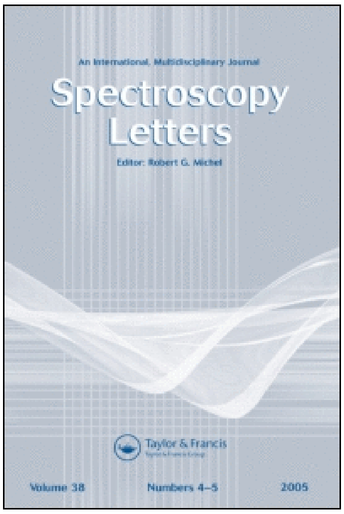

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A FT-IR STUDY OF THE HYDROLYSIS OF TETRAETHYLORTHOSILICATE (TEOS).

Key words:Infrared Spectroscopy, Sol-Gel, Deconvolution, Time Evolution

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ABSTRACT

The hydrolysis and polymerization of a non-catalyzed silica sol was investigated by Fourier Transform Infrared Spectroscopy (FT-IR) and deconvolution of the infrared spectra. The hydrolysis was followed by the 1168 and 812 cm^{-1} bands which have been observed that decrease continously with the reaction time, and they dissapear showing the complete hydrolysis. The bands located at 1200 and 1147 cm^{-1} are assigned to polymerization of Si-OH groups forming Si-O-Si bonds in cyclic or linear structures respectively. Both bands increase with time and are present simultaneously in the spectra showing that both kind of cross-linking of Si-OH groups are taking place in the sol to form the gel. In the gel the presence of Si-OH groups and $Si-O^-$ free broken bonds have been detected by means of the bonds located at 960 and 920 cm^{-1} respectively.

1.- INTRODUCTION.

In recent years there has been an important interest in the preparation of silica glass by the sol-gel process. This method is based on the hydrolysis and condensation of tetraethylorthosilicate (TEOS). By the sol-gel method, the formation of silica glass occurs at relatively low temperatures and ultrapure glasses of different composition can be obtained. Much effort has been carried out in order to understand the structural changes accompanying the silica sol-gel transformations (1,2). However, few works have been devoted to the study of the initial stages of the hydrolysis and polymerization of TEOS (3-6). Mulder and Damen (3) using Raman and ^{29}Si-NMR spectroscopies analyzed the initial stages of the hydrolysis and polymerization of TEOS. They found different silica oligomers, where the more characteristic band was observed at 654 cm^{-1} for the trimer and about 545 cm^{-1} for the tetramer of TEOS. Chu and Clark (4) studied by IR spectroscopy the influence of water content, pH level and aging in the sol to gel transformation as well as structure evolution of silica gels. They found that when low water content is used a more linear structure is obtained and it is characterized by an emerging peak located about 1160 cm^{-1} in the IR spectrum. During aging, this linear structure progressively formed a three-dimensional network with a peak above 1178 cm^{-1}. They also found that from pH=1.6 to pH=12 there was a decrease in the rate of hydrolysis although between pH=9 and pH=12 precipitation was observed.

Matos at al. (5) used simultaneously Fourier-Transform infrared (FT-IR) and Raman spectroscopies in order to study the time evolution of acid-catalyzed hydrolysis and polymerization of TEOS. The extent of hydrolysis was observed by the changes in intensity of the IR-active bands of TEOS at 793 cm^{-1}, 1102 cm^{-1}, 1168 cm^{-1} and 1400 cm^{-1} . This was also observed in the TEOS Raman active bands corresponding to the strongly polarized Si-O symmetric stretch (656 cm^{-1}) and the depolarized CH_2 rocking (960 cm^{-1}). Recently, Viart and Rehspringer (6) studied the influence of formamide on the acid-catalyzed sol-gel process. They studied two sols prepared from TMOS (tetramethoxyorthosilicate) methanol, water and formamide, and they concluded that in the presence of formamide condensation leads to small oligomers of less than six Si atoms. These oligomers condense increasing the degree of cross-linking of the gel network.

However, most frequently in obtaining silica gels is the use of TEOS and ethanol. In this case, some IR bands of TEOS, ethanol and Si-O-Si bonds are in the same position of the IR spectrum and the study is more difficulty. On the other hand, when a catalyst such as HCl is used in the reaction, the hydrolysis of TEOS molecule is obtained in a few minutes and then the polycondensation of $Si-(OH)_4$ groups is the only process in the sol-gel reaction.

In the present work we have used FT-IR spectroscopy in order to determine the hydrolysis of TEOS when no catalyst is added and therefore hydrolysis and polymerization reactions occur simultaneously. We propose a method to know when TEOS is hydrolyzed although polymerization can not to be completed and the sol not gelled.

2.- EXPERIMENTAL.

A solution of 200 cm^3 was prepared using TEOS (Merck, p.a.), ethanol (Merck, absolute p.a.) (EtOH) and deionized H_2O. The molar ratio used was

TEOS/EtOH/H_2O = 1/4/20. Firstly, two solutions were prepared, one using TEOS and half of EtOH volume, and the second H_2O and the other half volume of EtOH. Both solutions were stirred independently for 2 hours in a water bath at 25 ± 0,2°C covered by a plastic in order to avoid evaporation. After this time, the solution H_2O/EtOH was added drop-wise for 2 hours to the TEOS/EtOH solution. The obtained sol was continuously stirred until gelation which occurred in 28 hours. Therefore, we have given the name of addition and gelation to the stages of these reaction times: 2 hours and 28 hours respectively. During both stages, FT-IR spectra were recorded using FT-IR spectrometer (Perkin-Elmer Mod. 1720X) with a resolution of 2 cm^{-1}. For each spectrum a ratio of 10 sample scans to 10 background scans was used. The FT-IR measurements were carried out adding one drop of the sol between two KRS-5 crystals using a microburete. The spectra were stored in the computer and analyzed.

3.- RESULTS AND DISCUSSION.

The FT-IR spectra of TEOS, EtOH and TEOS/EtOH mixture are shown in figure 1. The assignments of all absorption bands are compiled from references 4, 5, 6 and 7 are given here in Table 1.

Some of these bands have been obtained when the spectrum was deconvoluted. All of these bands are unambiguously assigned to characteristic modes of TEOS, EtOH or Si-O-Si structures except for the IR peaks located at 1100 and 1086 cm^{-1} which corresponds to C-O stretching vibrations of ethanol and TEOS and Si-O-Si stretching vibrations in cyclic and linear structures (see Table 1). Therefore,

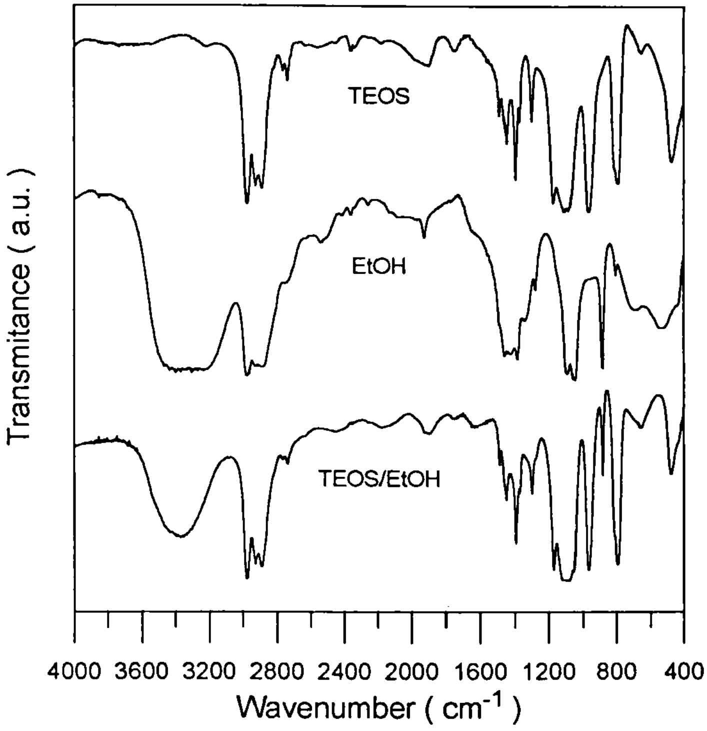

FIG1.- Infrared Spectra of TEOS, Ethanol and starting sol.

different IR bands of TEOS (1168 and 812 cm^{-1}) may be followed for studying the hydrolysis process and some others (1200 and 1147 cm^{-1}) for studying the polymerization process.

Figures 2 and 3 show the FT-IR spectra obtained for different times during the addition and gelation stages respectively. As may be observed in these figures, the main changes occurred in the gelation stage, confirming the slow hydrolysis rate of TEOS molecule when no catalyst is used. The decrease in intensity of TEOS bands (at 473, 1102 and 1168 cm^{-1}) are accompanied with the increase of new bands

TABLE 1

Infrared Absorption Bands Compiled from References 4, 5, 6 and 7.

Wavenumber (cm^{-1})	Assignement
3500-3000	O-H stertching (EtOH, H_2O, Si-OH)
2974	asym. C-H stretching (CH_3 in EtOH, TEOS)
2930	asym. C-H stretching (CH_2 in EtOH, TEOS)
2892	asym. C-H stretching (EtOH, TEOS)
1446	asym. C-H bendig (CH_3 in EtOH, TEOS)
1381	sym. C-H bending (CH_3 in TEOS, EtOH)
1416, 1324	O-H bending and C-H wagging (CH_2 in TEOS, EtOH)
1275	C-H twist/wagging (C-H in TEOS, EtOH)
1200	Si-O-Si asym. stretching in cyclic structures
1168	C-H rocking (CH_3 in TEOS)
1147	Si-O-Si asym. stretching in linear structures
1100	Si-O-Si sym. stretching in linear structures C-O asym. stretching (TEOS)
1086	Si-O-Si sym. stretching in cyclic structures C-O asym. stretching (EtOH)
1048	C-O sym. strethcing (EtOH)
960	C-H rocking (CH_3 in TEOS)
920	Si-O non-bridging free broken
881	CH_3 or CH_2 def. (EtOH)
812	CH_2 rock (TEOS)
793	SiO_4 asym. (TEOS) Si-O-Si bend (SiO_2)
473	O-C-C def. (TEOS) O-Si-O bend (SiO_2)

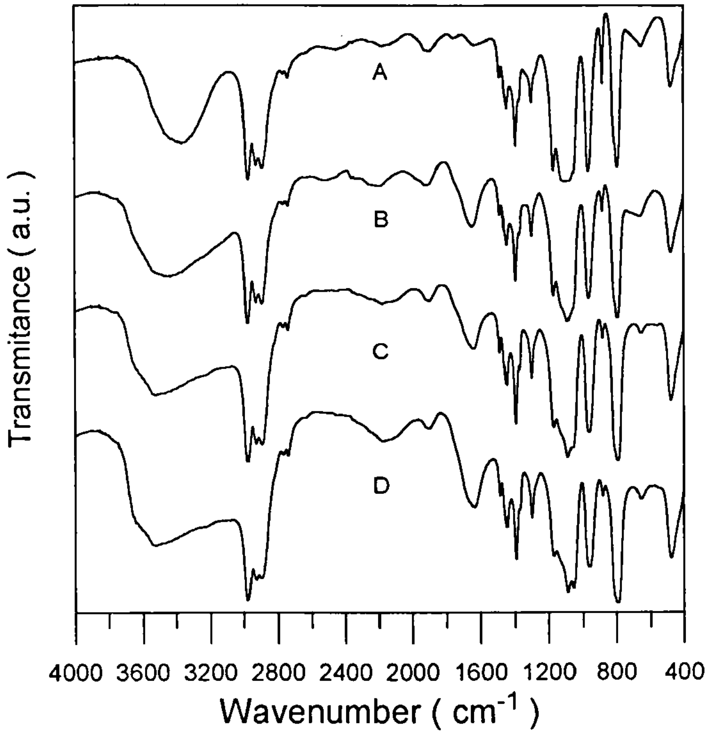

FIG2.- Infrared Spectra of the sol during the addition of H_2O. A- 0 hr, B- 0.5 hr, C- 1.5 hr and D- 1.9 hr.

of Si-O-Si bonds (at 460, 1168 and 1200 cm^{-1}). In addition, the TEOS IR bands located at 960 and 793 cm^{-1} change their intensity and wave number being now associated to Si-OH and $Si-O_4$ bonds in the xerogel (7). The EtOH bands located at 881 cm^{-1} and 1048 cm^{-1} increase in intensity in the first moments due to the addition of the H_2O/EtOH solution and the hydrolysis of the TEOS molecule.

The above results give only qualitative information about the hydrolysis of TEOS. In this work we have carried out a semiquantitative approach by a careful

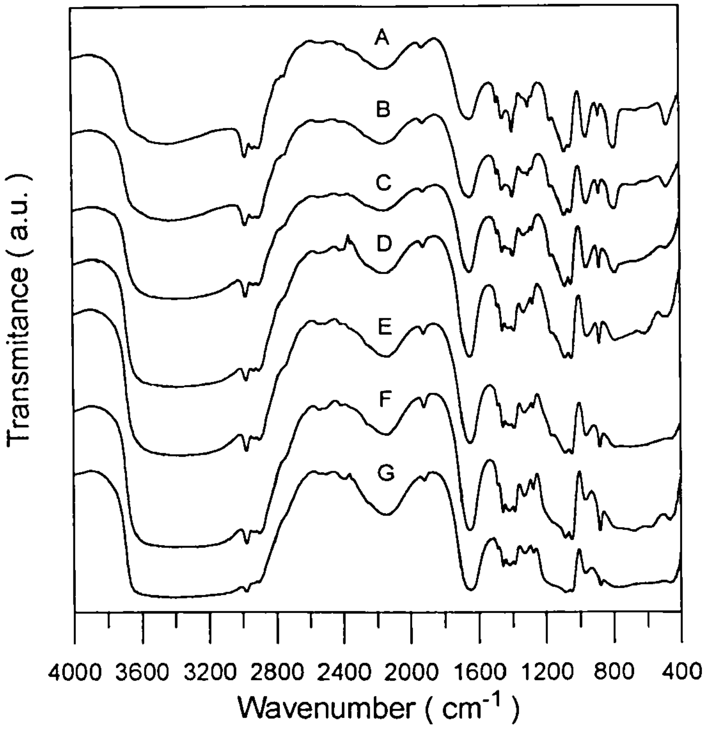

FIG3.- Infrared Spectra of the sol after addition of H_2O. A- 0 hr, B- 6 hr, C- 12 hr, D- 18 hr, E-24 hr and F-28 hr.

deconvolution of the IR profiles using a computer program. In this program each IR band is determined by three parameters: intensity, half width and wave number.In practice, we have chosen the minimum number of bands that give a reasonable agreement between experimental and calculated (deconvoluted) spectrum. We have adjusted the IR spectra with the bands given in Table 1. We have also assumed that the IR bands have a gaussian profile.

A typical example of spectral deconvolution is shown in Figure 4, for the solution after 40 minutes of addition. The difference between experimental spectrum and simulated curves were less than 1% in all cases.

The area of each IR deconvoluted band is taken as proportional to the concentration of associated bond. The individual band area has been normalized with respect to the total infrared absorption from 1400-600 cm^{-1}. Because the absorption coefficients are not known, the results are only a semiquantitative picture of the hydrolysis of TEOS molecule.

The results of the analysis are shown in the following figures. Figure 5 shows the time evolution of $-CH_3$ and $-CH_2-$ groups corresponding both to EtOH and TEOS. As it can be seen, an increase of both bands during the addition step because EtOH is added to the TEOS/EtOH mixture. During the gelation stage both bands do not change with time because the hydrolysis of TEOS produce EtOH but the concentration of $-CH_3$ and $-CH_2-$ groups remains constant in the solution.

The hydrolysis of TEOS molecule may be followed by the 1168 and 812 cm^{-1} bands assigned (see Table 1) to the rocking of $-CH_3$ and $-CH_2-$ groups of TEOS respectively as it is shown in Figure 6. Both bands show a fast decrease in the first two hours (addition stage) and a slow decrease between 2 and 24 hours. At this time, both bands disappear showing that the TEOS molecule must be completely hydrolyzed. When a catalyst such as HCl is used in order to hydrolize TEOS in aqueous medium, hydrolysis reaction is completed in the first moments (4). However, if not catalyst is used, the hydrolysis reaction depends on the water

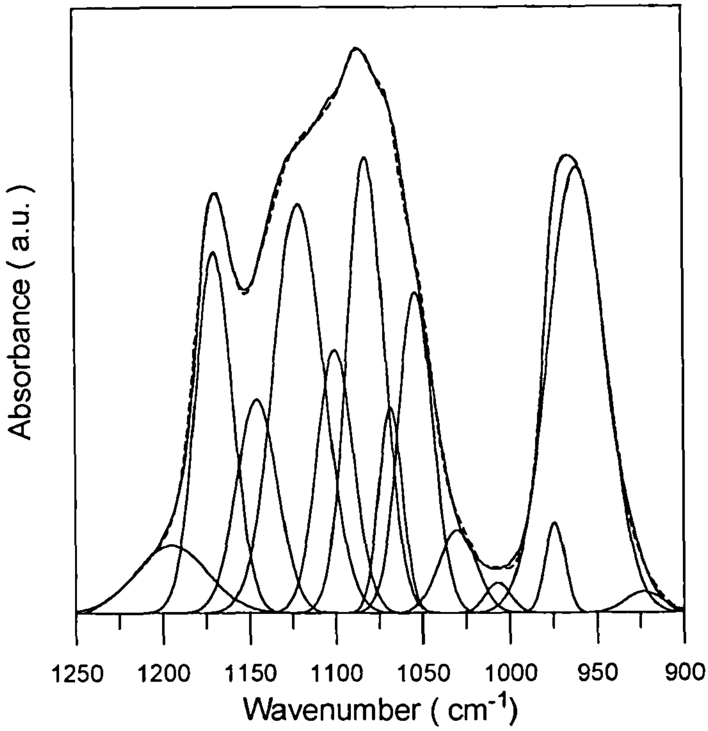

FIG4.- Deconvolution of the IR spectrum of the sol of 6 hr after H_2O addition.

concentration in the solution according to the simplified equation

$$Si - (O\text{-}CH_2\text{-}CH_3)_4 + 4H_2O \text{ ----------> } Si\text{-}(OH)_4 + 4\ CH_3\text{-}CH_2\text{-}OH \qquad (1)$$

If the H_2O concentration is high, this reaction is favoured to the right term, i.e. the hydrolysis of TEOS. Chu and Clark (4) have shown that TEOS is mostly hydrolized in short time when 20 moles of water for one mol of TEOS is used. According to the figure 6, both bands are characteristic of the ethoxy group of the TEOS molecule

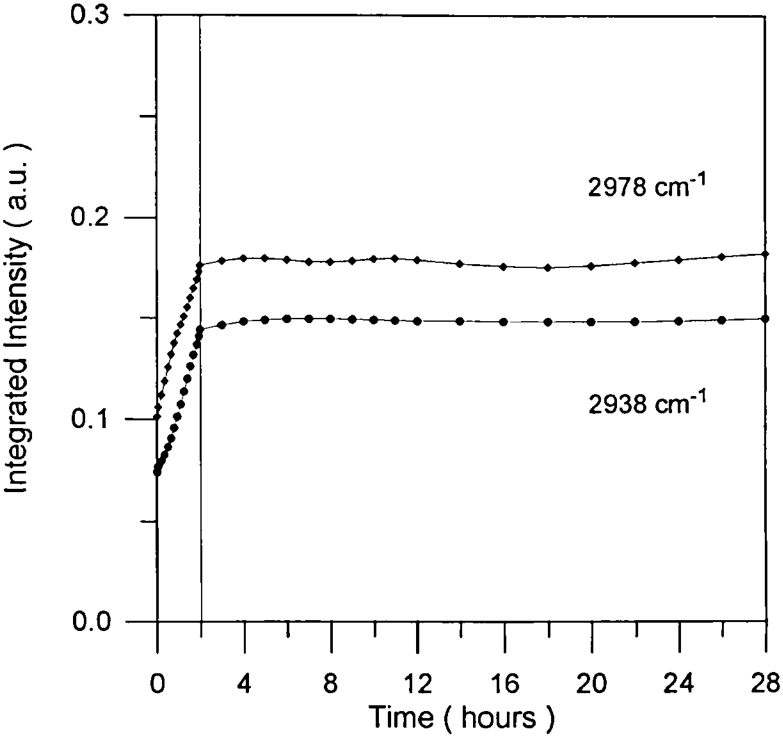

FIG5.-Time evolution of the integrated areas for 2978 and 2938 cm^{-1} bands during hydrolysis and gelation of TEOS.

(1168 and 812 cm^{-1}) disappear around 24 hours of the reaction, and therefore, we can consider that the TEOS molecule is fully hydrolyzed. It is interesting to emphasize that both bands show a similar trend although that at 1168 cm^{-1} is overlapped with other bands. On the other hand, the band located at 812 cm^{-1} is only slightly overlapped by other band situated at 793 cm^{-1}, and the deconvolution procedure is more easily in this last spectral region.

As it is well known, the hydrolysis of TEOS gives Si-OH groups which start to react with other Si-OH groups through a polycondensation reaction which gives

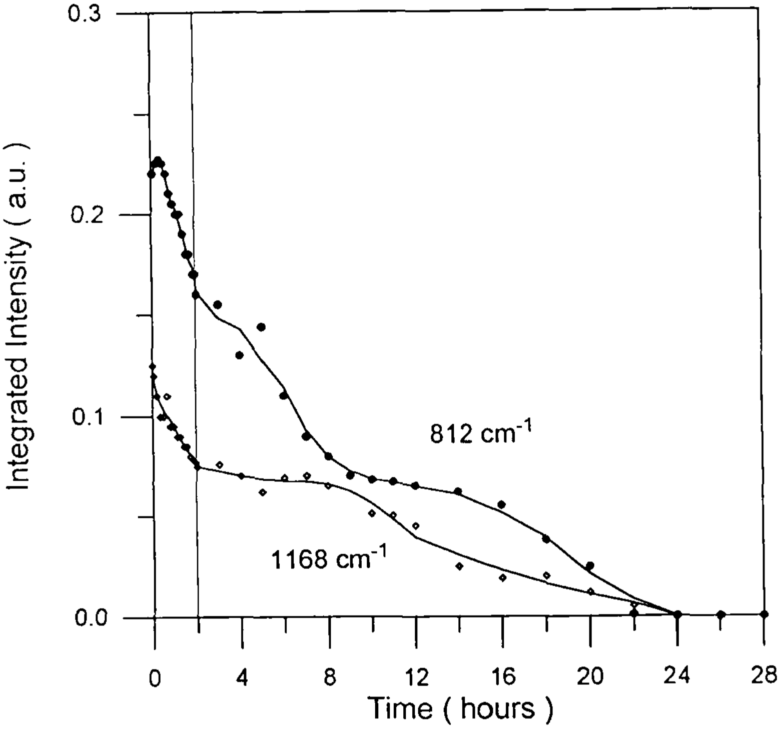

FIG6.- Time evolution of the integrated areas for 1168 and 812 cm^{-1} bands during hydrolysis and gelation of TEOS.

a three-dimensional silica network. This network may be heated at temperatures around 1000°C and a vitreous silica structure can be obtained (8,10,17). Several factors influence in the polycondensation reaction, and they are mainly pH, water/TEOS ratio and reaction temperature. The reaction temperature can change the reaction velocity and when the temperature is increased, the gelling time decrease, i.e. the polycondensation reaction increases in velocity and the solution gelled at lower times. This result can be assigned to a rapid threedimensional crosslinking of Si-OH groups.

On the other hand, the pH and H_2O/TEOS ratio can influence in such threedimensional crosslinking although there is no change in the reaction temperature. It has been observed that a low pH and when H_2O/TEOS ratio lower than 4 is used, the polycondensation of Si-OH groups occurs through linear -Si-O-Si- structures which gives long Si-O-Si chains (13,16). This result has been used for obtaining inorganic fibres through the sol-gel process (14,15). However, if the pH is high or the H_2O/TEOS ratio is higher than 4, the threedimensional crosslinking of Si-OH groups is favoured (16,17). Normally, both linear and threedimensional polycondensation occurs simultaneously.

The evolution of the polycondensation of Si-OH groups can be followed by the IR bands situated at 1200 and 1147 cm^{-1} corresponding to Si-O-Si asymmetric stretching in cyclic and linear structures respectively. Figure 7 shows the time evolution of both bands. It is observed in this figure that linear and cyclic structures increase continuously with the reaction time. Both kind of polycondensations occurs simultaneously as may be expected because the molar ration H_2O/TEOS is 20 and the pH of the solution is about 5.4 (measured in a pHmeter Radiometer by means of a glass electrode). The slope of the 1200 cm^{-1} band is higher than the corresponding to the 1147 cm^{-1} band, showing that a threedimensional crosslinking is more favoured than linear polymerization. This result is in accordance with the molar ratio H_2O/TEOS and solution pH employed. Chu and Clark (4) have shown that a more complex structure is formed in the sols with higher water concentration. This complex structure is associated to the threedimensional polymerization of Si-OH groups and therefore to the higher increase of the 1200 cm^{-1} band.

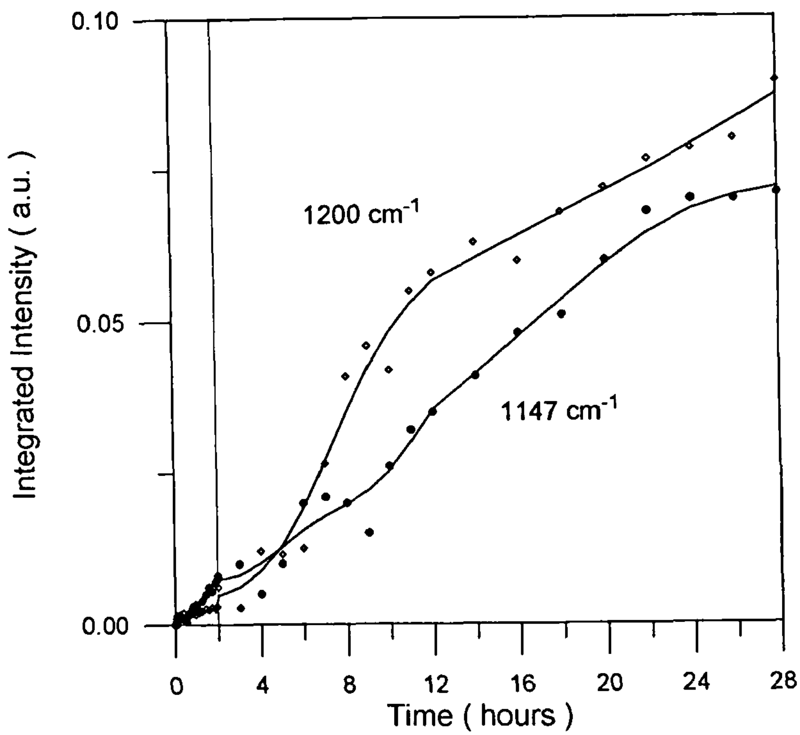

FIG7.- Time evolution of the integrated areas for 1200 and 1147 cm^{-1} bands during hydrolysis and gelation of TEOS.

Two other bands located at 1112 and 1086 cm^{-1} are also associated to Si-O-Si stretching in linear and cyclic structures respectively. However, both bands coincide in the same position with the C-O stretching of TEOS or EtOH and their evolution do not give new information about the polymerization process.

A similar situation occurs with the band located at 960 cm^{-1}. This band firstly corresponds to the CH_3 rocking of the TEOS molecule, and at the same position appears the Si-O(H) stretching (O-H stretching appears in the 3000-4000 cm^{-1}

spectral region). When a catalyst is added and the hydrolysis of TEOS molecule is completed in a few minutes, the evolution of the 960 cm^{-1} band may be used for studying the polymerization process of Si-OH groups. The position (wavenumber) of this band increases with the degree of cross-linking of the gel, because the wavenumber is directly linked to the strength of the Si-OH bond. Values of 950 cm^{-1} have been obtained for sols recently hydrolyzed, and this wavenumber shifts up to 975 cm^{-1} for the corresponding gels (6). In our study, a complete overlapping occurs between the $-CH_3$ rocking of TEOS molecule and the Si-(OH) stretching. The time evolution of this band is showed in figure 8. This evolution may be explained in the following form: the CH_3 rocking of TEOS must follow the same behaviour as the 1168 and 812 cm^{-1} bands (figure 6) corresponding to the CH_3 and CH_2 rocking in TEOS, and therefore must show a decreasing behaviour disappearing about 24 hours. At the same time, the hydrolysis of TEOS must give Si-OH groups which increase such band, but the polymerization of Si-OH groups which are forming finally the gel structure must give a decreasing behaviour of this band. In summary, the hydrolysis of TEOS and the polymerization of Si-OH groups give a decrease of the 960 cm^{-1} band, and this is the result observed in figure 8. An important observation have to be made of this band because it does not disappear when the sol is completely gelled, as it may be observed in this figure 8. If we consider that TEOS is fully hydrolyzed in accordance with the 1168 and 812 cm^{-1} bands (figure 6), the intensity of the 960 cm^{-1} observed in the gel after 28 hours must correspond to remaining Si-OH groups which have not yet polymerized. This result is in accordance with some other studies

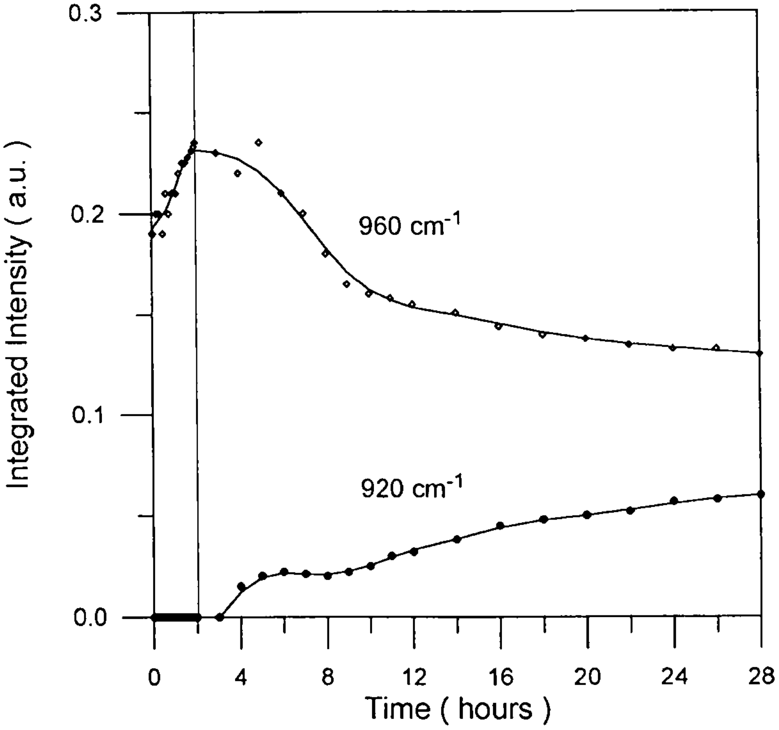

FIG8.- Time evolution of the integrated areas for 960 and 920 cm^{-1} bands during hydrolysis and gelation of TEOS.

of silica gels where the final polymerization of Si-OH groups is obtained by using temperatures higher than 1000°C (8,16,18).

Close to the band located at 960 cm^{-1}, the deconvolution procedure shows a low intensity band located at 920 cm^{-1}. This band has been observed in silica gels (6,11) and silica glasses (12) and has been assigned to non-bridging free broken Si-O bonds. Chmel et al (12) have shown that in gel derived silica glasses there exists a spectroscopically distinguishable amount of open rings in the silica network in which a great part are non-bridging bonds forming Si-OH groups giving the band located at 960 cm^{-1}, and there also exists a some part of broken Si-O bonds which remain free and gives the peak at 920 cm^{-1} in the Raman an IR spectra. This later band is hardly resolved in the spectra of large pore samples, but must be obtained by spectral deconvolution.

The time evolution of the 920 cm^{-1} band is also shown in figure 8. Due to the low initial concentration of Si-OH groups, they are produced by the hydrolysis of the TEOS molecule, this band is only detected after three hours of reaction. As it can be seen, this band increase continuously with time. This result shows the presence of $Si\text{-}O^-$ bonds in the gel, and therefore, there must exists Si-OH groups. The slow increase with time of 920 cm^{-1} band shows that polymerization of Si-OH groups must be the fundamental reaction taking place in the process.

Located at 790 cm^{-1} there appears a band which has some overlapping with the above mentioned 812 cm^{-1} band. The 790 cm^{-1} band has been assigned to SiO_4 asymmetric stretching in TEOS and Si-O-Si bending in SiO_2. Figure 9 shows the evolution of this band during the whole reaction time. It is observed a great decrease in the first hours of the reaction, which is a result of the hydrolysis of TEOS and later the slow decrease is due to the polymerization of Si-OH groups to form Si-O-Si bonds in cyclic or linear structures. This band does not disappear because the formation of Si-O-Si bonds. The low intensity of this band at the end of the reaction compared with the initial intensity is due to the difference in the extinction coefficients of $Si\text{-}O_4$ bonds in TEOS or in Si-O-Si bonds.

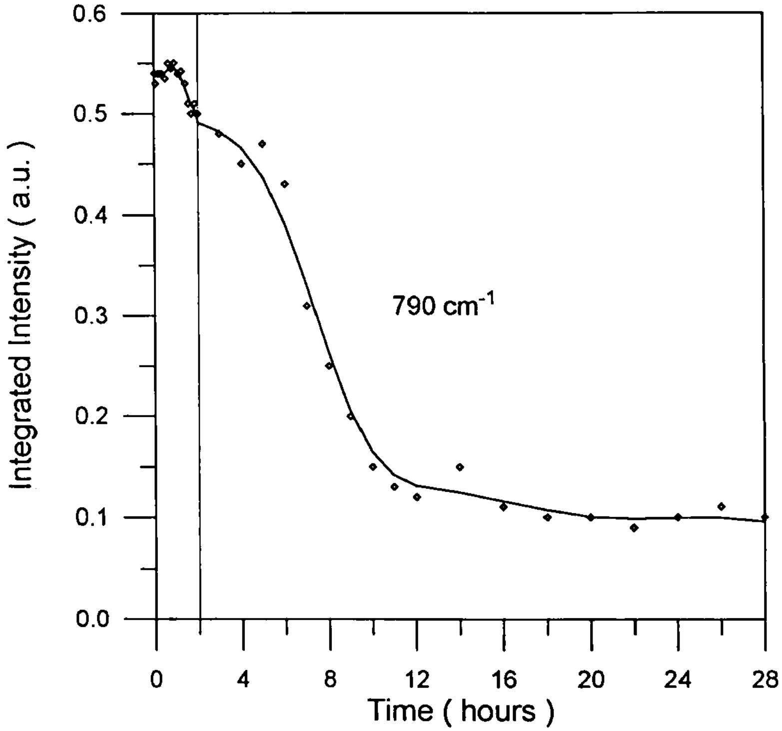

FIG9.- Time evolution of the integrated area for 790 cm^{-1} band during hydrolysis and gelation of TEOS.

4.- CONCLUSIONS.

In this work we have studied the hydrolysis and polymerization of TEOS and Si-OH groups in non catalyzed aqueous medium. We have used the FT-IR spectroscopy and the spectral deconvolution for a more direct examination of the sol-gel process. Some IR bands have been investigated in this study. The bands located at 1168 and 812 cm^{-1} can inform about the hydrolysis of TEOS. Both bands decrease continuously from the first moments of the reaction and disappear between 22-24 hours. At this time, the TEOS is hydrolyzed but the sol it is not yet gelled because this occurs between 4 to 6 hours later.

The polymerization process of Si-OH groups may be followed by the bands located at 1200 and 1147 cm^{-1} associated to Si-O-Si stretching in cyclic and linear structures respectively. Both bands increase with the reaction time showing a higher slope the band located at 1200 cm^{-1} and this result is assigned to a preferential threedimensional crosslinking of Si-OH groups.

The bands located at 960 and 920 cm^{-1} have been used in order to confirm that the silica gel obtained after 28 hours remains not polymerized Si-OH groups and there also exists some part of $Si\text{-}O^-$ free broken bonds.

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