metal oxides and silicates in equilibrium with atmospheric moisture consist of surface hydroxyl groups. The surface hydroxyl and oxide groups are important for the formation of each type of bonding.

The electrostatic surface potential (ζ-potential) depends on the concentration of H^+ ion. The isoelectric point of a surface is determined by the pH at which the potential of the surface is zero. Vanderbilt [11] indicated that different mineral surfaces have different interactions with the silane coupling agent. The pH of the treating solution of the glass fibers is an essential factor in controlling the

population of the acid sites. The chemical stability of silanol groups is highly pH dependent. Thus, the structure of the coupling agent in the treating solution is also strongly influenced.

Determination of the mode of silane adsorption on the glass fiber or mineral filler surfaces may be important in understanding the reinforcement mechanism of FRP. Plueddemann [12] studied the catalytic and electrostatic effects in bonding through silanes. He suggested that electrostatic forces at the mineral surface may be important in determining the orientation of silane molecules applied from an aqueous solution. Cationic organofunctional silanes are sensitive to the pH of the treating solution. The molecular orientation of cationic silane coupling agents is affected more than the nonionic coupling agents. At optimum condition of the treating solution, the cationic coupling agent may be more effective than the nonionic coupling agent due to the more favorable molecular orientation. The surface isoelectric point (IEP) also has an effect on the molecular orientation [12]. The deposited silane could be right side up (silanol on the mineral surface) or upside down (the functional group on the mineral surface) depending on both the IEP and pH of the solution.

Many researchers have studied the adsorption of silane on glass fibers and silicate surfaces. Ishida *et al* [13] utilized FT-IR to study the nature of vinyltriethoxysilane on fumed silica. They reported that the silane chemically reacted with the silica surface. Gent *et al* [14] showed that model silane compounds form chemical bonds with silica in the presence of *n*-propylamine probably via a base-catalyzed interchange reaction involving silanol groups on the silica surface.

Koenig *et al* [15] used Raman and infrared spectroscopy to study the reactions of silane with silica and glass surfaces. Different types of silanol groups of silica surface were detected. Kaas *et al* [16] studied the interaction of silane coupling agents with silica surfaces and found that the major forces holding the silane to the silica surface after application from dilute solution are primary chemical bonds. All these studies support the existence of chemical bonds at the glass/silane interface.

Both the optimum mechanical performance of composites and the amount of adsorbed silane on the surface of glass fibers depend on the concentration of the treating solution. It is well known that the structure of an aminosilane coupling agent is pH dependent and also affected by drying conditions [17]. With different structures that are influenced by the pH of the solution, the mode of adsorption of this coupling agent may vary and the amount of adsorbed silane may be influenced. Thus, the mechanical properties would be affected.

A high-surface-area silica was chosen to model the E-glass fiber since silica is the major component in E-glass fiber. Study of the interaction at the silica-coupling agent interface is facilitated by the use of high-surface-area silica. Fourier transform infrared spectroscopy (FT-IR) was chosen to obtain information about the molecular structure and the amount of silane coupling agent present on the surface of silica. Our aim is to elucidate the complex nature of the silane coupling agents on glass fiber surfaces and understand the reinforcement mechanism.

EXPERIMENTAL

A) FT-IR analysis of partially cured γ-APS

γ-aminopropyltriethoxysilane (γ-APS was purchased from Petrarch Systems Inc. γ-APS was mixed with deionized distilled water 20% by weight solution. The silane was hydrolyzed for 40 - 50 minutes. The hydrolyzed γ-APS was used at its natural pH or adjusted to the appropriate pH values by adding NaOH or HCl. The solution was cast onto a silver bromide (AgBr) plate and dried in air at room temperature. The dried γ-APS was then examined by FT-IR. Special precautions were taken for high pH samples. The solution was first allowed to be partially dried on a glass slide. When the solution became viscous, it was then quickly transferred to the AgBr plate for complete drying. This procedure prevented the possible decomposition of the AgBr plate.

B) Titration

Two ml of γ-APS were hydrolyzed in 20 ml of deionized distilled water. The solution was hydrolyzed for 40 - 50 minutes. One ml of solution was titrated with 0.1N HCl solution. After each addition of HCl, the pH of the solution was allowed to stand for ten minutes to reach equilibrium. The amount of HCl added was recorded along with the pH change. The pH of the solution was measured with a Beckman 3500 digital pH meter.

C) Silica wafers

Silica powder used in the experiment was obtained from Degussa Inc. The silica powder has a specific surface area of 130 m^2/g. The powder

was made into wafers by compressing the powder between aluminum foils under a pressure of 15,000 psi. Thin wafers with the thickness of approximately 0.1 mm were obtained. The wafers were then heated at 350°C for three days in an oven before being treated with coupling agents.

One percent by weight γ-APS solutions were prepared. The solution was adjusted to the appropriate pH by using either NaOH or HCl. Thin wafers were treated with hydrolyzed γ-APS in a Petri dish. The wafer of approximately 3 - 4 cm^2 was immersed in 50 ml of solution for 15 min. After the allocated time, the solution was decanted and the wafer was air dried overnight at room temperature.

Infrared spectra of the samples were obtained with a Digilab FTS-14 spectrometer at a resolution of 2 cm^{-1}. The number of scans was 200 for the sample and 100 for the reference. The wavenumber was calibrated with a helium neon laser with a reproducibility of 0.01 cm^{-1}. The spectra obtained were stored on a magnetic tape for further examination.

The same procedure was followed for other samples of silica wafers but the coupling agents used were γ-methacryloxypropyltrimethoxysilane or vinyltriethoxysilane.

D) Calibration curve of γ-APS

γ-APS coupling agent was smeared on a glass slide to be hydrolyzed by adsorbing the moisture from air. After exposure in air for ten days, the dried coupling agent was scraped from the glass slide. The dried powder was placed in an aluminum pan and the weight was measured by a Perkin-Elmer microbalance. The known weight of coupling agent was mixed with approximately 200 mg of KBr powder and compressed into a

pellet for infrared examination. Extra precaution was taken to ensure that all of the coupling agent powder was transferred from the mortar into the die of the pellet maker.

E) Calibration curve for silica

A high-surface-area silica powder was pressed into a thin wafer, and subsequently heated at 350°C for three days. The wafer was broken into an appropriate size and was placed between the two KBr plates in order to hold the wafer in place during infrared analysis. The wafer was removed from the sample holder and weighed with the electrobalance. The weight of silica wafer versus the absorbance at 1970 cm^{-1} was plotted.

F) E-glass fibers treated with 1% γ-APS at various pH

E-glass mats (Crane Glas, grade 50-01) were heat cleaned in air at 500°C for 24 hours prior to use. The pH-adjusted, 1% by weight γ-APS solutions were used. Glass mats were immersed into the silane solution for one minute and the excess solution was filtered off by using a house vacuum in order to improve the reproducibility of the experiment. The treated mat was dried in air at room temperature for one day. About 1 mg of glass mat was ground with approximately 200 mg of KBr powder for FT-IR analysis.

RESULTS

After hydrolyzing γ-APS, the pH of the solution was adjusted in order to study the effect of pH on the structure of the γ-APS. Figure 1 shows the spectra of the samples at various pH values. For the spectra in the pH range of 2 to 7, the bands at 1610 and 1505 cm^{-1} were assigned

to the NH_3^+ deformation modes [17]. These assignments can be supported by the presence of the broad bands at 2800 and 2400 cm^{-1} (not shown in fig. 1). As the pH value of the solution is raised to about 8, changes begin to occur. We will first focus our attention on the bands around 1600 - 1500 cm^{-1}, and later the band around 930 cm^{-1}.

A new peak begins to appear at 1570 cm^{-1} from pH 8 to 10. At pH 10, the peaks are clearly defined at 1575 and 1505 cm^{-1}. These two bands are assigned to the NH_3^+ deformation modes of aminebicarbonate salt [17]. The presence of the bicarbonate ion can be observed in the pH range of 7 and 10.8. The band at 1332 cm^{-1} was used to monitor the amount of the bicarbonate group. This band is due primarily to the OCO_2 mode. The intensity of this band (1332 cm^{-1}) increases noticeably as the pH value increases from 8.5 to 10.8. The increase in intensity is due to the increase in concentration of the bicarbonate salt. As we followed the changes further to a higher pH value, we observed that the bands at 1575 and 1485 cm^{-1} disappeared, leaving a prominent peak at 1592 cm^{-1}, which was assigned to the NH_2 bending mode. By following the structure changes due to the pH of the solution, we observed that the structure of the partially cured γ-APS hydrolyzate changed from NH_3^+ to $NH_3^+(HCO_3)^-$ and to NH_2.

The peak around 930 cm^{-1} which is assigned to the SiO stretching mode of the silanol [18] can also be followed. We monitor the frequency of the SiOH stretching mode and plot the peak position versus the pH of the solution as shown in fig. 2. The peak position of the SiOH mode remains constant at 902 cm^{-1} at pH 1 to about pH 8. In this region of pH, the silane is in the form of weakly hydrogen bonded SiOH and the amine group is in the form of NH_3^+. This result is in agreement with the result described earlier. As the pH of the solution becomes higher than 8, the frequency of the SiOH

peak shifts upward rapidly (fig. 2). In this region the amine group, which was in the form of NH_3^+ at low pH, changes its structure to form a hydrogen bond with the SiOH, which results in the upward shifting of the SiOH peak. Figure 3 shows the proposed structures of γ-APS in a partially cured state when prepared from solution at various pH's. The frequency of the amine deformation and SiO stretching modes were used as a guide to the proposed structures. At pH = 2, the two amine bands at 1610 and 1505 cm^{-1} are indicative of the NH_3^+ structure. The band at 902 cm^{-1} is the weakly hydrogen bonded SiOH stretching mode. The sample dried in air from a solution of pH = 10.6 has amine bands at 1575 and 1488 cm^{-1} which indicate the presence of the NH_3^+ structure. The SiOH peak is now shifted to 930 cm^{-1} from 902 cm^{-1}. This shifting is due to the existence of stronger hydrogen bonding of the SiOH group. With the presence of bicarbonate salt, the structures as shown in fig. 3 are proposed.

Titration was performed on the hydrolyzed γ-APS. The pH of the natural solution at 1% by weight of γ-APS has the value of 10.6. The pKa value of ethyl amine is 10.64. [19].

The pressed silica powder does not lose its specific surface area at this pressure [7]. Figure 4 shows the spectra of the silica wafer treated with γ-APS at various pH's. The bands at 2930 and 2860 cm^{-1}, which are due to the CH_2 stretching modes of the propyl chain, increase in intensity as the pH of the treating solution changes from 2 to 10.6. This indicates that more γ-APS is adsorbed at pH 10.6 than at pH 2. The silane uptake is lowered at the pH higher than 10.6.

In order to determine the number of γ-APS molecules adsorbed on the silica wafer versus the pH of the treating solution, the calibration curve,

the integrated absorbance of γ-APS versus the weight of γ-APS, must be established. Dried γ-APS was carefully weighted and pressed into a KBr pellet. The spectra were taken and the area of CH_2 stretching bands at 2930 and 2860 cm^{-1} were used to measure the amount of γ-APS. The area under the two peaks was plotted against the weight of dried γ-APS as shown in fig. 5. The slope of the line was found to be 280.7 cm^{-1}/mg by the least squares method. This indicates that 1 mg of γ-APS will have the area of 280.7 cm^{-1} due to the CH_2 stretching bands. From the calibration curve of silica (fig. 6), in which the absorbance of the peak at 1970 cm^{-1} was used to indicate the amount of silica powder, the weight of the silica wafer treated with coupling agent can be normalized. With the calibration curve of silica and the calibration curve of γ-APS, the number of γ-APS molecules deposited per milligram of silica can be obtained. Figure 7 shows the plot of the number of γ-APS molecules per milligram of silica versus the pH of the treating solution.

The same procedure was followed for the samples treated with γ-MPS and VS coupling agents (figs. 8 and 9). The specific absorptivity of C = C group of unhydrolyzed γ-MPS at 1720 cm^{-1} was measured to be 1.924×10^7 cm/mole and was used to calculate the number of molecules present on the silica surface. The specific absorptivity of VS coupling agent by using the C = C stretching mode at 1602 cm^{-1} was 2.87×10^5 cm/mole [20]. The number of γ-MPS and VS molecules adsorbed per milligram of silica powder are shown in figs. 10 and 11, respectively.

The adsorption of γ-APS on E-glass fiber was determined as a function of the pH of the treating solution (1% by weight). From digital subtraction of pure E-glass spectrum from the spectrum of the treated E-glass,

the amount of γ-APS adsorbed on the fiber was determined and plotted in fig. 12.

Figure 13 shows the difference spectra of untreated silica (fig. 13A) from the aminosilane-treated silica at pH 2 (fig. 13B), pH 10.5 (fig. 13C), and pH 12 (fig. 13D). The difference spectrum at pH 2 shows two peaks at 1610 and 1507 cm ^{1} which are indicative of the NH_3^+ structure of γ-APS. In the difference spectrum of pH 10.5, the peak at 1332 cm^{-1} is an indication that some of the amine groups form aminebicarbonate structures. In addition, the peak at 1596 cm^{-1} resembles that of the bulk sample made from the solution of pH 12. The difference spectrum of untreated silica from the treated silica of pH 12 solution (fig. 13D), shows a peak at 1592 cm^{-1} which is assigned to the free amine.

Figure 14 shows a difference spectrum of the γ-MPS on silica. The peak at 1705 cm^{-1} was assigned to the carbonyl of the methacryl group.

DISCUSSION

The structures of γ-APS hydrolyzate in solution and adsorbed on a glass surface are greatly dependent on the pH of the solution. It has been shown that γ-APS can be in the form of $NH_3^+C\ell^-$, $NH_3^+(HCO_3)^-$, free NH_2, and hydrogen bonded NH_2. From the frequency shifts of the SiOH peak and the assignment of the bands around 1600 cm^{-1}, the structures of γ-APS are proposed. From the IR experiments, we observe that there is a change in the structure of partially cured γ-APS above pH 8.5, which is indicated by the frequency shift of the SiOH peak from 905 to 930 cm^{-1}. The influence of the carbon dioxide on the formation of aminebicarbonate is also noticed between pH 6 and 12. The amount of bicarbonate salt shows a maximum at

the natural pH of the solution. When the amount of γ-APS adsorbed on silica is examined, the maximum adsorption is also found at the natural pH of the solution. The number of molecules adsorbed on silica from γ-APS solution at natural pH is one order of magnitude higher than the sample treated from acidic solution. With a change of the pH from 10.6 to 2, an amine salt ($NH_3^+Cl^-$) is formed. It can be seen that the amount of adsorption is highly dependent on the structure of the amine group itself. The high adsorption of γ-APS on silica at the natural pH of the treating solution may be explained by the difference in the interaction of the amine group with the surface silanol of silica. At low pH, the amine group has a strong interaction with the added acid and forms an amine salt ($-NH_3^+Cl^-$). The SiO^- concentration of the silica surface species decreases at low pH, whereas, the concentration of the surface silanol increases. At natural pH the concentration of SiO^- on the silica surface is higher. The positively charged amine group prefers to interact with a negatively charged silica surface. However, at low pH the tendency for the $NH_3^+Cl^-$ to interact with SiOH is lower. Therefore a greater adsorption is observed at natural pH than in an acidic solution. At high pH (above 11), some of the γ-APS silanol groups may be in the form of SiO^- which will have a tendency to repel the negatively charged surface SiO^-. The adsorption of γ-APS at pH 12 is lower than at natural pH.

When γ-MPS and VS were used to treat silica wafers, their adsorption characteristics showed little pH dependency except at pH above 10. VS adsorbs more on silica surface than γ-MPS. The high adsorption of VS on silica may be explained by the size effects. The VS molecule is smaller

than γ-MPS, thus the silica surface can adsorb more molecules per unit area. From the plot in figs. 12 and 13, 1.13×10^{17} molecules of VS are adsorbed per milligram of silica compared with 6.21×10^{16} molecules for γ-MPS. The VS molecules are small and can be trapped in the cavities of the rough silica surface. Knowing the specific surface area of silica powder (130 m^2/g), the number of molecules on the surface, and an approximate molecular size, the equivalent number of layers can be calculated. The estimated area occupied by a VS and a γ-MPS molecule are 40 $Å^2$/molecule [13] and 50 $Å^2$/molecule, respectively [21]. The calculation shows that VS and γ-MPS form 0.35 and 0.24 equivalent layers on silica when treated with a 1% by weight solution, both of which correspond to nearly effective monolayer coverages.

The adsorption of γ-APS on E-glass mat shows a trend similar to the adsorption on silica wafer. The maximum adsorption occurs when the treating solution is at its natural pH. However, the absolute amounts of adsorbed molecules at natural pH and at acidic pH do not differ as much as for the silica wafer. This is probably due to the fact that the nearly effective monolayer coverage on silica results in direct interaction between the surface and the silane. Whereby, with E-glass fibers, the multilayer adsorption shows the reduction of the surface effects; however, the orientation of the silane in the first layer influences the adsorption of the next layer and so on, thus resulting in the observation of the surface effects on the adsorption curve but less than the silica sample.

γ-APS adsorbed on silica surface may very well have more than one structure. From the difference spectrum (fig. 13B), the peak at 1332 cm^{-1} is evidence that the amine bicarbonate structure is present. The

peak at 1596 cm^{-1} is also present when the sample is treated from solution at natural pH. This band is due to the hydrogen bonded amine. Preliminary results show that about 50% of the amine group is in the form of the bicarbonate. Figure 14 shows that the carbonyl group is hydrogen bonded. In general the carbonyl peak of γ-MPS appears at 1720 cm^{-1} and can be shifted as much as 1740 cm^{-1} upon polymerization of the C = C functional group. The band at 1705 cm^{-1} indicates that the carbonyl is hydrogen bonded. No direct evidence has been obtained thus far on the hydrogen bonding of the amine group with the surface though all indirect evidence suggests the interaction with the surface. In the case of γ-MPS, the hydrogen bonded C = O has a frequence at 1705 cm^{-1}. The partially cured hydrolyzate of γ-MPS contains a significant amount of SiOH which intermolecularly hydrogen bonds with the C = O group of the methacryl moiety. For this hydrogen bonding, the C = O stretching mode occurs at 1700 cm^{-1} [20]. This frequency shift can be considered as the evidence that the C = O group is in fact interacting with the silica surface.

The structures of partially cured γ-APS are proposed based on the bands around 1600 cm^{-1} and the SiOH band around 930 cm^{-1}. The shifting of the SiOH mode is due to hydrogen bonding. When the γ-APS sample is dried in a nitrogen atmosphere, the SiOH peak shifts to 934 cm^{-1}, even higher than the sample dried in air which gives rise to the SiOH mode at 930 cm^{-1}. This indicates that the sample dried in nitrogen forms stronger hydrogen bonds than the sample dried in air since stronger hydrogen bonding increases the SiO stretching frequency of the silanol whereas the OH stretching frequency decreases under the same circumstance.

It is reasonable that the sample dried in air will have less hydrogen bonding since the bicarbonate structure is also present. At pH 12, the amine group is mostly in the form of NH_2 as indicated by a single peak at 1595 cm^{-1}. However, there are some residual SiOH groups indicated by the presence of the band at 925 cm^{-1}.

The influence of carbon dioxide on the formation of the bicarbonate salt with the amine group is noticeable at pH 6. When γ-APS is applied at a solution pH higher than 6 onto glass surface, the bicarbonate salt may be formed during the drying process. It is not known whether the bicarbonate structure can alter the reactivity of the amine group with the resin matrix. It was found that the strength of a silica-filled polyester composite may be improved more than 100% by changing the pH of silane application from 12 to 2 [12].

CONCLUSIONS

The structure of γ-APS is highly dependent on the pH of the treating solution. The maximum number of molecules are adsorbed when the silica is treated with a solution at its natural pH (10.6). It is evident that the mode of adsorption of γ-APS on silica and E-glass fibers is pH dependent. The amount of γ-MPS and VS adsorption, however, is independent of the pH of the treating solution below pH 10. With 1% by weight solution, the number of molecules of VS and γ-MPS on a high-surface-area silica are 1.13×10^{17} and 6.21×10^{16}, respectively. Various structures were proposed based on the amine deformation bands around 1600 cm^{-1} and the SiOH stretching band around 930 cm^{-1}. The peak of SiOH can shift from 905 cm^{-1} of acidic sample to 930 cm^{-1} of the natural pH sample. This shifting is due to the variation in the strength of hydrogen bonding.

The structure of γ-APS changes noticeably in the pH range of 6 to 12. At the natural pH of the treating solution, the maximum amount of bicarbonate formation as well as the maximum amount of adsorption were observed.

The structure of γ-APS on the silica surface treated at pH = 2 is in the form of a protonated amine. At natural pH (10.6), two structures are observed, namely hydrogen bonded NH_2 and amine bicarbonate. At pH = 12, γ-APS is mainly in the form of NH_2.

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FIGURE CAPTIONS

Fig. 1 FT-IR spectra of partially cured γ-APS. The solution at various pH was dried on AgBr plate in room environment.

Fig. 2 The position of SiOH peak of partially cured γ-APS shifts as a function of pH of the solution.

Fig. 3 Proposed structures of partially cured γ-APS as a function of pH of the solution and drying conditions. Amine deformation and SiOH vibrational modes were used to derive the structures.

Fig. 4 FT-IR spectra of (A) untreated silica wafer and (B) treated silica with 1% weight γ-APS at pH = 2, (C) pH = 9, (D) pH = 10.6, (E) pH = 12.

Fig. 5 Calibration curve of partially cured γ-APS by using area under CH_2 stretching bands.

Fig. 6 Calibration curve of silica wafer. The absorbance at 1970 cm^{-1} was plotted versus the weight in milligrams of silica.

Fig. 7 Number of γ-APS molecules adsorbed on silica as a function of pH of the treating solution. Highest adsorption occurs at pH = 10.6.

Fig. 8 FT-IR spectra of γ-MPS (1% weight) at (A) pH = 2, (B) pH = 5, (C) pH = 12 treated on silica wafer.

Fig. 9 FT-IR spectra of vinyl silane (1% weight) at (A) pH = 2, (B) pH = 7.5, (C) pH = 12 treated on silica.

Fig. 10 Number of γ-MPS molecules on silica treated from 1% weight solution at various pH.

Fig. 11 Number of vinyl silane molecules on per milligram of silica treated from 1% weight solution at various pH.

Fig. 12 Number of γ-APS molecules deposited on E-glass as a function of pH of the treating solution (1% weight).

Fig. 13 FT-IR difference spectra: (A) silica treated with 1% weight γ-APS at pH = 2, (B) pH = 10.6, (C) pH = 12 minus the untreated silica. Various γ-APS structures, depending on pH of the treating solution, present on silica surface.

Fig. 14 FT-IR difference spectra of γ-MPS treated on silica minus untreated silica. The band at 1705 cm^{-1} indicates hydrogen bonded carbonyl group.

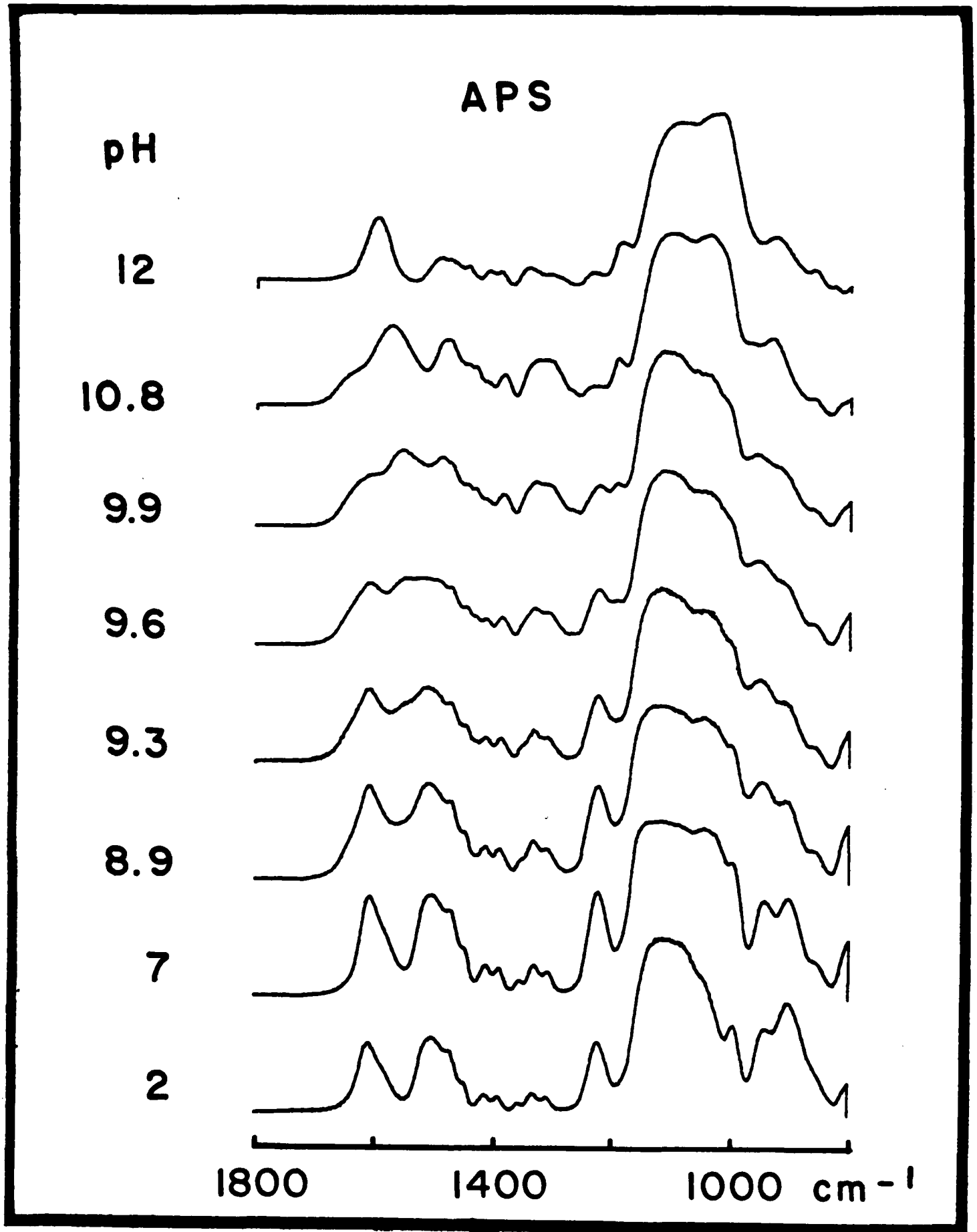


Fig. 1

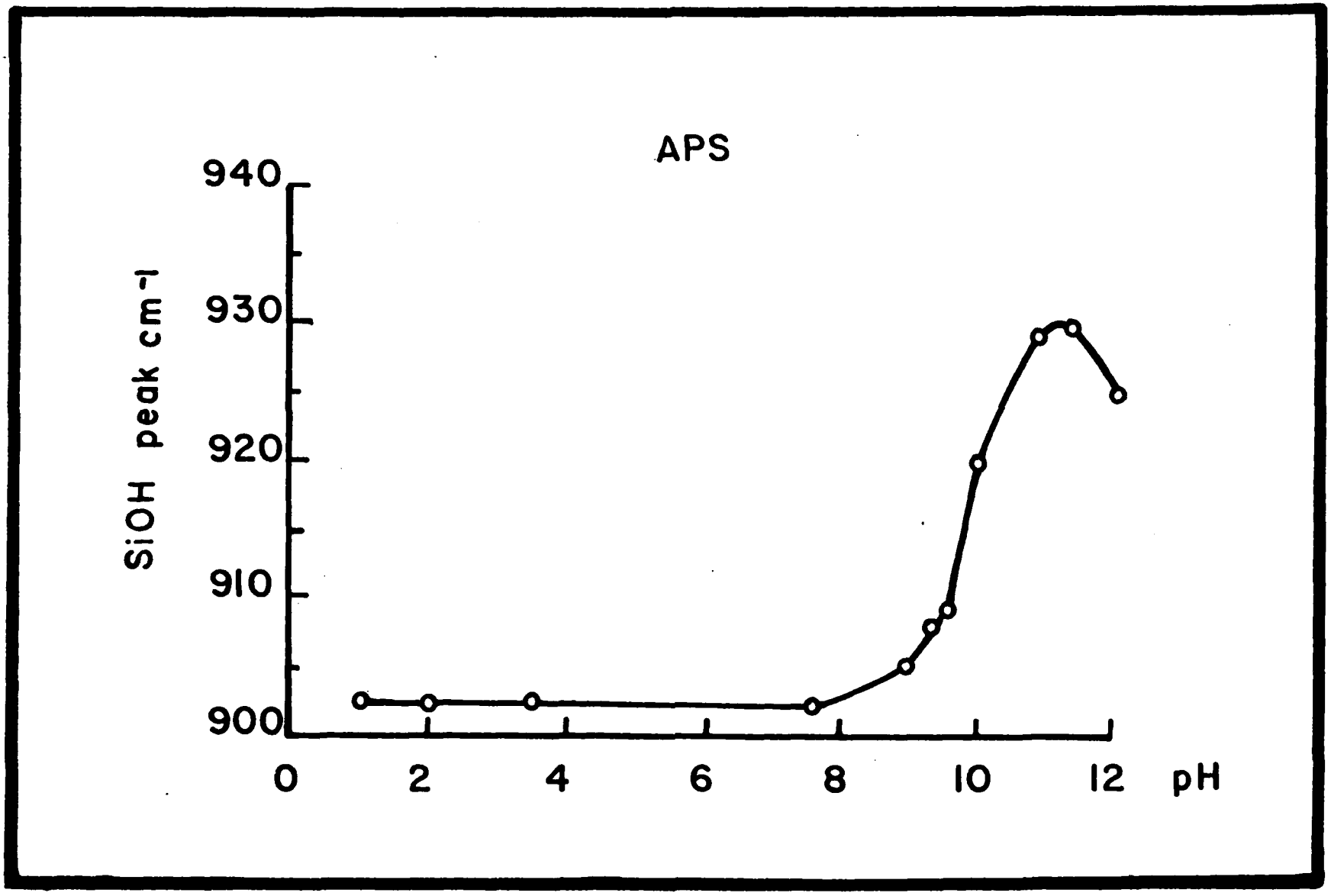


Fig. 2

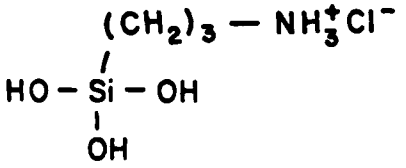
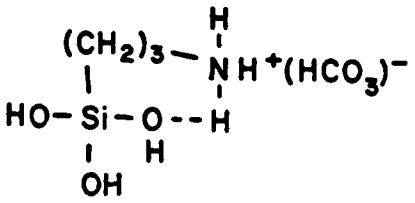
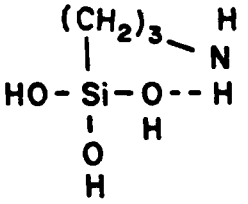
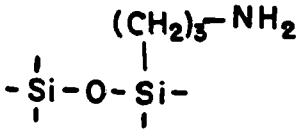
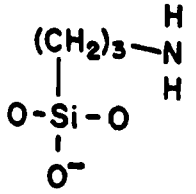
pH		Amine def. (cm^{-1})	SiOH (cm^{-1})
2		1610, 1505	902
10.8			
Air dried		1575, 1488	930
N_2 dried		1601	934
Heated		1591	—
12		1595	925

Fig. 3

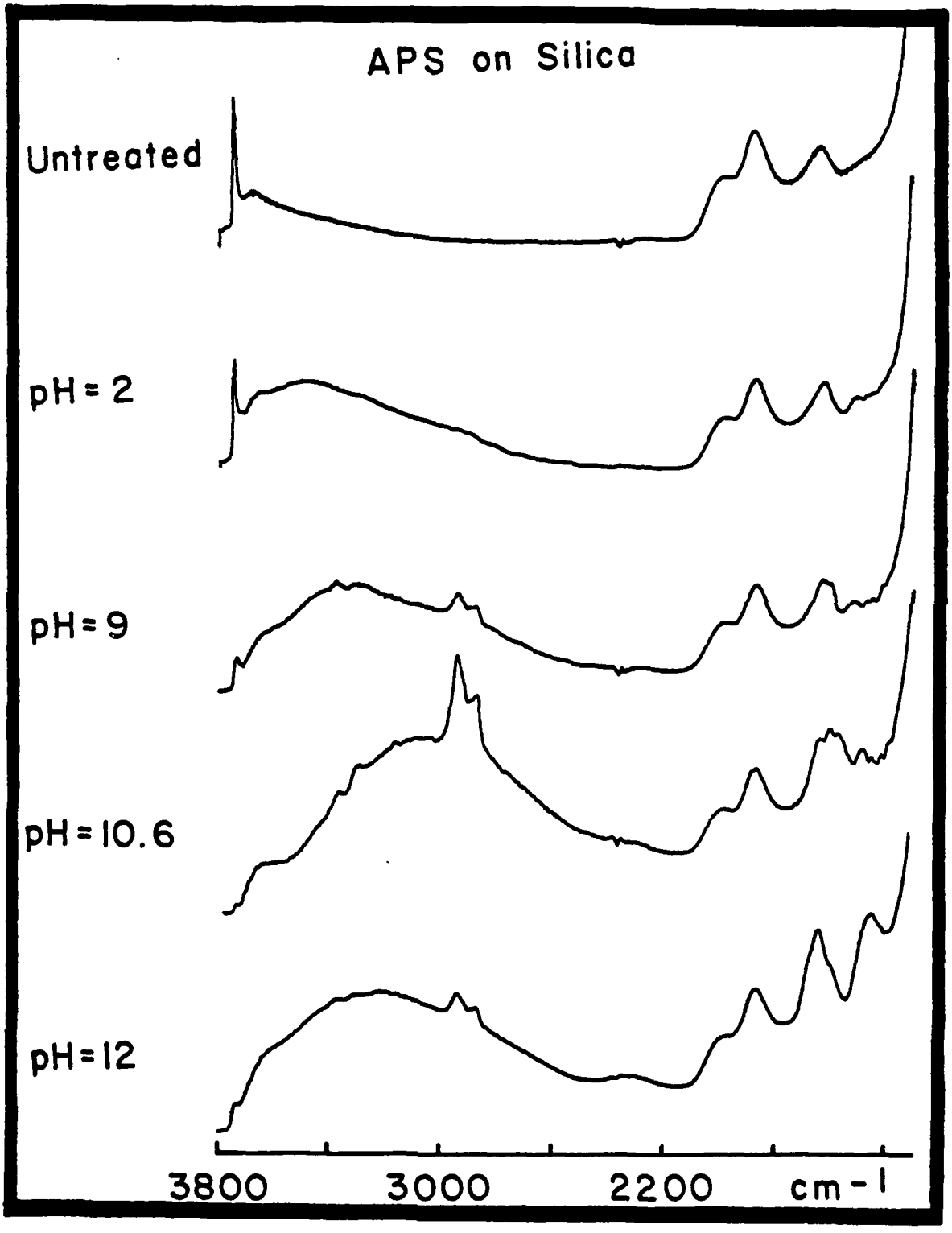

APS on Silica
Untreated
pH = 2
pH = 9
pH = 10.6
pH = 12
3800
3000
2200
cm-1

Fig. 4

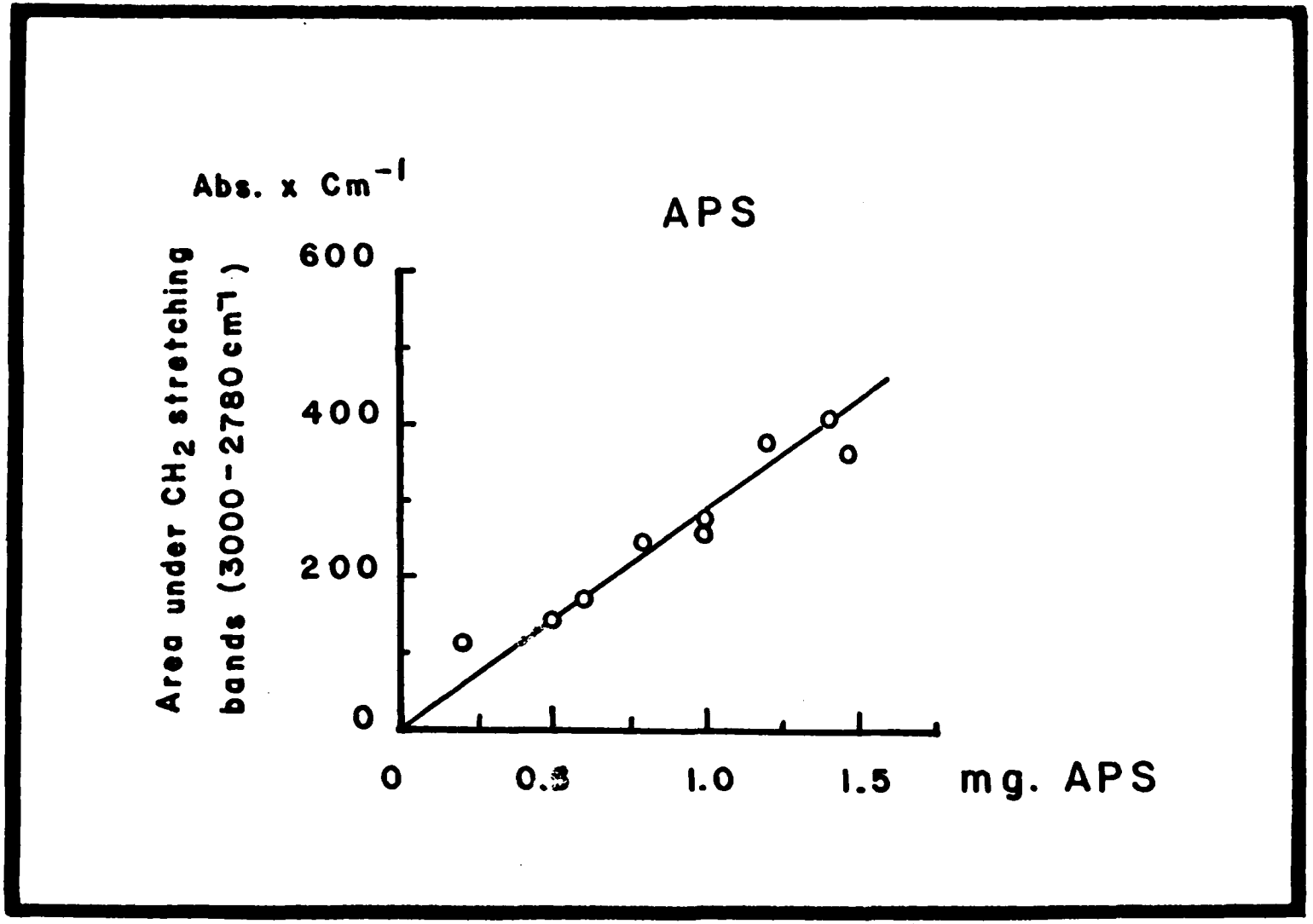

Abs. x Cm⁻¹
APS
Area under CH2 stretching bands (3000-2780 cm⁻¹)
600
400
200
0
0
0.5
1.0
1.5
mg. APS

Fig. 5

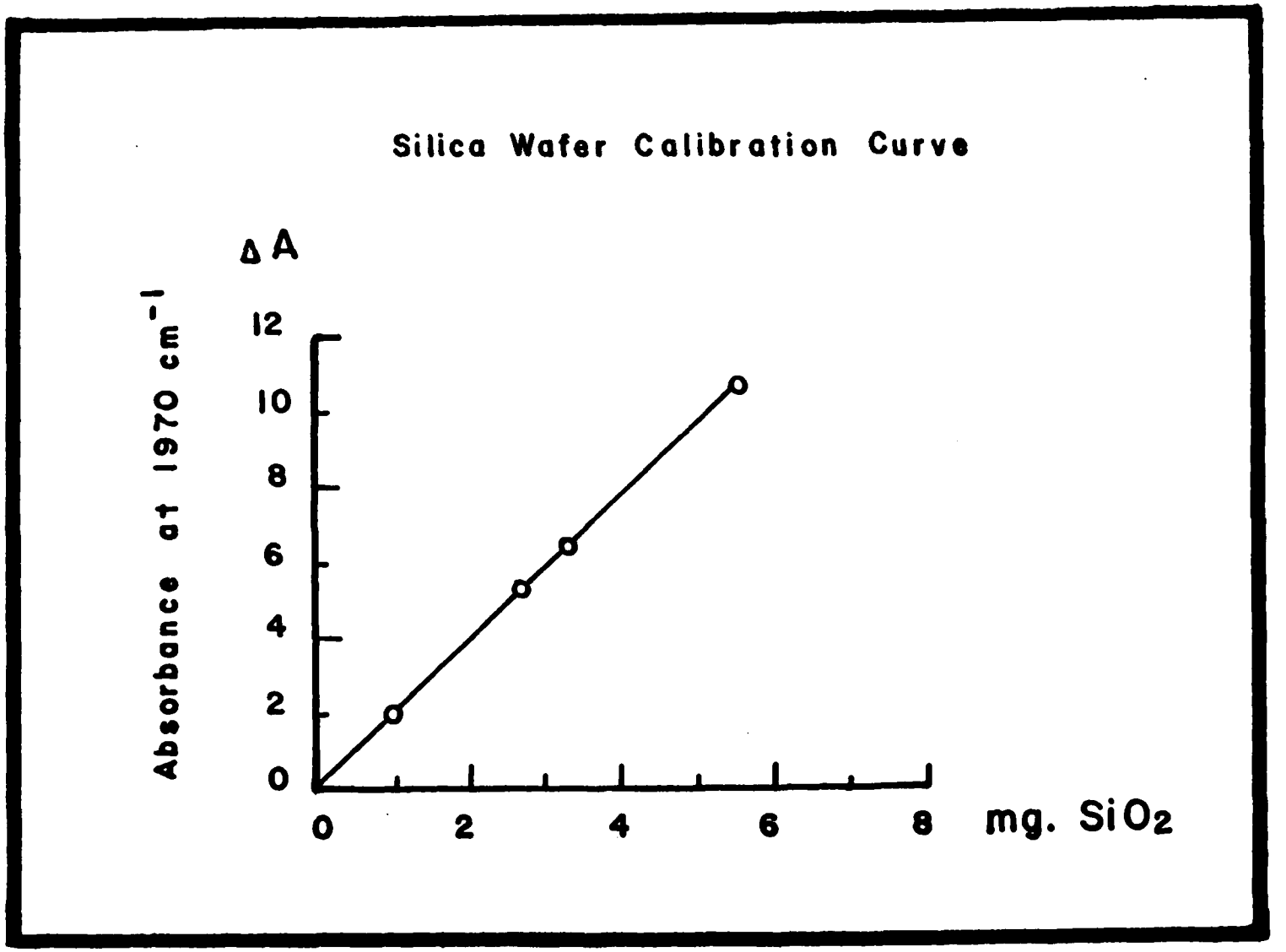

Silica Wafer Calibration Curve
ΔA
Absorbance at 1970 cm⁻¹
12
10
8
6
4
2
0
0
2
4
6
8
mg. SiO2

Fig. 6

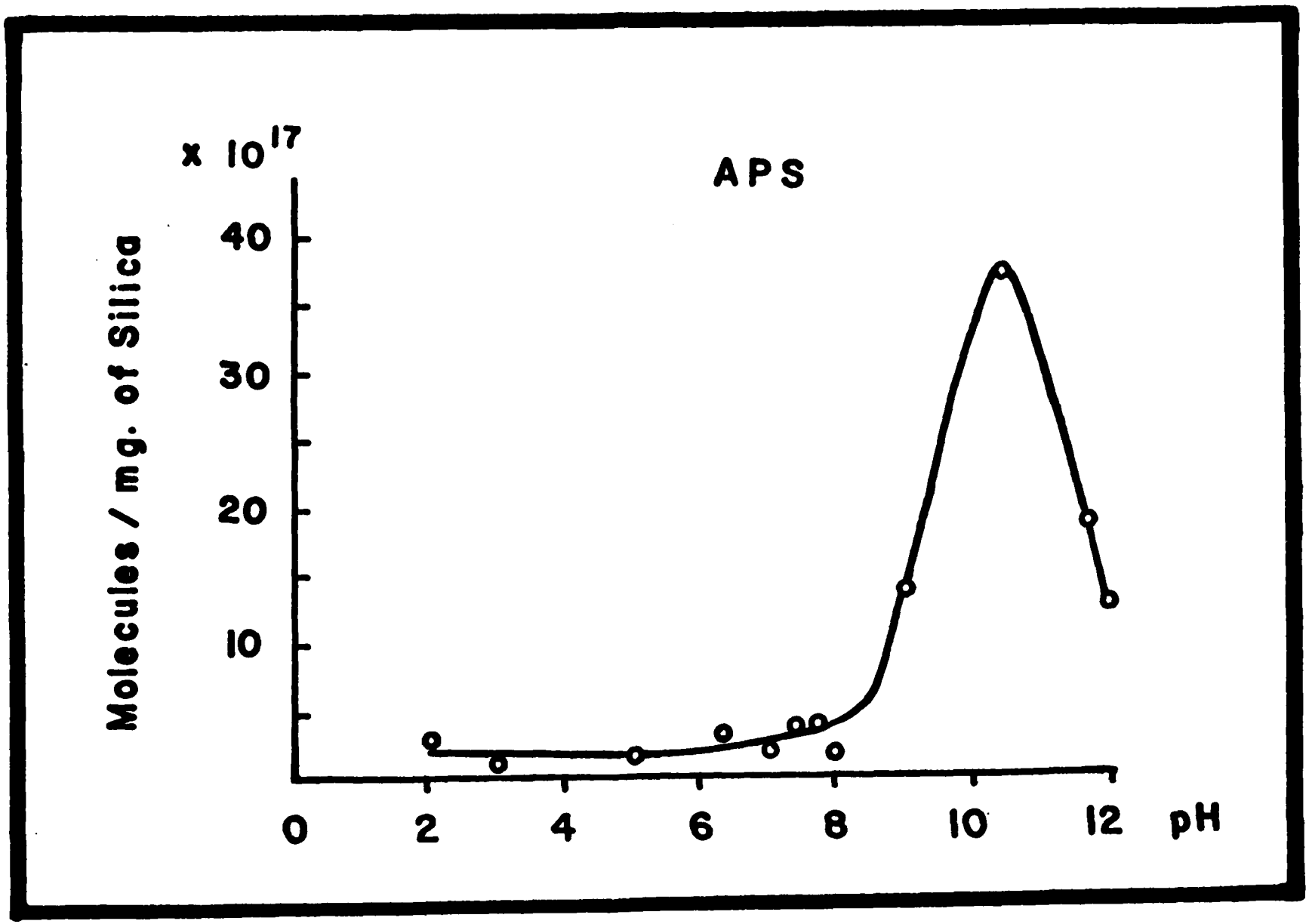


Fig. 7

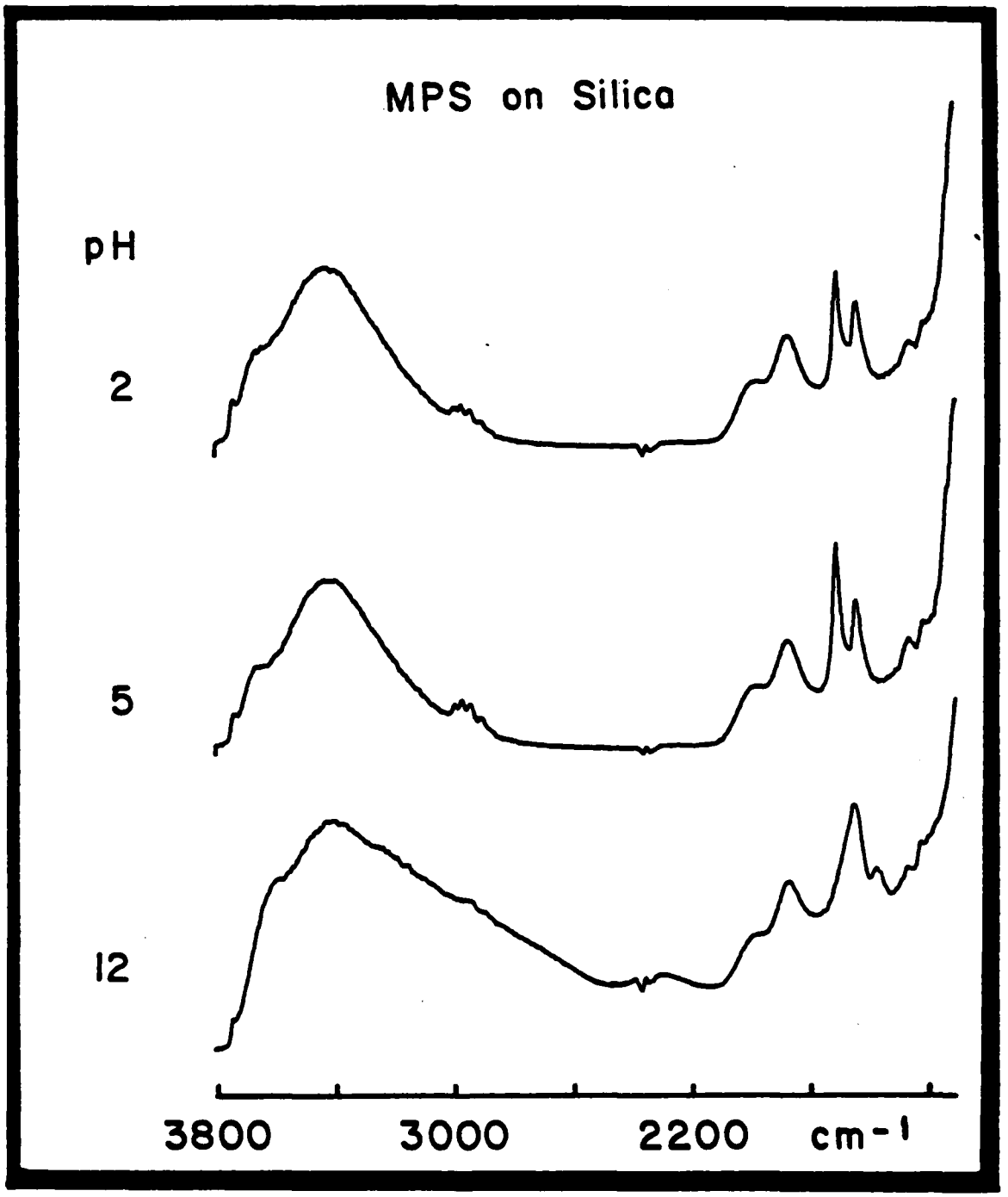


Fig. 8

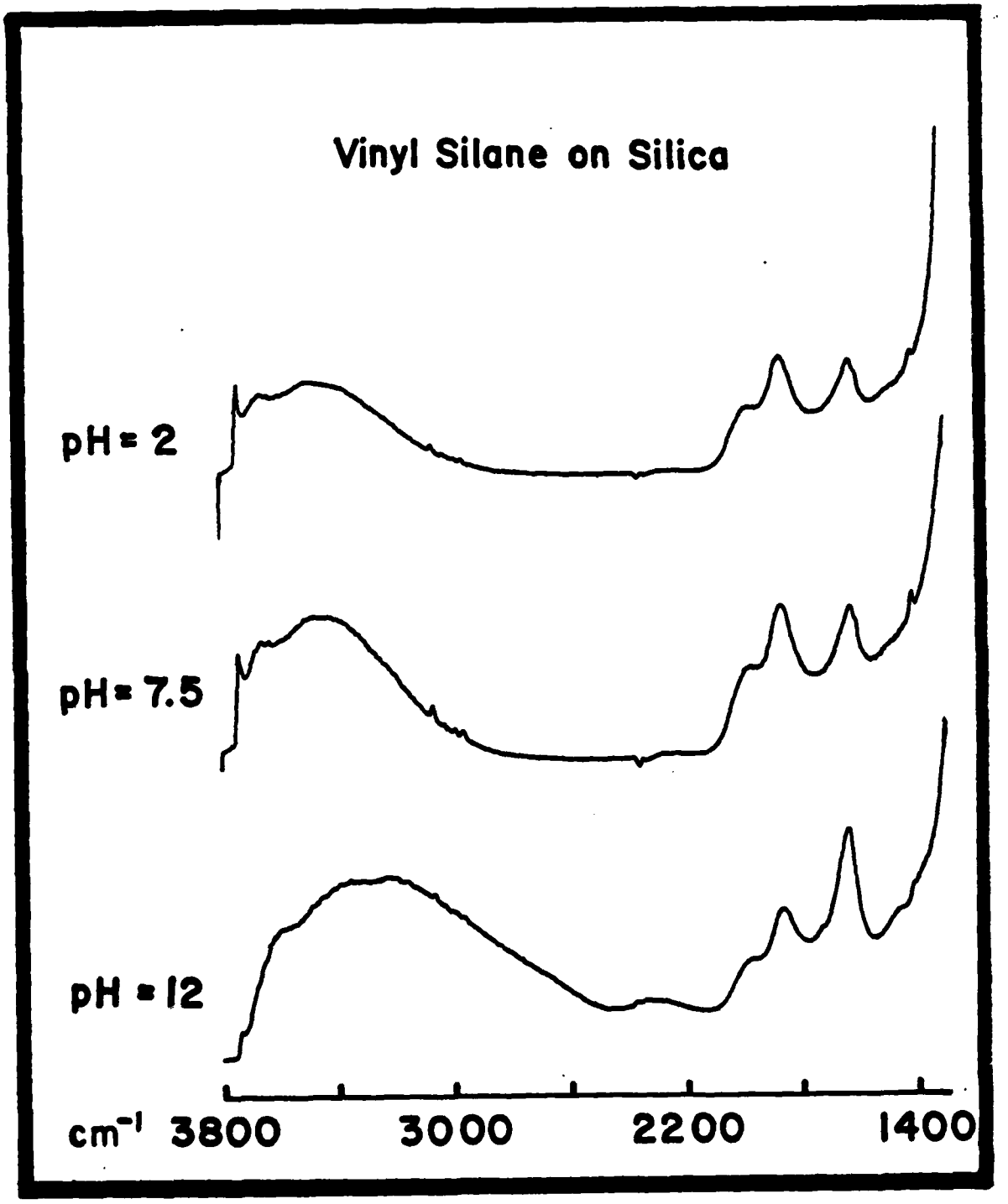


Fig. 9

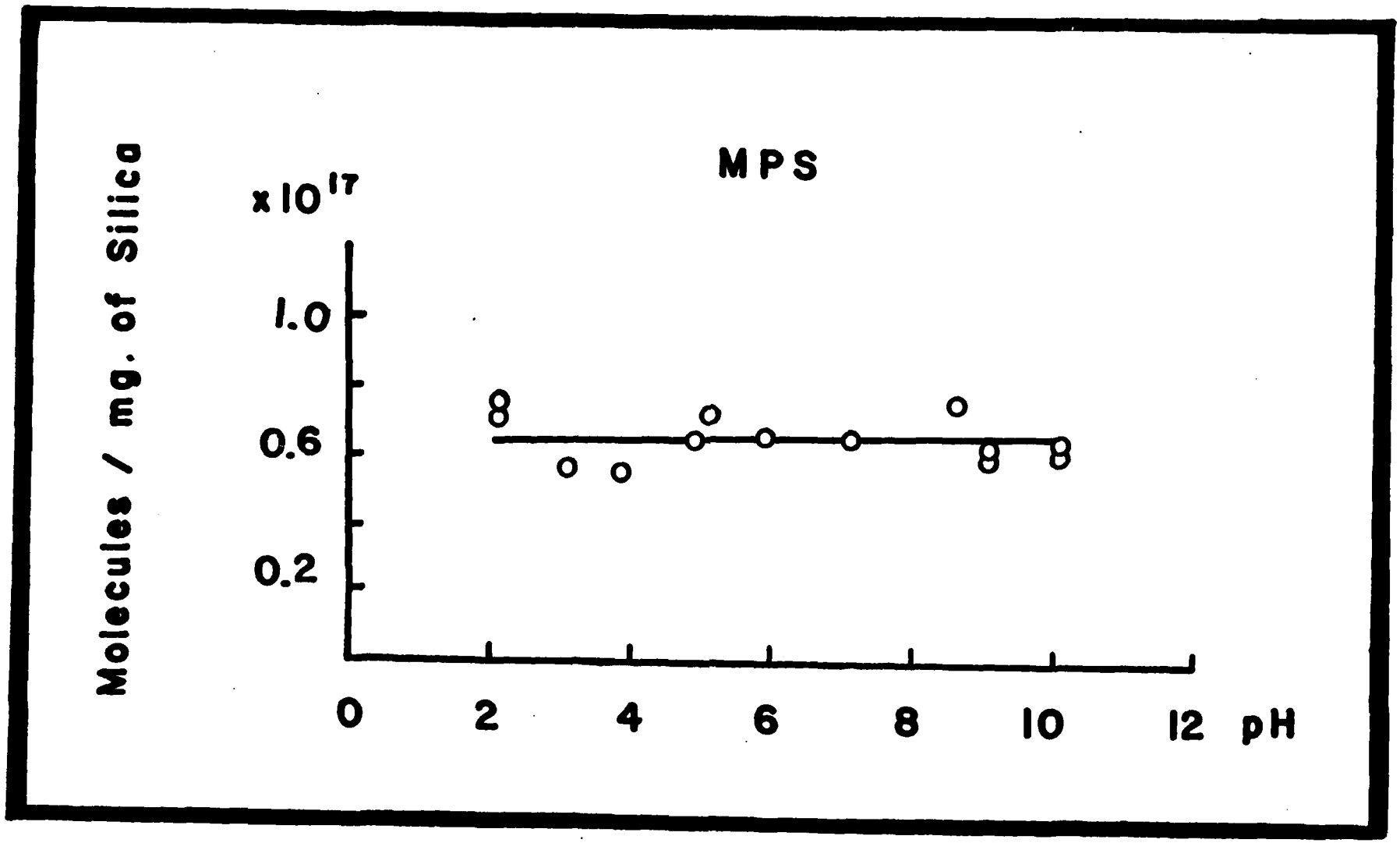


Fig. 10

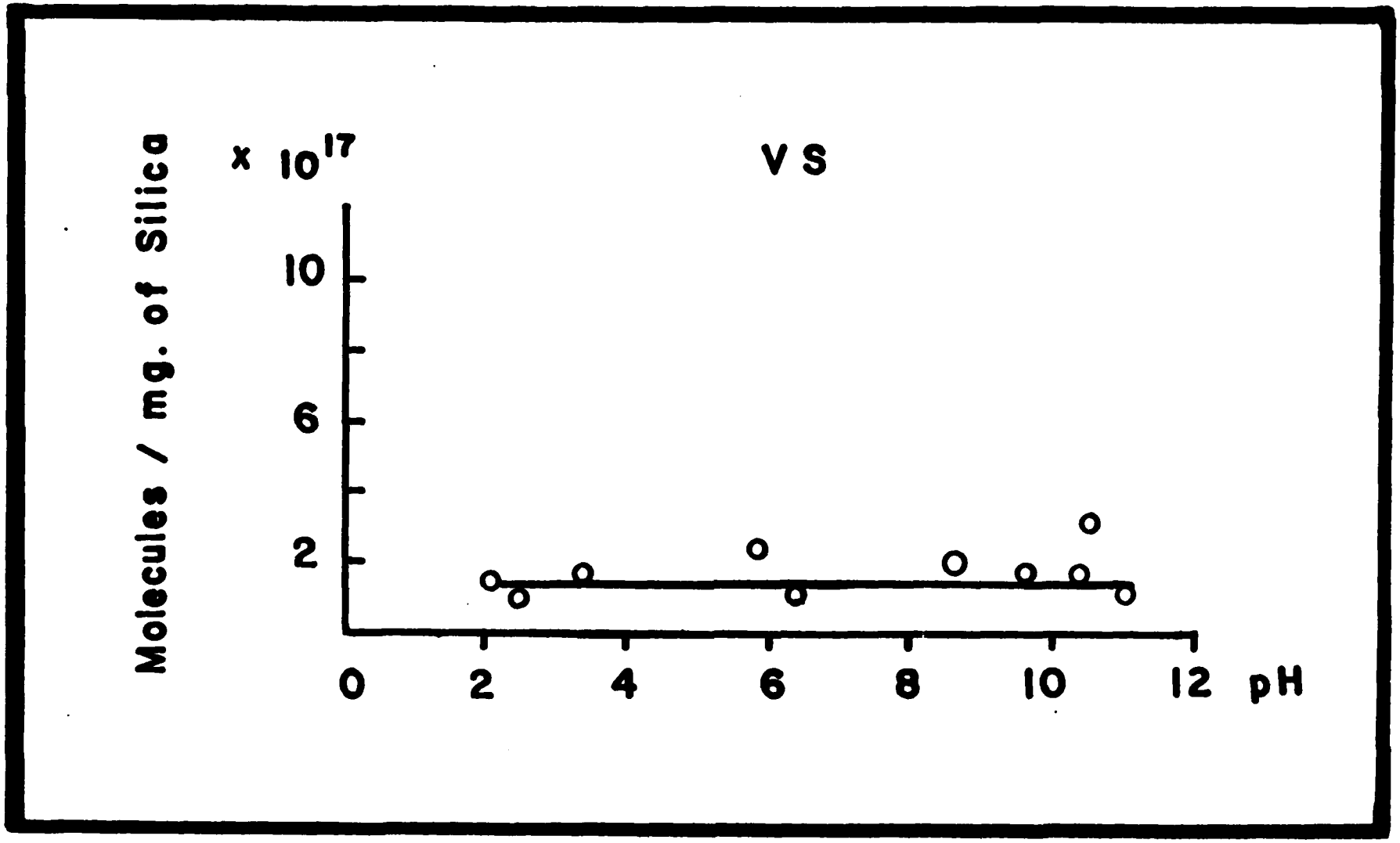


Fig. 11

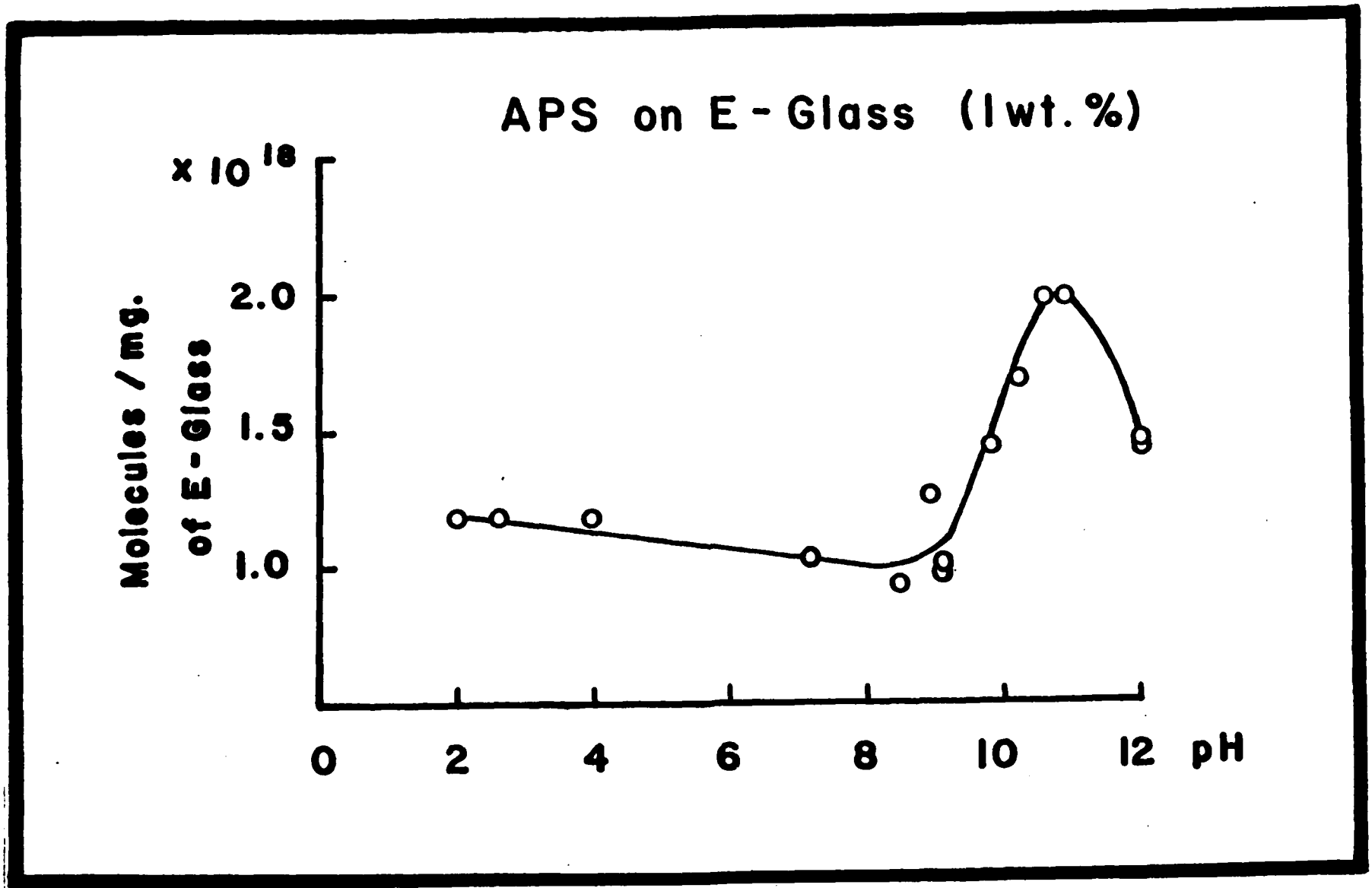

APS on E-Glass (1wt.%)
x 10^18
Molecules / mg. of E-Glass
2.0
1.5
1.0
0
2
4
6
8
10
12
pH

Fig. 12

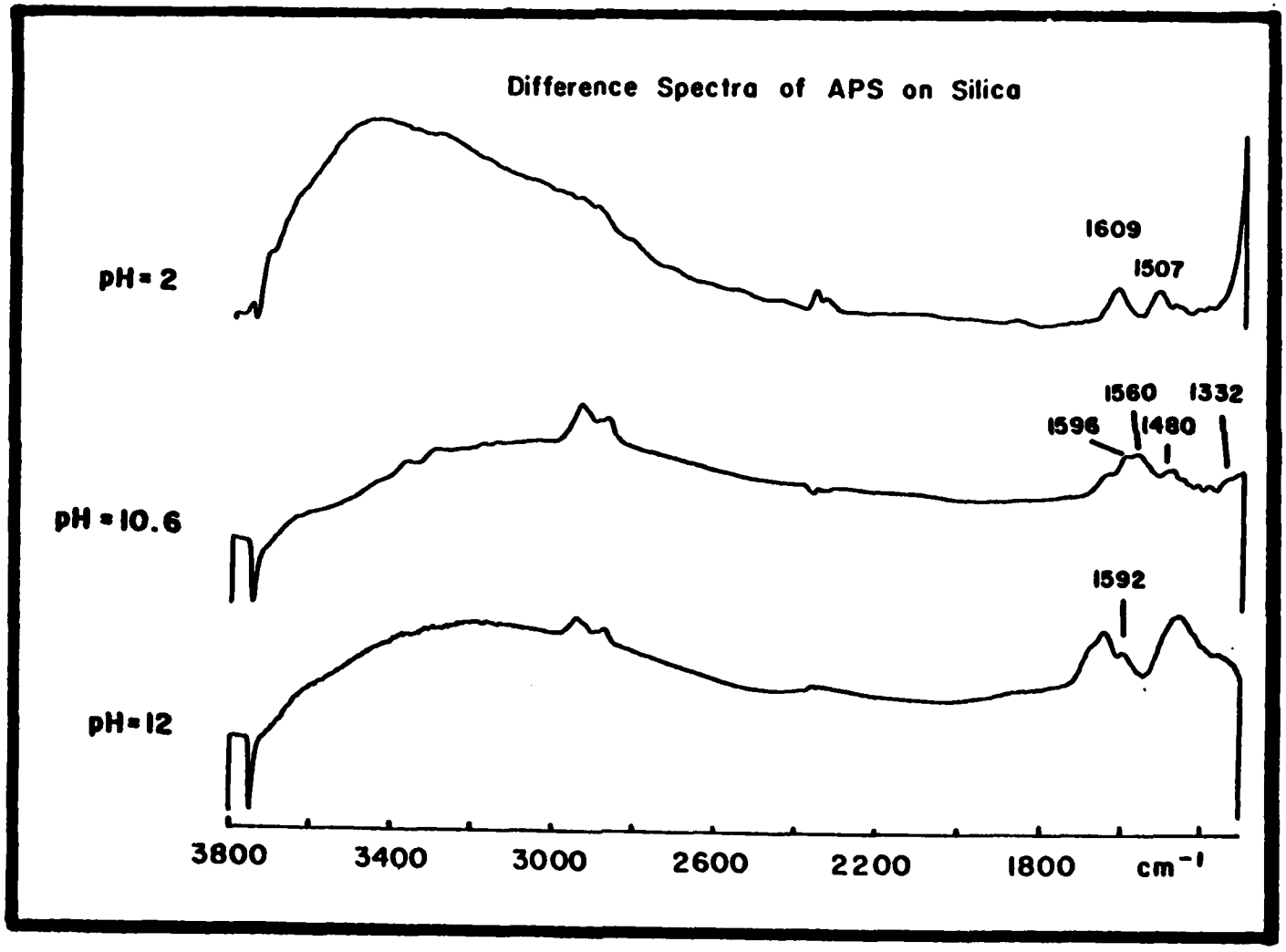

Difference Spectra of APS on Silica
pH = 2
1609
1507
1560
1332
1596
1480
pH = 10.6
1592
pH = 12
3800
3400
3000
2600
2200
1800
cm⁻¹

Fig. 13

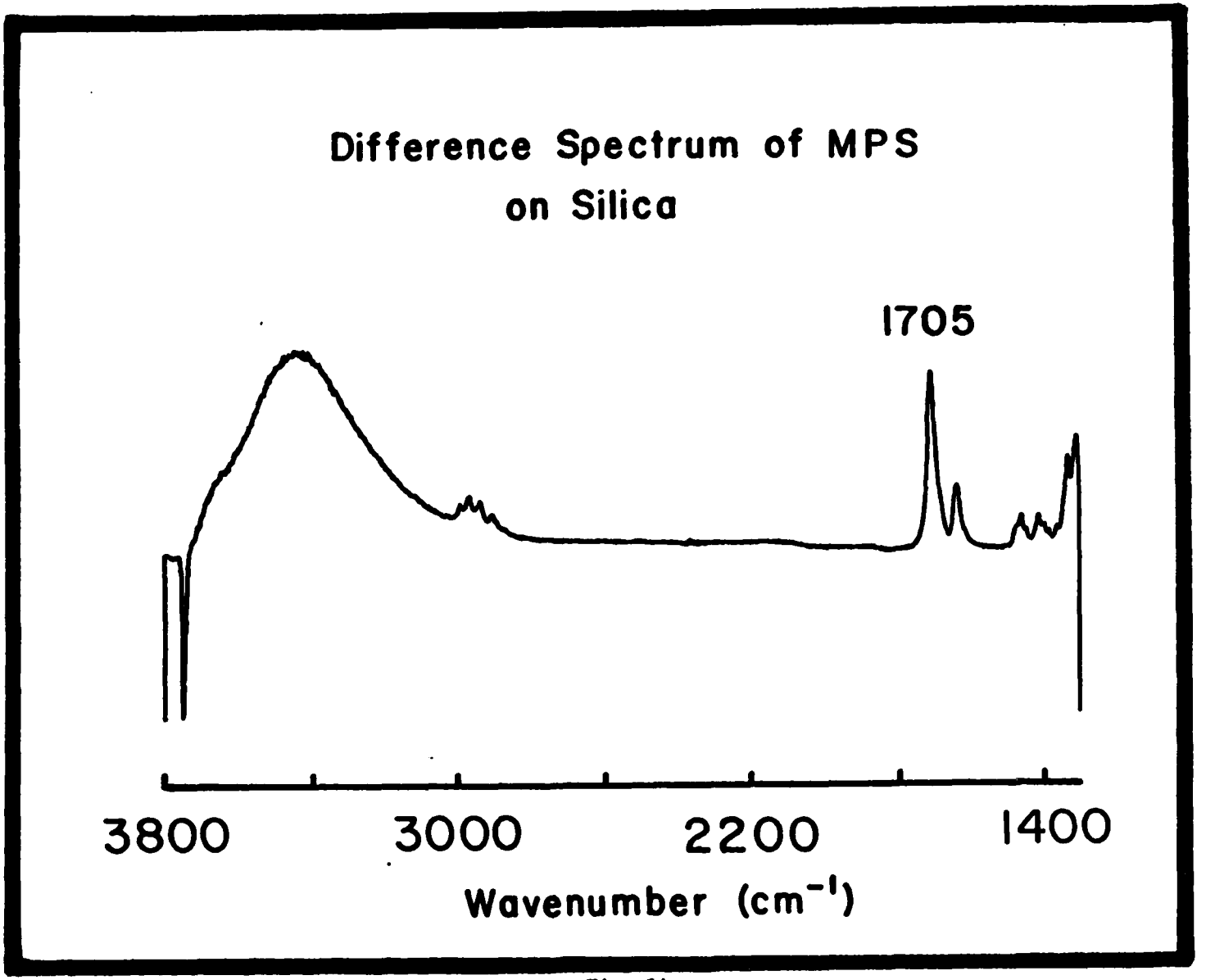

Difference Spectrum of MPS
on Silica
1705
3800
3000
2200
1400
Wavenumber (cm⁻¹)

Fig. 14