

The structure of aminofunctional silane coupling agents: 1. γ -Aminopropyltriethoxysilane and its analogues

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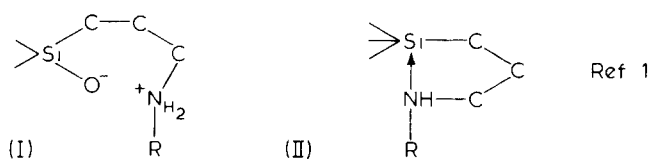
Gamma-aminopropyltriethoxysilane (γ -APS) and its analogues are studied as aqueous solutions as well as solids by Fourier transform infra-red spectroscopy (FT i.r.) and laser Raman spectroscopy. Emphasis was placed on a determination of the nature of the interaction between the amine groups and the residual silanol groups in partially cured solids. Comparison with γ -aminopropyltrisilanolate and partially cured solids obtained from γ -aminopropylmethyldiethoxysilane and γ -aminopropyl-dimethylethoxysilane lead us to conclude that the residual silanol groups are strongly hydrogen bonded to the amine groups as $\text{SiOH} \cdots \text{NH}_2$ rather than $\text{SiO}^- \cdots {}^+\text{NH}_3$. Hydrolysis of γ -APS at concentrations ranging 2–80% by weight showed that the solutions below 40% by weight have a few unhydrolysed alkoxy groups. The amine groups are mutually hydrogen bonded in unhydrolysed silane. However, in an aqueous solution and highly cured solids, the amine groups are either free or are interacting predominantly with water molecules.

Keywords Spectroscopy; infra-red; Raman, solutions; γ -aminopropyltriethoxy silane; hydrolysis; amines, interaction

INTRODUCTION

Aminosilanes have applications in a number of areas as silane coupling agents for fibre-glass reinforced plastics. To date, however, the molecular structures of the hydrolysates of aminosilanes are not known. Aminosilanes show a complicated molecular nature and they are often sensitive to the conditions of sample preparation.

Unlike many other organotrialkoxysilanes, aminosilanes exhibit a remarkable stability in aqueous solutions even at high concentrations. In order to explain this stability, Plueddemann¹ first postulated either five or six membered rings in which either the nitrogen atom interacts with the silicon atom or one of the silanols.

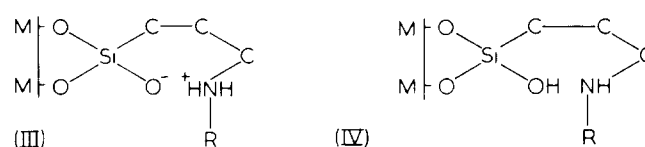


Extensive effort has been made to elucidate the macroscopic nature of aminosilanes on substrates^{2–7}. Bascom⁸ using infra-red attenuated total reflection spectroscopy (a.t.r.) and Shih and Koenig⁹ using laser Raman spectroscopy pioneered the study of the molecular structure of aminosilanes. The aminosilanes deposited on germanium plates from both aqueous and cyclohexane solutions showed multilayers of polymerized silane⁸.

Boerio and others¹⁰ utilized infra-red reflection-absorption spectroscopy to study an aminosilane deposited on electropolished metal surfaces. They assigned the observed infra-red band at 1510 cm^{-1} to the NH_3^+ as a consequence of the six membered ring structure (I) and the band at 1575 cm^{-1} to the five membered ring

structure (II) which leads to a penta-coordinated silicon atom. Unfortunately, due to the unavailability of proper model compounds, no unambiguous evidence for the penta-coordinated silicon was reported.

Anderson *et al.*¹¹ used X-ray photoelectron spectroscopy for chemical analysis (e.s.c.a.) and observed the N 1s e.s.c.a. band of an aminosilane on a silicon wafer as a doublet. They attributed the higher energy peak to the protonated amine, $-\text{NH}_3^+$. Addition of hexafluoroisopropanol reduced the NH_3^+ species and, as a result, increased the population of the SiOH groups of the hydrolysate of the aminosilane. Moses *et al.*¹² also used e.s.c.a. to study the aminosilanes on electrode surfaces. They realized the multiplicity of the structures of aminosilanes depended upon the environments and proposed the following two structures.



The N 1s e.s.c.a. band at 401.9 and 400.3 eV are assigned to the protonated and free base, respectively. The population of free base increases at higher pH values of the environment. Our previous work¹³ showed that the aminopropyl chain can be either a ring structure or extended chain shown below depending on the degree of curing.



Ion scattering spectroscopy (i.s.s.) and secondary ion mass spectroscopy (s.i.m.s.) have been applied by DiBenedetto and Scola¹⁴ in order to study the structure of an aminosilane on S-glass fibres. The depth profile of the structure of a multilayer of aminosilane on the fibres cured at 100°C for 45 min was studied employing the sputtering technique by ³He ion beam. They reported that the aminosilane at the air/silane interface consisted of a high molecular weight polysiloxane layer and the middle of the silane layer consisted of oligomeric polysiloxanes. The region near the silane/glass interface had a high molecular weight polysiloxane layer. The effect of humidity at elevated temperature was reported to enhance polymerization of the oligomeric layer of the aminosilane.

Preliminary results of inelastic electron tunnelling spectroscopy¹⁵ by Diaz *et al.* and Auger electron spectroscopy¹⁶ by Cain and Sacher on aminosilanes deposited on aluminium oxide and silicon wafers, respectively, have been reported. γ -Aminopropyltriethoxysilane formed a more dense polymerized layer when deposited from the silane hydrolysed by water only when deposited from the 50:50% mixture in volume of water and methanol.

The results described above reveal the complicated nature of aminosilanes. Apparently, further investigation is needed to elucidate the molecular structures of aminosilanes and understand the mechanism of their effectiveness as adhesion promoters. Since the structures of the silane layers on the glass surfaces are strongly influenced by the structure of a silane in an aqueous solution¹⁷, it is essential to investigate the structure of aminosilanes in aqueous solutions. To date, the molecular structure of aminosilanes in aqueous solutions and the polymers without substrate have not been studied. Fourier transform infra-red spectroscopy (FTi.r.) is extremely useful for studying aqueous solutions of silanes^{13,18,19}. The weak interference by water is also advantageous in laser Raman spectroscopy¹⁸⁻²⁰ and the information from infra-red and Raman spectra are complementary. Therefore, we will utilize the combination of FTi.r. and laser Raman spectroscopy in order to study the structures of amine and silanol groups in greater detail.

EXPERIMENTAL

A Fourier transform infra-red spectrophotometer (Digilab FTS-14^R) and laser Raman spectrometer (Spectra Physics Ar⁺ ion laser; model 165 and Spex holographic grating double monochromator) are the same as our previous papers^{18,19}. Spectral resolution of 2 cm⁻¹ and 4 cm⁻¹ are the common set ups for infra-red and Raman spectra, respectively. All infra-red spectra in this paper are shown in the absorbance mode. The difference between the maximum and the minimum absorbances of the spectrum is designated as ΔA .

γ -Aminopropyltrimethoxysilane, γ -amino-propyltriethoxysilane, γ -aminopropylmethyl-diethoxy-silane and γ -aminopropyldimethylethoxysilane were purchased from Petrarch Systems and only freshly purchased samples which had been stored under nitrogen were used. Vinyltrimethoxysilane was kindly provided by Dr E. P. Plueddemann, Dow Corning Co. The silanes were hydrolysed with deionized distilled water and the spectral examination was undertaken usually between 20 and 45

min after the hydrolysis unless kinetic experiments were to be performed. The polyaminopropylsiloxane film was prepared by depositing the aqueous solution of 20% by weight aminopropyltriethoxysilane onto a AgBr plate and dried at room temperature for 30 min. γ -Aminopropyltrisilanolate and vinyltrisilanolate were prepared by adding the starting silanes slowly with rigorous agitation into the KOH solution at a mole ratio of 1:6 (silane:KOH) yielding H₂N(CH₂)₃ Si O₃ and CH₂=CH Si O₃⁻³, respectively. The concentration of the silanes was 20% by weight.

RESULTS

The Raman spectrum of γ -aminopropyltrimethoxysilane (Figure 1) shows two strong lines at 645 and 614 cm⁻¹ due to the symmetric SiOC stretching mode of the trialkoxy group. This splitting is commonly observed when the organic chain has more than three carbons due to vibrational interactions along the C-C-C-Si-O skeleton. The magnitude of separation of the two frequencies is strongly influenced by the nature of the attached alkoxy groups²¹. The symmetric SiO stretching mode is usually one of the strongest Raman lines in organotrialkoxysilanes as well as organosilanetriols. A strong line at 645 cm⁻¹ is unique to the structure RSi(OX)₃ where R represents organofunctionality and X is the species such as CH₃ or H. The dimer does not show this mode nor any explicit characteristic lines, thus, Raman spectroscopy, using the strong lines in the range 750-620 cm⁻¹, can verify the existence of organosilane monomers in solutions.

The Raman spectrum of hydrolysed γ -aminopropyltriethoxysilane as a 20% by weight aqueous solution is shown in Figure 2. Spectrum A does not show this strong symmetric SiO stretching mode of the Si(OH)₃ group in the range 750-650 cm⁻¹ nor the characteristic bands due to the SiO bending modes of the Si(OH)₃ group in the range 450-350 cm⁻¹ indicating absence of silanetriol monomer. The very strong line at 1021 cm⁻¹ is due to the ethanol produced as a byproduct of the hydrolysis of the ethoxy groups. Figure 2 also includes the spectrum (B) of γ -aminopropyltriethoxysilane in concentrated KOH solution. Spectrum A resembles the spectrum of a highly crosslinked polyaminopropylsiloxane (Figure 3) as a powder except for the lines due to water and ethanol. The band at 525 cm⁻¹ in Figure 3 is due to the symmetric SiOSi stretching mode and its relative intensity to the CH₂ bending mode of the propyl chain at 1455 cm⁻¹ is similar to the polyaminopropyl-

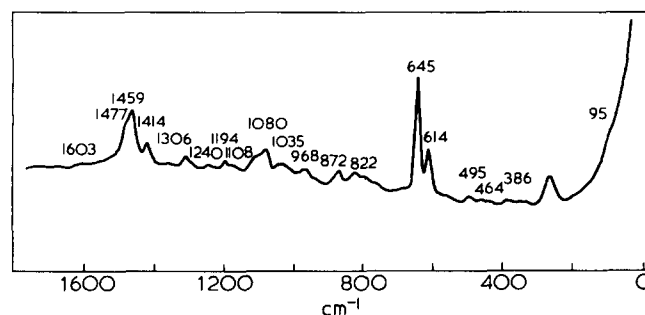


Figure 1 The Raman spectrum of unhydrolysed γ -aminopropyltrimethoxysilane

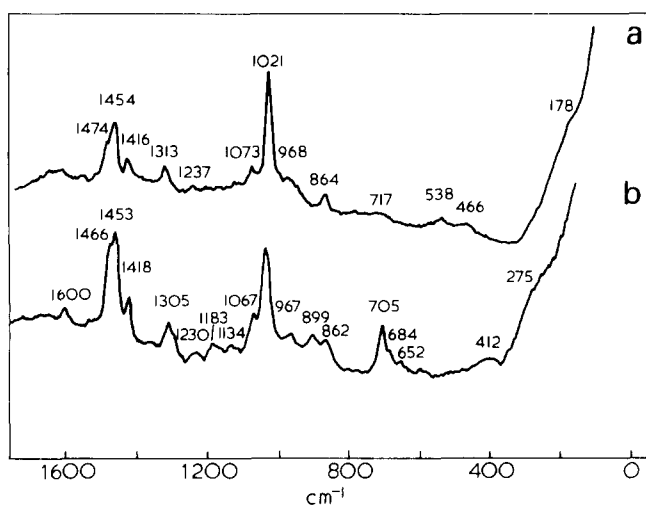


Figure 2 The Raman spectra of the hydrolysate of γ -aminopropyltrimethoxysilane. a, 20% by weight in H_2O . b, 20% by weight in KOH solution. The mole ratio of the silane and KOH is 1:6

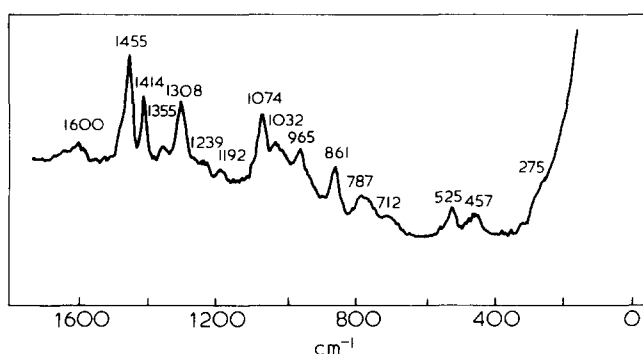


Figure 3 Completely cured polyaminopropylsiloxane treated at $110^\circ C$ for 1 h under vacuum

siloxane in the solid state indicating that the aminosilane in the solution at this level of concentration exists predominantly as condensed oligomers.

In general, when the concentration of silane solutions is low, the size of silane oligomers is small. It is thus useful to study the effect of silane concentration on the spectral changes. The difference spectra of hydrolysed γ -aminopropyltriethoxysilane at concentrations 2, 5, 10, 20, 40, 60, and 80% by weight hydrolysed for 0.5 h are shown in Figure 4 where the contributions of ethanol as a byproduct of hydrolysis and water are excluded. Slight frequency shifts of the ethanol bands, for example around 1020 cm^{-1} , are due to the different environments of ethanol in the silane solution compared to ethanol in water. More detailed spectral features can be seen in Figure 5 which shows the spectrum of 20% solution of the silane by weight. An expanded spectrum of the solution of 2% by weight is also shown in Figure 6 in order to examine the spectral features of the silane at low concentrations.

From Figure 4 one observes that the band around 1115 cm^{-1} due to the SiOSi antisymmetric stretching mode increases in intensity with respect to the intensities of other bands as the concentration increases. However, in spite of the wide range of concentrations, i.e. from 2 to 80% by weight, the relative intensities of the band around 920 cm^{-1} which is due to the SiO stretching mode of the SiOH groups and the band around 1115 cm^{-1} mentioned above do not show large differences. As a result, one can

assume similarity in the oligomers of aminosilane in water throughout the concentration range studied here in contrast to the observation of the aqueous solution of 10% by weight vinyltrimethoxysilane as predominantly monomers^{1,18}. This difference probably arises from the self-catalysed condensation of the aminosilane even at low concentrations.

A band around 960 cm^{-1} , obvious at concentrations above 40% by weight, is associated with the unhydrolysed ethoxy groups. Another ethoxy band at 1390 cm^{-1} is also present in these spectra indicating that the aminosilane contains a small amount of unhydrolysed ethoxy groups at concentrations above 40% by weight when hydrolysed for 0.5 h. No evidence of unhydrolysed species was detected at low concentrations. The band at 1006 cm^{-1} in Figure 5 is probably due to the propyl group attached to the silicon atom because ethyltrimethoxysilane shows a band at 1010 cm^{-1} , *n*-propyl-trimethoxysilane at 1005 cm^{-1} and *n*-butyltrimethoxysilane at 1000 cm^{-1} (ref 21). Neither the methoxy group nor the methyl group give rise to a band in this frequency range. Hence, it is attributed to the propyl groups which still exist after the hydrolysis of the aminosilane. According to Murata *et al.*²², an infrared band at 1001 cm^{-1} of butylsilane can be assigned to the C-C stretching mode. In the spectra of polyamino-

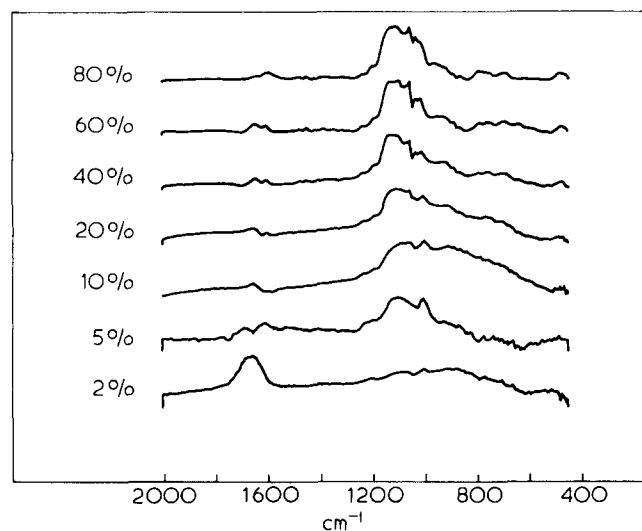


Figure 4 The FT i.r. difference spectra of hydrolysed γ -aminopropyltriethoxysilane in H_2O at various concentrations. The absorbance contributions of the ethanol and water are subtracted

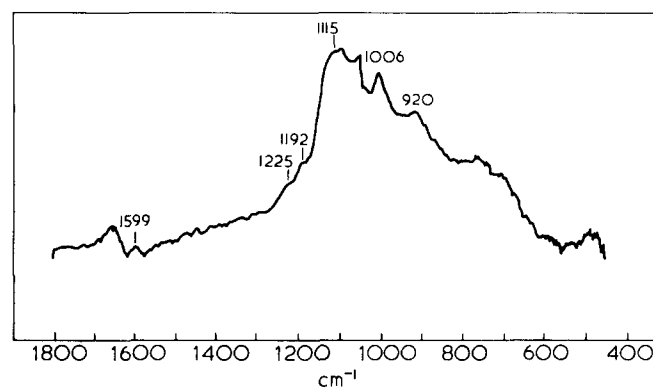


Figure 5 The FT i.r. difference spectrum of hydrolysed γ -aminopropyltriethoxysilane in H_2O at 20% by weight. $\Delta A = 0.0972$

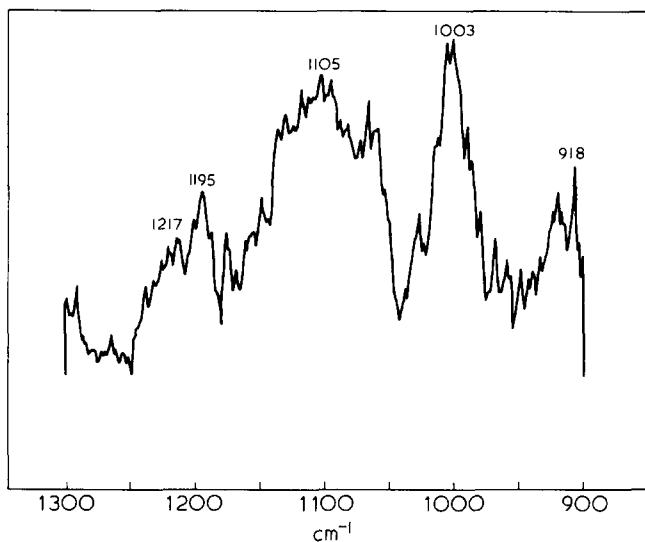


Figure 6 The FT i.r. difference spectrum of hydrolysed γ -aminopropyltriethoxysilane in H_2O at 2% by weight. $\Delta A = 0.0052$

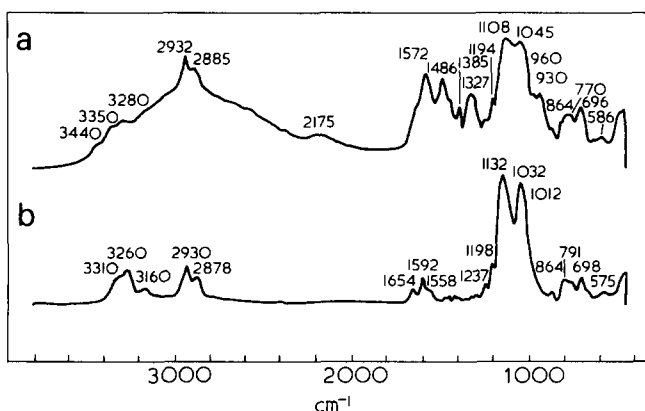


Figure 7 The FT i.r. spectra of polyaminopropylsiloxane. a, partially cured. b, completely cured at 110°C for 1 h under vacuum

propylsiloxane (Figure 7) this mode is obscured by the very strong SiOSi antisymmetric stretching mode around $1200\text{--}1050\text{ cm}^{-1}$.

A band around 920 cm^{-1} occurs in the general range of the SiO stretching modes of SiOH groups^{18,19}. The highest frequency observed from a study of 10 organosilanetriols is at 930 cm^{-1} (ref 21) and this frequency decreases to around 890 cm^{-1} when the silanetriol condenses to a silanediol or silanol. However, strong hydrogen bonding may increase this frequency.

Organotrisilanolates, RSiO_3^{-3} , were prepared using vinyltrimethoxysilane as a model system because detailed band assignments have been reported. Figure 8 compares the Raman spectra of 20% by weight vinyltrimethoxysilane in water (spectrum A) and in KOH solution (spectrum B) at a mole ratio of 1:6 (silane:KOH). Thus, the silanes are predominantly $\text{CH}_2=\text{CHSi}(\text{OH})_3$ and $\text{CH}_2=\text{CHSiO}_3^{-3}$, respectively. The three SiO stretching modes at 933 , 848 and 678 cm^{-1} for the $\text{Si}(\text{OH})_3$ group are shifted to 956 , 907 and 664 cm^{-1} for the SiO_3^{-3} group. The stretching mode at 664 cm^{-1} due to the SiO_3^{-3} group considerably weakens while the $\text{Si}(\text{OH})_3$ mode at 678 cm^{-1} shows one of the strongest lines in the spectrum. The vibrational modes of the $\text{Si}(\text{OH})_2$ or SiOH groups of

the vinyl functional silane appear very close to the average value of the two SiO antisymmetric stretching modes of the $\text{Si}(\text{OH})_3$ group. Namely, the SiO stretching mode of the polyvinylsiloxanol appears at 890 cm^{-1} and an average of 888 cm^{-1} is calculated using the 927 and 848 cm^{-1} lines ($927 + 848/2 = 888$) observed for the $\text{Si}(\text{OH})_3$ group. By analogy, it is reasonable to expect the modes due to the $\text{CH}_2=\text{CHSiO}_2^{-2}$ or $\text{CH}_2=\text{CHSiO}^-$ groups around 936 cm^{-1} ($965 + 907/2 = 936$).

A 20% by weight aminopropyltriethoxysilane in KOH solution at a mole ratio of 1:6 (silane:KOH) was also prepared and the Raman spectrum of the solution is shown in Figure 2 as spectrum B, where the Raman spectrum of 20% by weight γ -aminopropyltriethoxysilane in water (spectrum A) is also shown for purposes of comparison. As previously cited, no obvious SiO symmetric stretching mode of the silanetriol in the region $720\text{--}650\text{ cm}^{-1}$ is seen in the spectrum of the aminosilane in water. A resemblance is seen between the spectra of vinyl and amine functional silanes in KOH solutions suggesting that the aminosilane in KOH is predominantly aminopropyltrisilanolate, $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_3^{-3}$.

The FTi.r. difference spectrum of the $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_3^{-3}$ obtained from the solution used for the Raman experiment is shown in Figure 9. The difference spectrum again confirms that the condensation of the aminosilane is minimal since there is no noticeable band around 1115 cm^{-1} due to the SiOSi groups. A very strong broad band at 972 cm^{-1} with a shoulder at 909 cm^{-1} has been observed. These two bands can be assigned to the antisymmetric SiO^- stretching modes and the line at 705 cm^{-1} in the Raman spectrum (Figure 2) to the symmetric SiO^- stretching mode of the SiO_3^{-3} groups. Using an analogy previously described for the vinyl functional silane, the SiO^- stretching mode of the $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_2^{-2}$ or $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}^-$ is expected to be in the vicinity of 941 cm^{-1} which is slightly too high for the mode observed in the amino-silane in water (920 cm^{-1}), again implying that the band around 920 cm^{-1} is due to the strongly hydrogen bonded SiOH group instead of SiO^- groups.

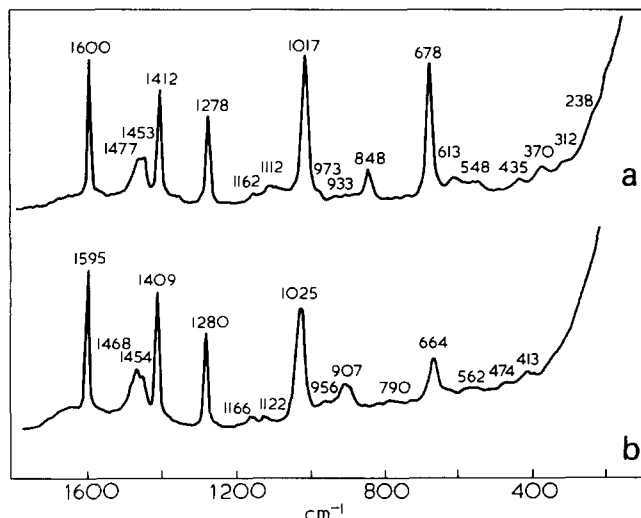


Figure 8 The Raman spectra of the hydrolysate of vinyltrimethoxysilane. a, 20% by weight in H_2O . b, 20% by weight in KOH solution. The mole ratio of the silane and KOH is 1:6

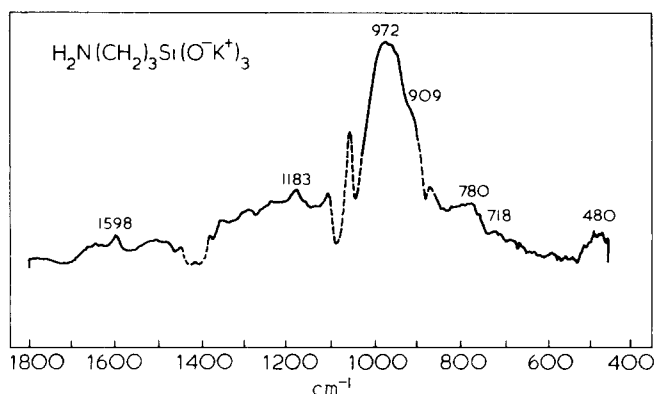


Figure 9 The FT i.r. difference spectrum of γ -aminopropyltri-silanolate in KOH solution. The concentration of the original silane is 20% by weight and the mole ratio of the silane and KOH is 1 : 6. The absorbance contributions of the ethanol and KOH solution are subtracted

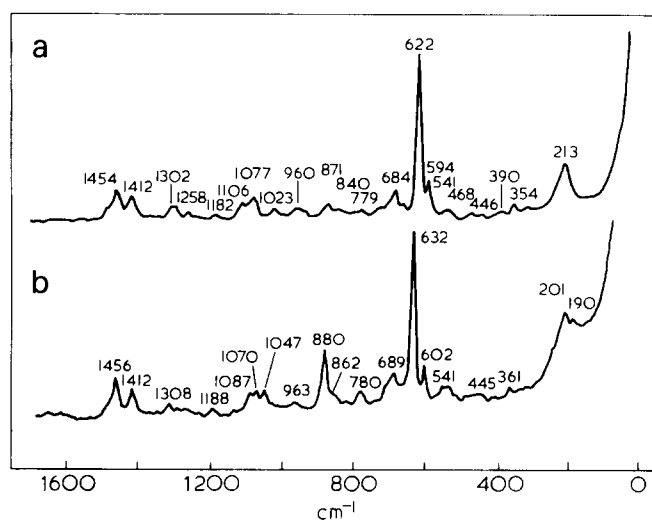


Figure 10 The Raman spectra of γ -aminopropyltrimethylethoxysilane (a) and its hydrolysate in H_2O at a concentration of 20% by weight (b)

In order to study further the possible interaction between the NH_2 and $SiOH$ groups, a model compound, γ -aminopropyltrimethylethoxysilane, was used. This silane yields only one silanol group after hydrolysis so that the condensation product consists only of a dimer. Hence, it is much simpler to follow the structural changes.

The Raman spectra of γ -aminopropyltrimethylethoxysilane and its 20% by weight aqueous solution are shown in *Figure 10* where the strongest mode at 622 cm^{-1} due to the symmetric SiC_3 stretching mode shifts to 632 cm^{-1} upon hydrolysis. The spectrum was taken within 45 min after the hydrolysis. After 1 h, the homogeneous solution showed a phase separation and the oily top layer consisted mainly of the dimer, $H_2N(CH_2)_3Si(CH_3)_2O-(CH_2)_3NH_2$, with a small amount of monomer. The oily layer was heated at $80^\circ C$ for 30 min to ensure the complete condensation of residual monomers. The Raman spectrum of the dimer (*Figure 11*) clearly shows the evidence of dimerization characterized by the strong broad line at 533 cm^{-1} due to the symmetric $SiOSi$ stretching mode, which is analogous to the same mode at 523 cm^{-1} of $(CH_3)_3SiOSi(CH_3)_3$ (ref. 23). The absence of

this strong line in the spectrum of the aqueous solution in *Figure 10* indicates that most silane molecules exist as monomers.

The FT i.r. difference spectrum of the 20% by weight of γ -aminopropyltrimethylethoxysilane aqueous solution along with the spectra of the original silane solution and ethanol/water mixture are illustrated in *Figure 12*. An interesting fact is that a strong band appears at 874 cm^{-1} which is a normal SiO stretching frequency of the $SiOH$ groups. A comparison with the FT i.r. spectrum of the dimer (*Figure 13*) reveals that the band at 874 cm^{-1} is unique to the hydrolysed monomer. The amine band of the hydrolysed monomer at 1598 cm^{-1} is essentially unchanged in frequency upon dimerization. However, a frequency decrease from 1607 to 1597 cm^{-1} is seen as one compares the unhydrolysed monomer and the condensed dimer. This frequency change is not due to the hydrogen bonding with water or silanols because no hydroxyl groups are available in these samples. Probably the unhydrolysed aminosilane exists as hydrogen bonded amines which are then hydrated and separated from each other in aqueous solutions. The unhydrolysed amines show a doublet indicating the hydrogen bonding of the

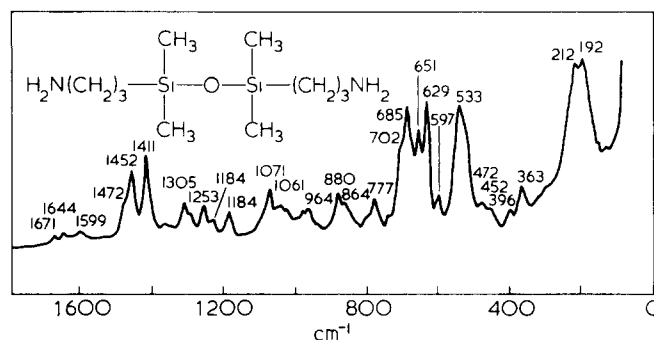


Figure 11 The Raman spectrum of the condensed dimer of the hydrolysate of γ -aminopropyltrimethylethoxysilane

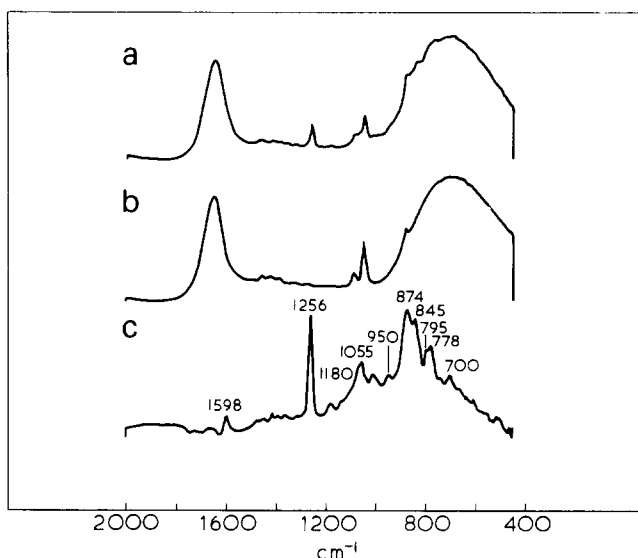


Figure 12 The FT i.r. spectra of the hydrolysed γ -aminopropyltrimethylethoxysilane a, 20% by weight aqueous solution of the silane; $\Delta A = 0.529$. b, 20% by weight aqueous solution of ethanol; $\Delta A = 0.722$. c, the difference spectrum showing predominantly γ -aminopropyltrimethylsilanol; $\Delta A = 0.116$

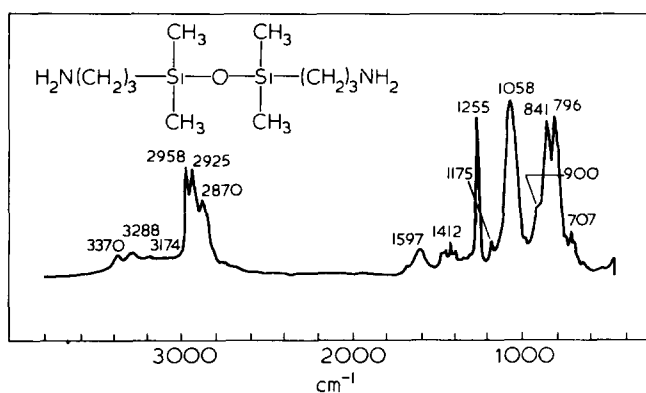


Figure 13 The FTIR spectrum of the condensed dimer of the hydrolysate of γ -aminopropyldimethylethoxysilane

type, $\text{NH}\dots\text{N}$, where one amine is a donor and the other is an acceptor.

Another model aminosilane is γ -aminopropylmethyldiethoxysilane, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$. This silane yields linear polysiloxane chains with varying lengths upon hydrolysis and subsequent condensation. Therefore, only the amine groups at both ends of the chain can hydrogen bond intramolecularly with silanols. This silane is difficult to dissolve in water and requires an alcohol/water mixture to hydrolyse. Partially cured oligomers (Figure 14: spectrum A) show two bands at 960 and 930 cm^{-1} .

DISCUSSION

The major question of this paper concerns the structures of the amine and silanol groups in solution and the partially cured solid. There are spectral differences between the partially condensed aminosilanes as an aqueous solution and a solid even though the degree of condensation is similar. The amine group in solution usually shows a single band around 1599 cm^{-1} regardless of the degree of condensation. However, when the solvents evaporate and either a viscous liquid or solid form, this weak amine band gains intensity and shifts down to around 1570 cm^{-1} . A new strong band appears at 1484 cm^{-1} . A symmetry analysis predicts two bands from the NH_3^+ group and, therefore, it is thought to arise from an interaction of the type, $\text{SiO}^-\dots^+\text{NH}_3$. This structure would lead to the observation of the SiO^- stretching mode. All primary amine salts show these two strong modes²⁴ though the frequencies depend on the counter ions. In addition to the two modes mentioned above, amine salts show further characteristic features. A very broad intense band appears in the range 3200–2800 cm^{-1} and its low frequency side often shows fine structure. Moreover, a weak to medium but characteristic band arises \sim 2300–2000 cm^{-1} due to the combination band of the NH_3^+ bending and torsional modes. All these modes are not observed in the solution spectra. Spectral features of the amine bands favour the existence of the NH_3^+ group though not necessarily conclusively.

As mentioned above, the formation of amine salt requires the observation of SiO^- groups. An incompletely cured polyaminopropylsiloxane (Figure 7) shows two bands around 960 cm^{-1} and 930 cm^{-1} which may be assigned to the SiO^- and SiOH groups, respectively. The 960 cm^{-1} band overlaps with the previously discussed band at 960 cm^{-1} of the unhydrolysed silanes. However,

the sample shown in Figure 7 is prepared from a well hydrolysed low concentration solution. However, a series of hydrolysed and incompletely cured γ -aminopropyltriethoxysilane, γ -aminopropylmethyldiethoxysilane and γ -aminopropyldimethylethoxysilane, show the two modes at 960 and 930 cm^{-1} , 960 and 914 cm^{-1} , and 960 and 874 cm^{-1} , respectively. It is reported that the SiO^- stretching mode decreases in frequency when the oxygen atoms are replaced by carbon atoms²⁵. The modes at higher frequency are, however, insensitive to the replacement of oxygen atoms to carbon atoms. If these are assigned to the SiO^- stretching modes, a similar tendency is expected since the effect of electronegativity of the carbon atoms on the silicon atom is the same for the SiO^- and SiOH groups. On the contrary, no frequency shift is observed, which leads us to postulate that the band at 960 cm^{-1} is a vibrational mode of a group unaffected or far from the silicon atom. No amine bands are known in this range. Moreover, a medium intensity Raman line around 964 cm^{-1} is seen in the spectra of completely cured polyaminopropylsiloxane and the dimer of the hydrolysate of γ -aminopropyldimethylethoxysilane. Hence, the C–C group next to the amine group is probably responsible for this mode. Accordingly, only one band is assignable either to SiO^- or SiOH vibration.

The band at 920 cm^{-1} of the polyaminopropylsiloxane in water is lower than the expected SiO^- stretching mode by 21 cm^{-1} as described earlier. In addition, the partially cured polyaminopropylsiloxane condenses and forms SiOSi bonds even in dry air and shows a decrease of the intensity of the band at 930 cm^{-1} indicating that the 930 cm^{-1} is due to the SiOH groups. Furthermore, the difference spectrum shows a broad band at 3300 cm^{-1} which decreases, corresponding to the decrease in the 930 cm^{-1} band, and almost no intensity change at the 1635 cm^{-1} band which is probably due to the adsorbed water. The weakening of the bands at 3300 and 930 cm^{-1} are, therefore, due to the OH stretching mode and SiO^- stretching mode of the residual SiOH groups²⁶. Weakening of hydrogen bonding of the $\text{SiO}^-\dots\text{H}\dots^+\text{NH}_2$ also leads to similar effects. However, it should be noted that a weakening of the hydrogen bonding results in a frequency increase of the OH stretching mode. The resultant spectral feature of the difference spectrum is, therefore, a derivative appearance instead of the observed monotonous intensity decrease.

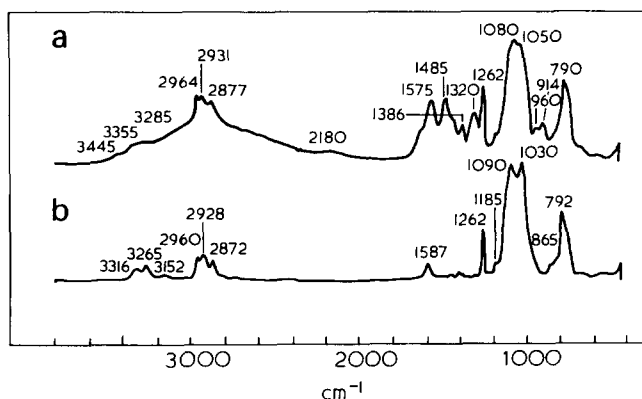


Figure 14 The FTIR spectra of the hydrolysate of γ -aminopropylmethyldiethoxysilane. a, partially cured silane. b, completely cured silane at 110°C for 1 h under vacuum

CONCLUSIONS

We have studied the FTi.r. and Raman spectra of the γ -aminopropyltriethoxysilane (γ -APS) and its analogues before and after hydrolysis and condensation reactions. The band at 930 cm^{-1} of the partially cured γ -APS is assigned to the residual SiOH groups. There is no evidence of the existence of SiO^- groups under the conditions examined. One may picture $\text{SiO}^- \dots \text{NH}_3^+$ as an extreme case of $\text{SiO} \dots \text{H} \dots \text{NH}_2$. However, the perturbations of the SiO stretching mode are not strong enough to compare with such ionic groups as $\text{RSi}(\text{O}^- \text{K}^+)_3$. In light of the mild conditions required for complete elimination of SiOH groups, the structure $\text{SiO}^- \dots \text{H} \dots \text{NH}$ is favoured instead of $\text{SiO}^- \dots \text{NH}_3^+$.

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