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Multinuclear NMR Study of Aluminosilicate Sol-Gel
Synthesis Reasons for the Homogeneous Gelation Using
the Prehydrolysis Method

by

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**Multinuclear NMR Study of Aluminosilicate Sol-Gel Synthesis-Reasons
for Homogeneous Gelation Using the Prehydrolysis Method**

submitted to Chemistry of Materials, 6/93

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Abstract

Aluminosilicate gels have been utilized in numerous optical, dielectric, and catalytic applications. These applications require a high degree of molecular homogeneity, but reproducible means of achieving this remain unobtainable for many compositions^{1,2,3}. In this work, reactions occurring in one of the most successful sol/gel processes are examined by means of both liquid and solid ^{13}C , ^{29}Si , ^{17}O , and ^{27}Al NMR. The synthesis process studied was the method, optimized by Krol, of prehydrolyzing tetraethylorthosilicate, TEOS, in ethanol, and subsequently adding aluminum sec-butoxide, and then further water⁴.

After prehydrolysis and addition of aluminum sec-butoxide, an aluminosilicate precursor is formed in which the aluminum is tetrahedrally coordinated to four silicate ligands. After adding further water, gelation is accompanied by the expansion of the tetrahedral aluminum to octahedral coordination; this apparently occurs by nucleophilic attack of silanol groups on the aluminum in the aluminosilicate precursor. At sufficiently low water to silicon molar ratios, where transparent gels and longer gel times result, this coordination expansion is preceded by condensation of the silicate ligands to form Si-O-Si bonds between the aluminosilicate intermediates. At high water levels, though, coordination expansion proceeds before the formation of Si-O-Si bonds.

Introduction

Aluminosilicate gels have a number of current and potential applications in optics, dielectrics, and catalysis^{1,2,3}. Ideally one would want homogeneity on the molecular scale. The unique processing advantages offered by sol-gel techniques, where dissolved inorganic precursors are mixed in solution, can in principle ensure such homogeneity⁵. However, these methods have been unable to consistently produce homogeneous gels over a broad composition range. In fact, few methods provide even transparency, i.e., uniformity of composition over a length scale of $\sim 0.5 \mu\text{m}$ ⁵. It is worthwhile to investigate why certain preparation protocols produce more transparent gels.

If one simply mixes tetraethyl orthosilicate, TEOS, aluminum sec-butoxide, and water, one will in general not obtain a clear gel; this protocol typically leads to the precipitation of alumina rich phases. The reason is thought to be that the hydrolysis of the aluminum alkoxide is several orders of magnitude faster than that of the silicon alkoxide, and this then leads to the early formation of Al-OH-Al bridges and the subsequent phase separation of bayerite or pseudo-boehmite. To allow the silicate precursors a headstart in forming Al-O-Si bonds, the silicate alkoxide can be prehydrolyzed, as suggested by Yoldas⁷. Subsequent addition of the aluminum precursor and slow addition of the remaining water for hydrolysis and condensation reactions has been found to produce transparent gels^{7,8,9,10}.

Even with this protocol, a recent study revealed that more homogeneous gels were synthesized by decreasing the water to silicate molar ratio, R. The gelation rate for R equal to 4 was 24 minutes, and the resulting gel was inhomogeneous. For R values of near 2.0, though, gelation was delayed for a week, and the resulting gels were transparent⁶.

Although NMR studies have been performed on gels synthesized by the prehydrolysis method^{7,8,9,10,11}, it is not yet clear why only certain prehydrolysis techniques increase homogeneity and decrease gel time. Pouxviel has used ^{29}Si NMR on prehydrolysis solutions before and after addition of aluminum sec-butoxide; it was found that the prehydrolysis of the silicon alkoxide forms various condensed silicates in addition to the expected hydrolyzed species. However, no other nuclei were observed, and the value of R was higher than that which would ensure homogeneous gelation^{6,7}. Jonas and Irwin have used ^{27}Al MAS NMR on such gels and have found unusually high amounts of tetrahedral aluminum^{9,10}, but Fahrenholtz and co-workers have found both tetrahedral and octahedral aluminum environments in these sols before gelation¹¹.

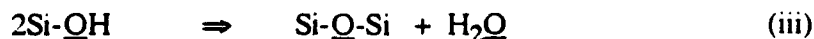
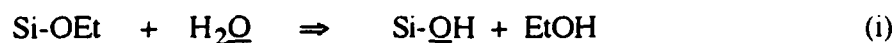
In this work, ^{27}Al , ^{17}O , ^{29}Si and ^{13}C NMR are observed at several key steps in the synthesis to investigate the relationship between the hydrolysis ratio ($R=\text{H}_2\text{O}/\text{Si}$) and

homogeneity. The gels synthesized were prepared by the prehydrolysis method of Krol, illustrated in Figure 1⁴. The preparation method is identical for different R values until the last step (C), so it may be possible to clearly discern processes responsible for to more homogeneous gels. A molar ratio of aluminum to silicon of 1/4 and the molar ratio of HCl to silicon of 0.006 were used; these are typical values that produce transparent gels at $R = 2$ ⁶. Total water to silicate molar ratios, R, varied from 2.0 to 4.0, but the prehydrolysis ratio was maintained at 1.2. Gelation rates and homogeneity were similar to those previously reported⁶.

Experimental

NMR spectra were obtained with a GE 11.77 T spectrometer. MAS NMR experiments were performed using a Doty 5mm MAS probe using Si_3N_4 rotors spinning at 10 kHz. Spectrometer parameters for each nucleus are given in Table 2. ^{27}Al NMR spectra were referenced to an external sample containing $\text{Al}(\text{H}_2\text{O})_6^{3+}$. ^{17}O NMR spectra were referenced to water. Both ^{29}Si and ^{13}C NMR spectra were referenced to trimethylsilane (TMS).

For ^{17}O enrichment, water enriched in ^{17}O to 10% atom content, obtained from Aldrich Chemical, was substituted for normal abundance water (0.037% ^{17}O). For prehydrolysis, water at 5% enrichment was used, while additional water at stage C was at 10% enrichment. ^{17}O occupies sites of interest as follows^{12,13}:



Since alkoxide oxygens are not enriched, they are not observed in the ^{17}O NMR spectra.

Results

The processing of all solutions remains identical up to point C in Figure 1. The amount of added water at C was varied so that the total water to silicate ratio (R) ranged from 2 to 4. The gelation time is on the order of weeks at R=2, but is only minutes at R=4, as shown in Table 1⁶.

Stage A

Prehydrolyzed silicate solution

The ^{29}Si NMR spectrum of the prehydrolysis mixture at stage A in the synthesis is shown in Figure 2. Most of the TEOS has been hydrolyzed and condensed. Q_0 , Q_1 , and Q_2 connectivities are shown, and 60% of the Si present bears silanol groups. The ^{17}O NMR spectrum (Figure 3) shows unreacted water (-3 ppm), ethanol (6 ppm), silanol groups, Si- OH (18 ppm), siloxane bridges Si- O -Si (32 ppm), and siloxane bonds in cyclic species (Si- O -Si)_{cyc} (44 ppm)[14-19]. These ^{17}O environments are consistent with the ^{29}Si NMR spectrum. The ^{17}O shift of unreacted water is 3 ppm lower than for pure H_2O because in the synthesis solution it is participating in hydrogen bonding and exchange with ethanol.

Aluminum sec-butoxide

The ^{27}Al spectrum for aluminum sec-butoxide is shown in Figure 4; it is dissolved in benzene since the pure butoxide liquid is too viscous to produce narrow peaks. The spectrum displays two broad peaks at 35 and 58 ppm, corresponding to tetrahedral and penta-coordinated aluminum, and two peaks at 4 and 6 ppm, each corresponding to octahedrally coordinated aluminum. This spectrum supports the suggestion that the butoxide is actually a mixture of polynuclear complexes with a variety of aluminum coordination states²⁰. Quadrupolar nutation spectra of the solution showed no additional peaks.

Figure 5 shows the ^{13}C NMR spectrum. Bridging sec-butoxide ligands are observed at 25, 34, and 73 ppm, confirming that aluminum sec-butoxide is oligomeric. Peaks at 68.7, 32, 22.6, and 10 ppm are associated with the terminal sec-butoxide ligands. The ^{17}O NMR spectrum for the aluminum sec-butoxide was not obtained since it was not possible to enrich the oxygen of the butoxide.

Stage B

Immediately following addition of aluminum sec-butoxide to the prehydrolyzed silicate solution

After addition of aluminum sec-butoxide to the prehydrolyzed silicate solution, the ^{29}Si NMR spectrum (Figure 6) shows that all Si-OH groups are consumed. New ^{29}Si peaks are observed at -85, -91, and -95 ppm. The peak at -95 ppm has been previously assigned to an Al-O-Si environment⁸. Those at -85 and -91 ppm are new, and presumably also represent Al-O-Si environments.

The ^{27}Al spectrum (Figure 7) shows two broad peaks at 56 ppm and 4 ppm; corresponding to tetrahedral and octahedral aluminum²¹. The disappearance of pentacoordinated aluminum suggests reaction of the aluminum sec-butoxide precursor. For comparison, the spectrum of a solution with an aluminum to silicon ratio of 3/8 is shown in Figure 8. The pentacoordinate peak at 38 ppm, similar to that of the original aluminum sec-butoxide, suggests that with insufficient silicon, butoxide does not completely react with the prehydrolyzed silicates.

A decoupled ^{13}C NMR spectrum at stage B is shown in Figure 9. It exhibits peaks associated with the silicon ethoxide groups (13, 59 ppm), ethanol and the aluminum sec-butoxide groups (68.7, 32, 22.6, and 10 ppm). 2-butanol might also result from alcohol producing condensation of the aluminum sec-butoxide with the hydrolyzed silicates, but its resonance cannot be distinguished from that of the aluminum sec-butoxide. While the peak at 59 ppm is the ethoxide ligand of the TEOS, the peak at 58.4 ppm is assigned to a bridging ethoxide group between a silicon and an aluminum. The peak at 13 ppm is assigned to the methyl group of the ethoxide for both the TEOS and the ethanol. Peaks at 68.7, 32, 22.6, and 10 ppm are carbon environments in the sec-butoxide ligand. The peaks of the bridging sec-butoxide groups in the aluminum precursor have disappeared, confirming the oligomeric nature of the aluminum precursor has been disrupted^{5,20}.

Although ^{13}C NMR does not help to determine the number of sec-butoxide ligands still attached to the aluminum, the ^{17}O NMR spectrum (Figure 10) indicates a large amount of enriched ^{17}O incorporation into the Al-O-Si site at 29 ppm, so many of the sec-butoxide ligands on the aluminum must have been removed^{14,19}. The peak at 44 ppm corresponds to a siloxane environment, but it is not formed in large amounts. The ^{17}O NMR spectrum also shows peaks at 7.5, and 80 ppm. The peak at 7.5 ppm falls in

the shift range for neither Si-O-Si, Al-O-Si, nor Si-OH environments¹⁴⁻¹⁹. Since triply bonded oxygens in Al-OH-Al environments occur at 0 ppm^{15,18}, though, we tentatively assign this peak to a Si-OH-Al environment, which is the only enriched site possible that would correspond to this shift. The peak at 80 ppm is associated with neither network siloxane nor aluminate environments¹⁴⁻¹⁹, but it does fall into the shift range for pyroxene siloxane environments¹⁹, so it is assigned to a linear Si-O-Si bridge in a new aluminosilicate species.

The chemical shift of the tetrahedral peak in the ^{27}Al spectrum of the prehydrolysis mixture (Figure 5) conforms to a $\text{Al}(\text{OSi})_4$ site^{21,22,23}. The large number of Al-O-Si bridges formed in solution (Figure 10) support this assignment.

Without further addition of water, the solution at stage B will be stable for up to 3 months. Even without addition of the aluminum precursor, the prehydrolyzed TEOS solution would also gel in approximately 3 months. It is evident, then, that at stage B, the aluminum sites are "protected"; without further addition of water, gelation seems to be governed by silicate condensation kinetics.

Stage C

Following Addition of Final Water

Solution Spectra

Solution spectra were obtained at stage C only for $R=2$, since gelation was much too rapid for $R=3$ and 4.

The ^{29}Si NMR spectrum (Figure 11) immediately after final water addition at point C for $R=2$ shows some hydrolyzed Q_0 , Q_1 and Q_2 silicate sites. No aluminosilicate peaks remain in solution. After one day of reaction, though, only the Q_1 and Q_2 species remain in the solution spectra.

The progression of the ^{27}Al NMR spectra for a gelling solution is shown in Figure 12. Addition of water causes a change in the chemical shift of octahedral aluminum (4-6 ppm, in Figure 7) to 0 ppm (Figure 12). The tetrahedral aluminum chemical shift remains unchanged at 56 ppm, but the intensity is lower. The intensity of both the tetrahedral and octahedral aluminum peaks decrease with time with no apparent change in proportion, but ^{27}Al MAS NMR of the gelling solution (Figure 13) shows conversion to the octahedral aluminum environment as gelation proceeds. The signal of the MAS spectrum

is low compared to the liquid NMR spectrum because the sample size in the MAS rotor is much smaller.

The ^{13}C NMR spectrum of the solution after water addition (Figure 14) shows coalescence of the peaks of the bridging ethoxide and TEOS ethoxide groups into a broad peak at 58 ppm. The ^{17}O NMR spectrum (Figure 15) shows an increased number of Si-OH groups at 18 ppm, Al-OH-Si sites at 7.5 ppm and Al-O-Si bridge sites at 29 ppm. The Al-O-Si sites are evident in the ^{17}O spectra but not the ^{29}Si spectra due to the poor sensitivity of the ^{29}Si nuclei.

Gels

The ^{27}Al MAS NMR spectra of wet gels at water ratios of R=2 and 4 are shown in Figure 16. They both show a broad peak corresponding to octahedral aluminum and a small amount of tetrahedral aluminum; typical of aluminum hydroxides and oxides¹⁵. No ^{27}Al chemical shift difference is seen between these gels, although the R=2 gel is much more transparent.

^{13}C and ^{17}O NMR are more helpful in showing structural differences. ^{13}C MAS NMR of the two gels is shown in Figure 17. At R=4.0, only carbon associated with the sec-butoxide and ethanol are present, but at R=2.0, unhydrolyzed ethoxide groups on the TEOS at 58 ppm are also present. The ^{17}O MAS NMR spectra of the R=2.0 and 4.0 gels are shown in Figure 18. At both R values, three broad peaks at 24, 7.5, and -5 ppm are observed. At R=2.0, though, a peak also appears at ~85 ppm. The peak at 7.5 ppm corresponds to the triply bridging silanol in both gels; it is increased in intensity compared to the prehydrolysis mixture in Figure 10. The peak at 24 ppm is the Al-O-Si bridge. The peak at -5 ppm is assigned to a Si-OH environment since no unhydrolyzed ethoxide groups remain in the gel and since no bridging oxygen environments are present at R=4. The new peak at 80-90 ppm is assigned to a pyroxene-like siloxane bridge. Thus, whereas the aluminum coordination expansion occurs for all R values, the more transparent, more slowly gelling, solutions retain ethoxides on Si sites and produce Si-O-Si bonds.

Discussion

Stage B

After Aluminum Sec-Butoxide Addition

The ^{27}Al and ^{17}O NMR spectra (Figures 7 and 10) of the solution after addition of the aluminum sec-butoxide suggests sites of tetrahedral aluminum surrounded by four silicate ligands. The ^{13}C NMR spectrum (Figure 9) suggests a Si-OEt-Al environment. This bridging ethoxide is not observed in the ^{17}O NMR spectrum only because it is not an enriched site.

Since the aluminum precursor is only sparingly soluble in ethanol alone, the presence of prehydrolyzed silicate acts to allow aluminum sec-butoxide to be dissolved in solution. A deficiency of prehydrolyzed TEOS will not allow complete reaction of the aluminum sec-butoxide precursor, as shown in Figure 8.

The number of hydrolyzed silicate groups corresponds well with the number of tetrahedral aluminums surrounded by silicate ligands. There are also competing reactions to form pure Si-O-Si bridges and Si-OH-Al bonds; both are seen in the spectrum of the prehydrolysis mixture in Figure 10. There is no distinction, though, between the Al-O-Si environment bonded to tetrahedral versus octahedral aluminum¹⁴.

Thus it is apparent that a new alumino-silicate species is formed at point B in the synthesis. This species is shown schematically in Figure 19. The ^{17}O and ^{13}C NMR spectra suggest this species probably has three Al-O-Si bonds and a fourth bond occupied by either a bridging silanol or ethoxy ligand.

Stage C

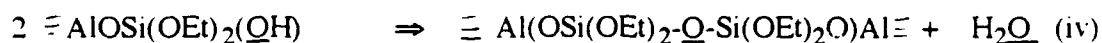
After Final Water Addition

The idealized precursor shown in Figure 19 can help to explain the homogeneity and gelation rates as the hydrolysis ratio, R is changed. It is helpful to consider the

amount of water added at stage C. Table 3 shows the relation between the overall water content in the procedure (R) and the amount of water added in stage C (R').

R=2

At R=2, the functionality, f, of the new precursor at stage C after hydrolysis with the remaining water should be less than two. This would suggest that linear polymerization can occur between the new precursors in solution as shown in Figure 20, and these Si-O-Si bridges are shown by the ^{17}O NMR spectra in Figures 10 and 18. This Si-O-Si bridges may be the result of polymerization of the aluminosilicate precursors is shown at site a in Figure 20. This is a site which may be enriched with ^{17}O as follows:



The ^{17}O NMR spectra also suggest coordination expansion of the aluminum by nucleophilic attack of silanol groups. Figure 18 shows the silanol peak at -5 ppm in the gel is decreased in intensity, more than can be accounted for by Si-O-Si formation. The Al- $\underline{\text{O}}$ -Si bridge is shifted upfield by 5 ppm to overlap with the triply bridging silanol group at 7.5 ppm. The triply bridging silanol group now has twice the intensity of the Al- $\underline{\text{O}}$ -Si site.

In the sequence shown in Figure 20, the hydrolysis of a single ethoxide group of each silicate ligand can lead to linear polymerization between the precursors. This can be followed by nucleophilic attack of silanols on the aluminum to expand its coordination from tetrahedral to octahedral. Gelation may be slow because it is controlled by the condensation reactions between the alumino-silicate precursors, the kinetics of which are similar to acid catalyzed TEOS gels.

R=4

For R=4, the ^{17}O MAS NMR spectrum in Figure 18 shows that silicate condensation reactions do not occur to any appreciable degree. However, octahedral aluminum is still formed. This conversion from a tetrahedral to octahedral coordination coincides with gelation at both high and low R values, but the greater concentration of the attacking silanol group at higher R apparently causes silanol attack on aluminum to

happen faster than silanols can condense with each other, and this may be associated with lower homogeneity.

At both high and low water contents, gelation is accompanied by the tetrahedral to octahedral conversion of aluminum, but it is not yet clear why this expansion of coordination occurs.

Although the reason for the relationship between gel homogeneity and aluminum coordination also is not yet clear, the following is proposed. The coordination shift of aluminum from tetrahedral to octahedral coordination proceeds by nucleophilic attack of silanols on the aluminum. The coordination shift is then dependent on the number of silanol groups present in solution. At low R values, the silanol groups form siloxane bridges by condensation reaction (iv) before the coordination expansion occurs. The coordination expansion then is rate limited by the low amount of silanol groups left in solution. The initial concentration of silanol groups is decreased by reaction (iv) as more condensed aluminosilicate species are formed. Although water is produced in reaction (iv) and can form silanol groups by hydrolysis of the ethoxide ligands in solution, there is only one silanol group formed from the water in reaction (v). The consumption of two silanol groups in reaction (iv) in a condensation reaction generates only one silanol group from the water produced, so the concentration of silanol groups is effectively halved, which slows the rate of coordination expansion. The condensed aluminosilicate species formed at low R values are also larger and bulkier than the aluminosilicate species formed at high R values, which introduce steric factors into the reaction.

These silanols which attack the aluminum and expand its coordination become unavailable for condensation reactions to form siloxane bridges between aluminosilicate precursors, so the presence of tetrahedral aluminum in a gel is evidence that a high number of siloxane bridges between precursors have been formed. Aluminum in a tetrahedral coordination may also fit more easily into the silicate net to form a more continuous, molecularly homogeneous polymeric network.

Conclusion

The prehydrolysis method of preparation allows the formation of aluminosilicate precursors in solution in which the aluminum is protected from hydrolysis. At low water ratios, polymerization between the silicate ligands of these precursors can occur. This polymerization seems to delay aluminum coordination expansion and gelation.

At high water ratios, all ethoxide groups are hydrolyzed and the resulting silanol groups attack to expand the aluminum coordination much more rapidly; there is evidently

no time to form siloxane bridges. The lack of homogeneity of these gels is linked to the fast expansion of coordination of aluminum from tetrahedral to octahedral coordination.

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Table 1

R (Molar Ratio of Water/TEOS)	Gel Time (Hours)
2.0	114
2.5	23
3.0	0.5
4.0	0.4

Table 2: Spectrometer Parameters

Nucleus	Spectral Frequency (MHz)	Sweep Width (kHz)	90° Pulse Width (μs)	Relaxation Delay (sec)
²⁷ Al	130.433	30	18	0.5-1.0
¹³ C	125.760	20	30	2.0
¹⁷ O	67.808	30	61	0.10-0.20
²⁹ Si	99.364	10	26	12

Table 3

Overall R	R' (Stage C)
2.0	0.8
2.5	1.3
3.0	1.8
4.0	2.8

Figure 1: Procedure for Synthesis of Aluminosilicate Gels by Krol Method [Ref. 4]

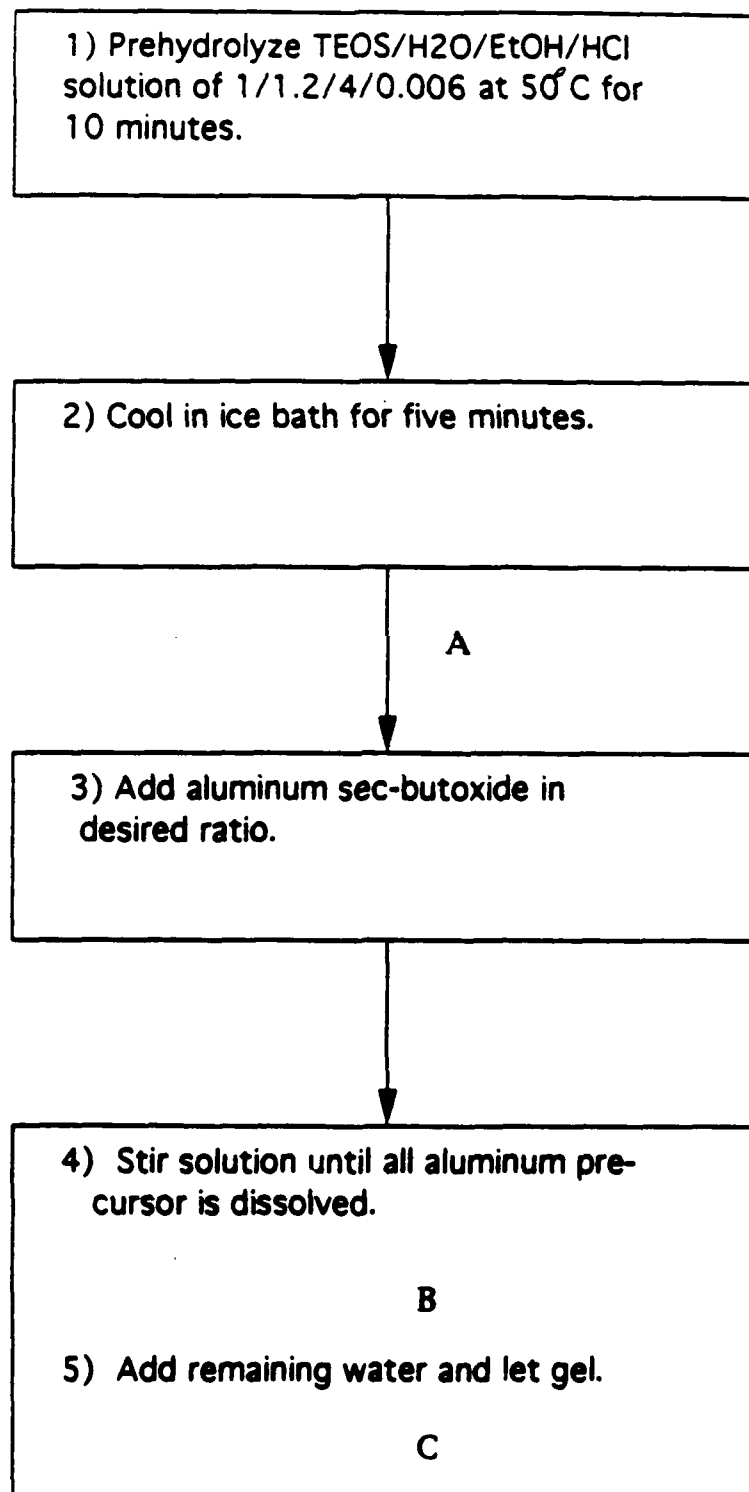


Figure 2: ^{29}Si NMR of Prehydrolysis Solution

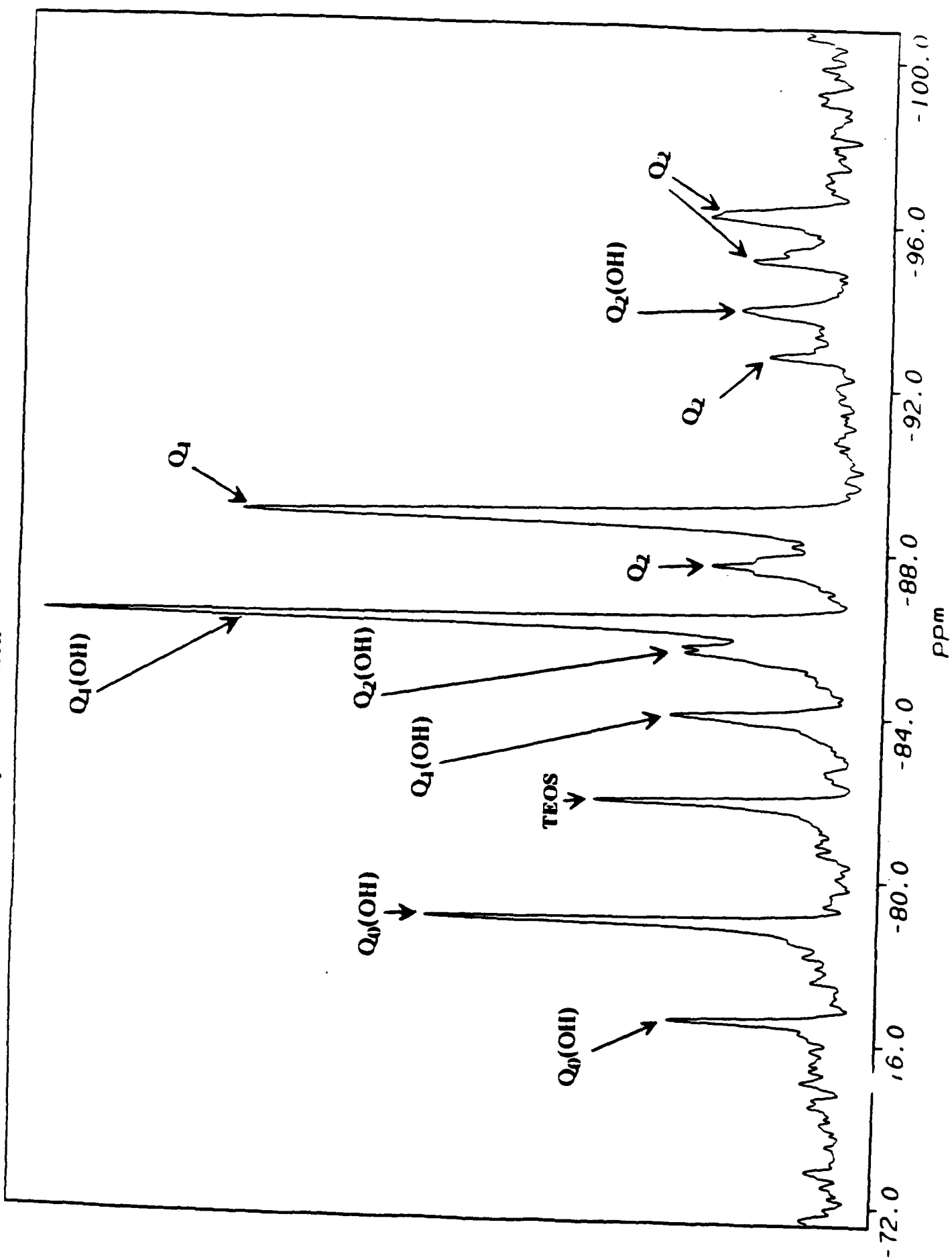


Figure 3: ^{17}O NMR of Prehydrolysis Solution

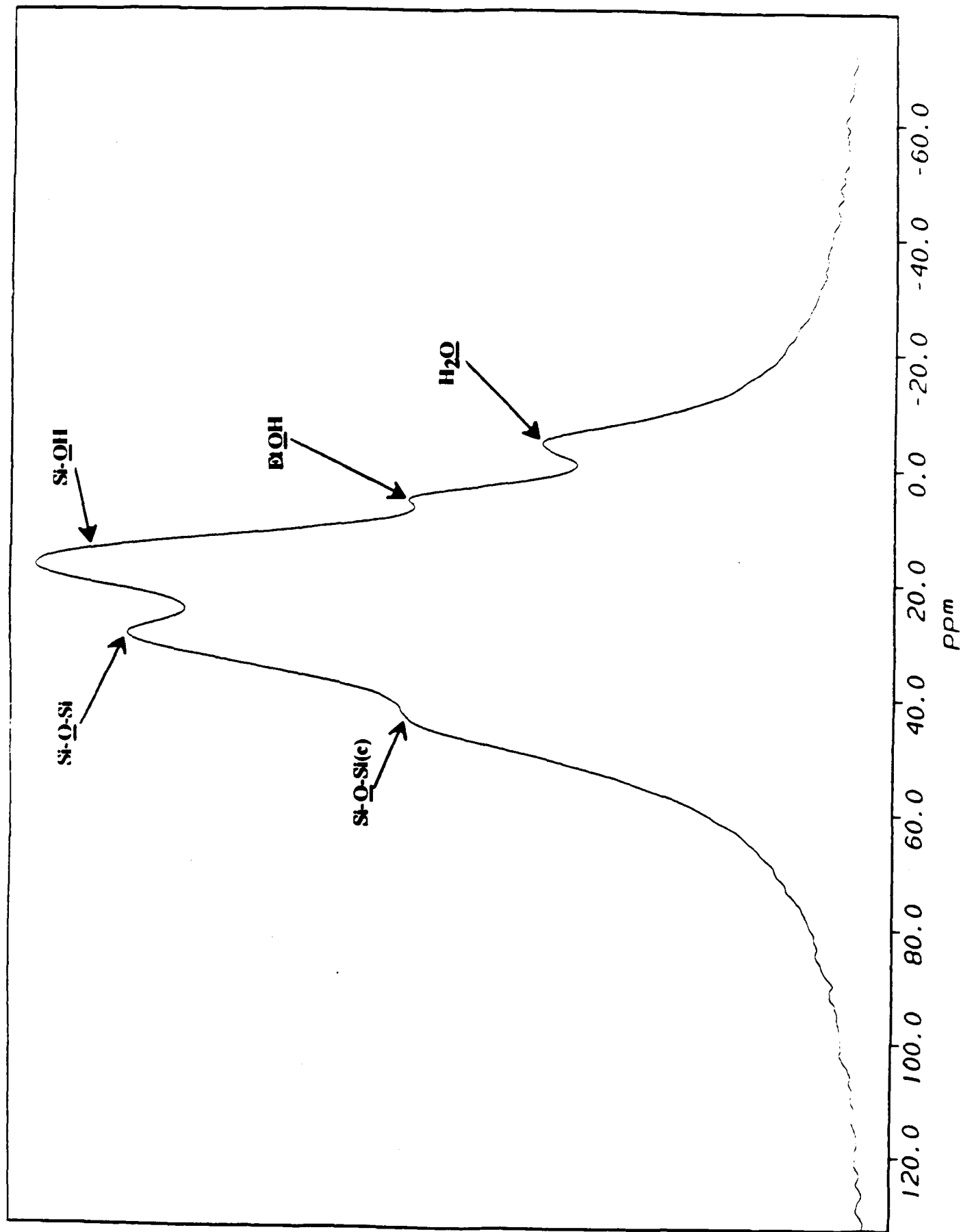


Figure 4: ^{27}Al NMR of Aluminum Sec-Butoxide in Benzene

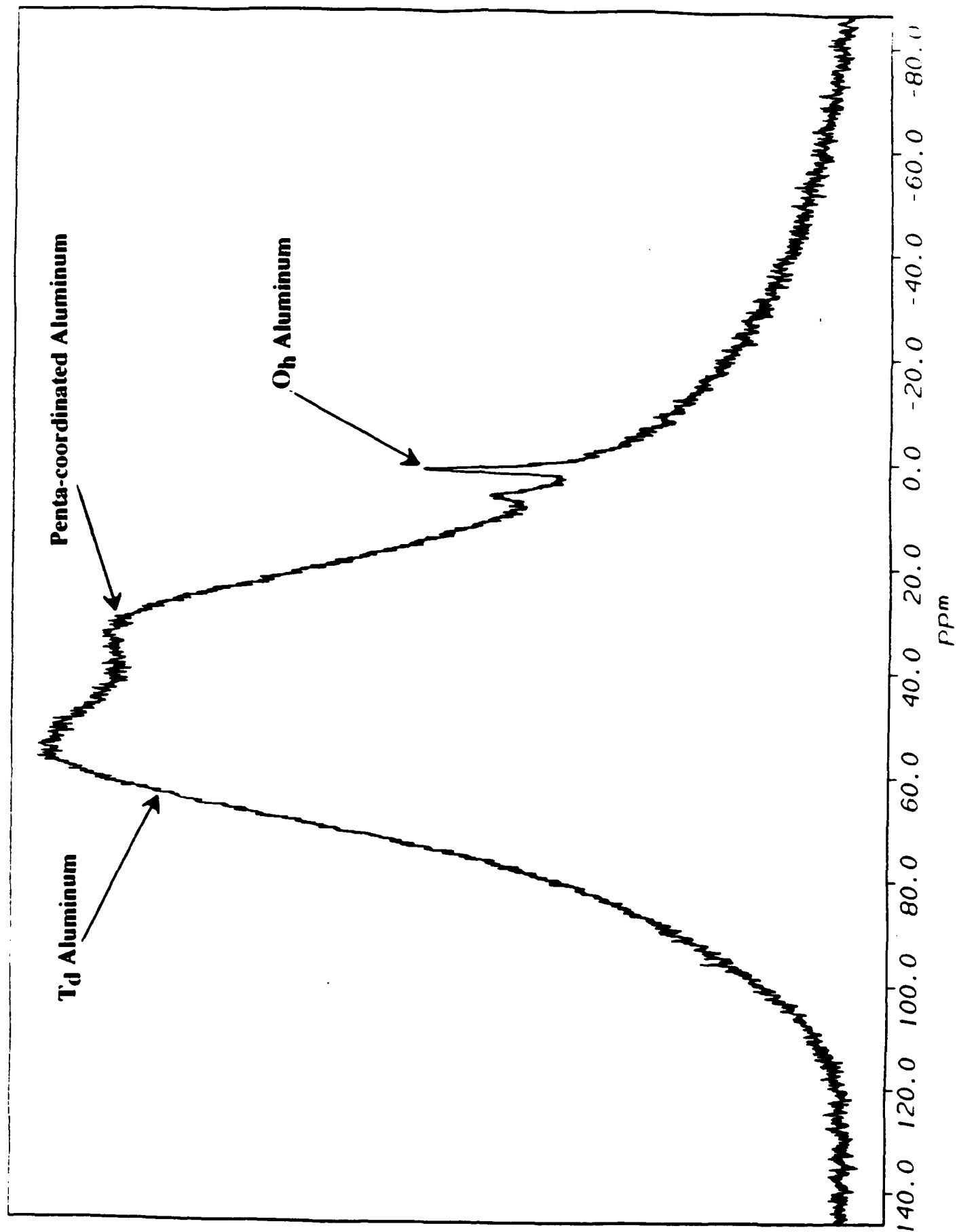


Figure 5: ^{13}C NMR (Decoupled) of Aluminum Sec-Butoxide in C_6H_6

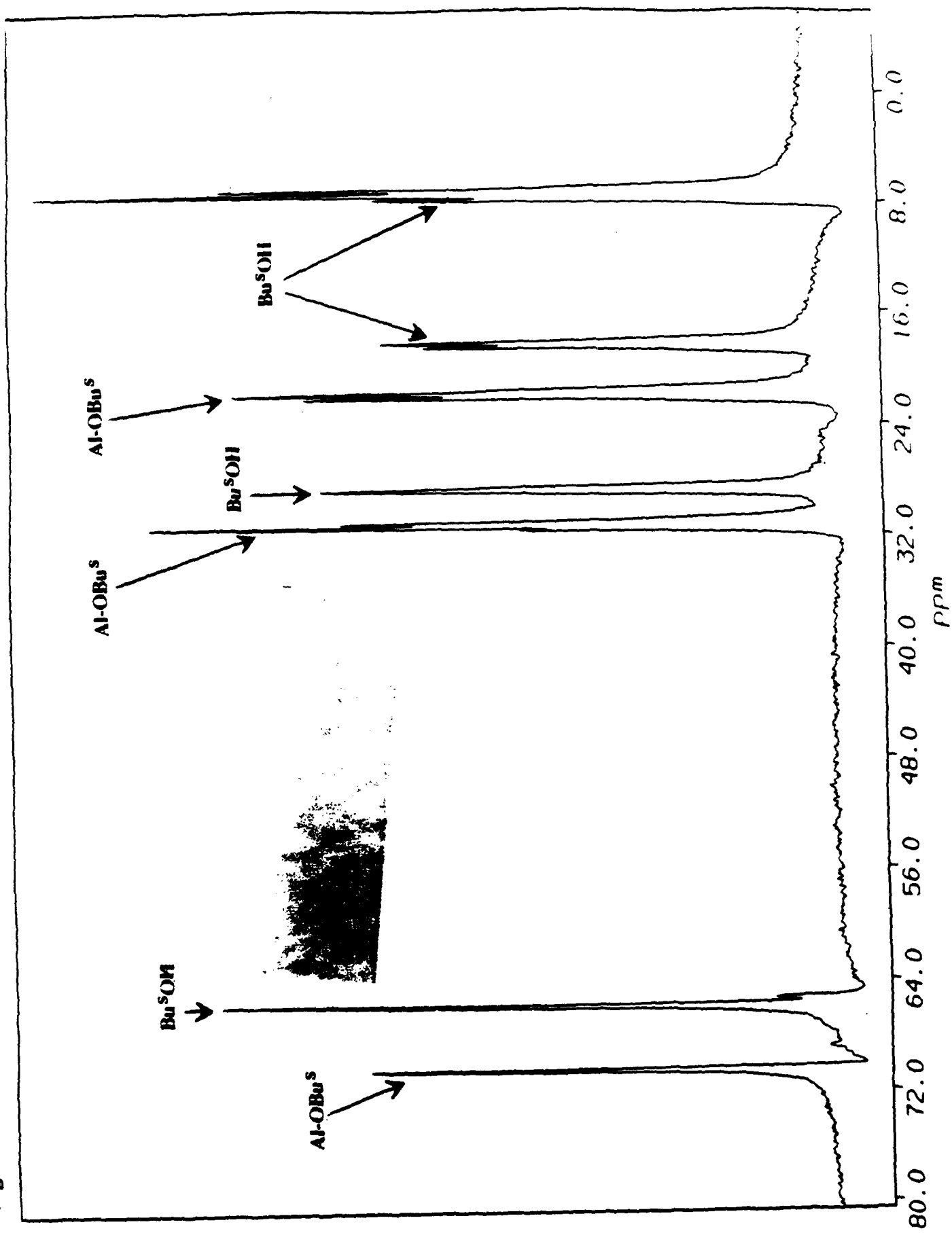


Figure 6: ^{29}Si NMR of Solution at B

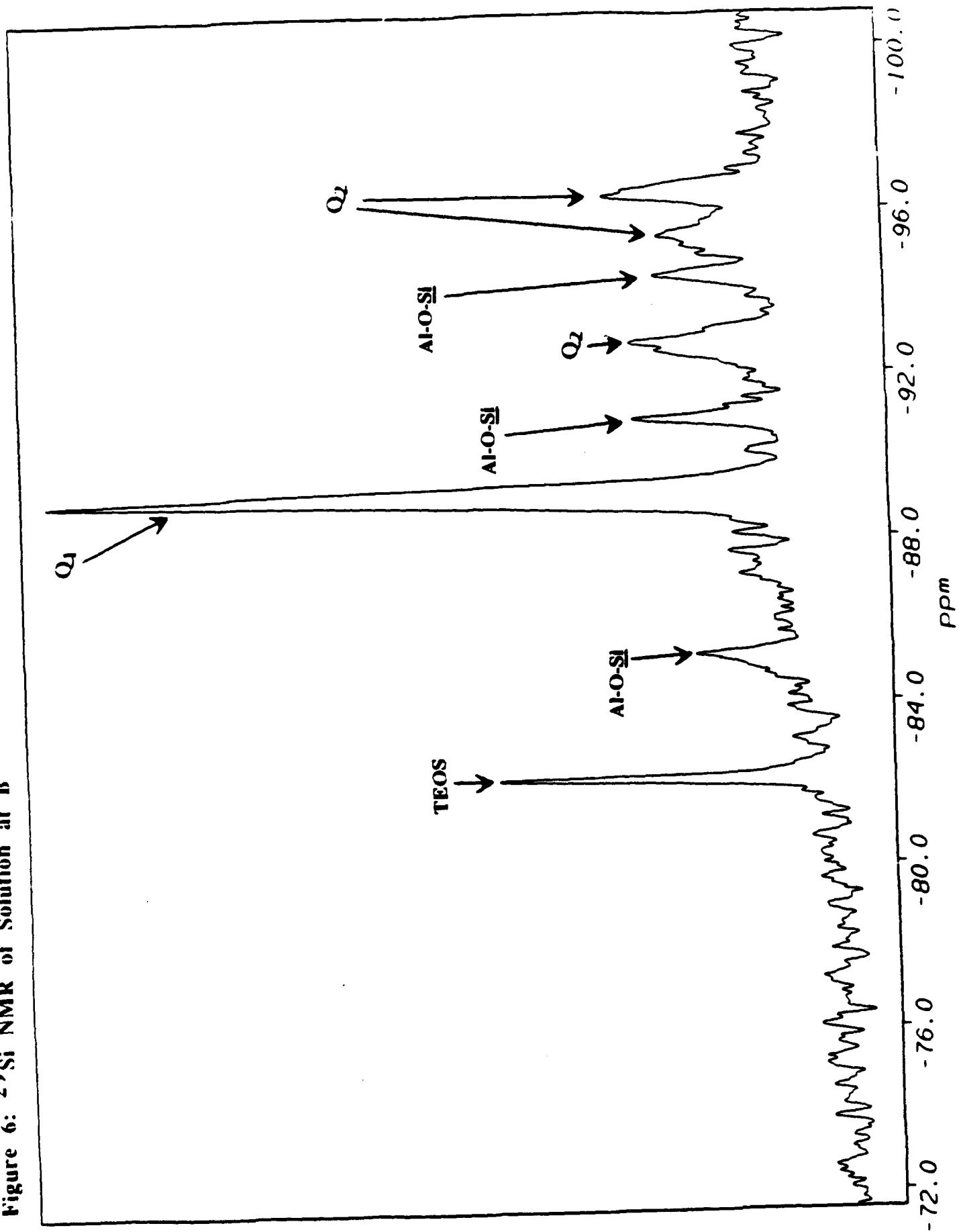


Figure 7: ^{27}Al NMR of Solution at B

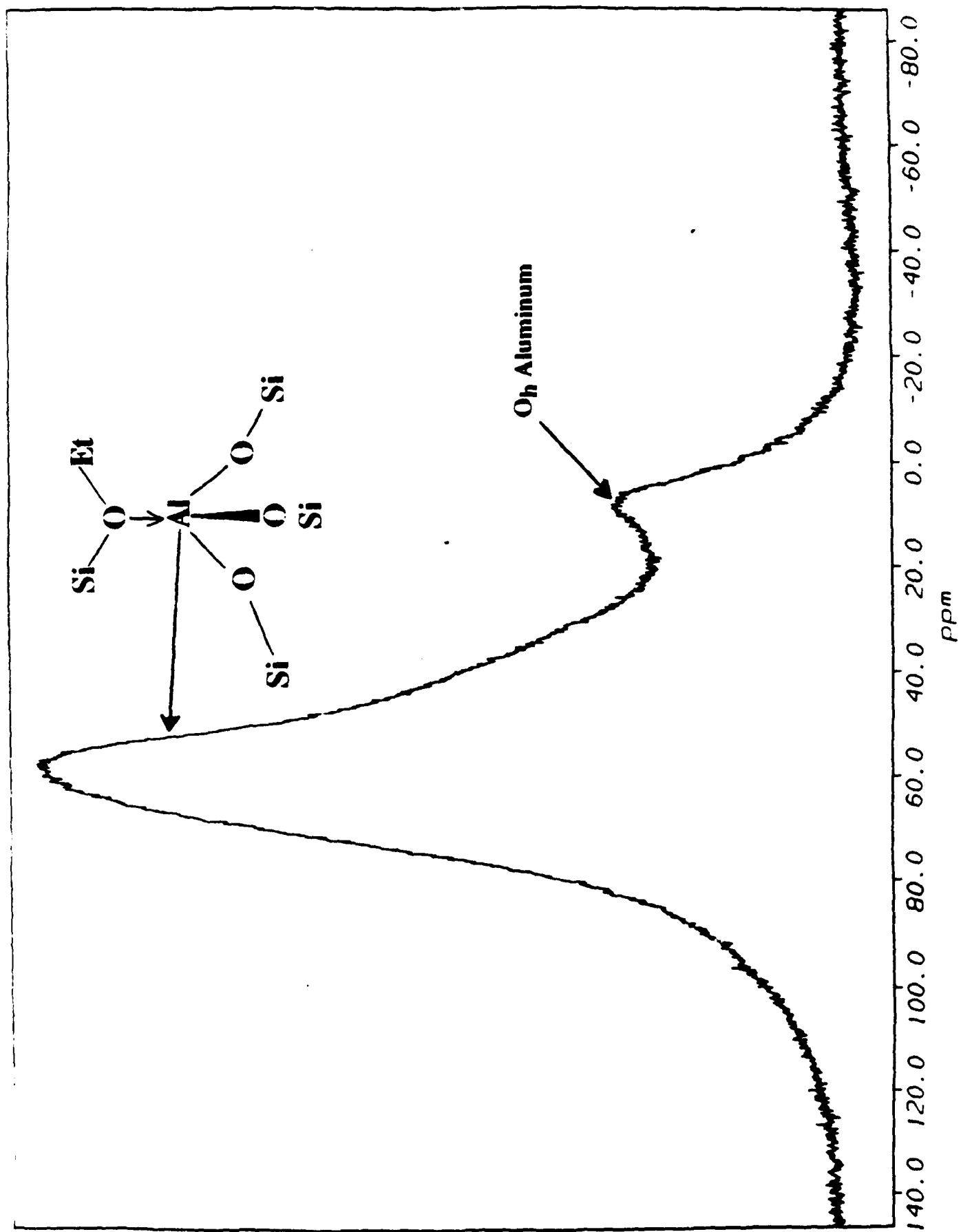


Figure 8: ^{27}Al NMR of Solution B Using $\text{Al/Si}=0.375$

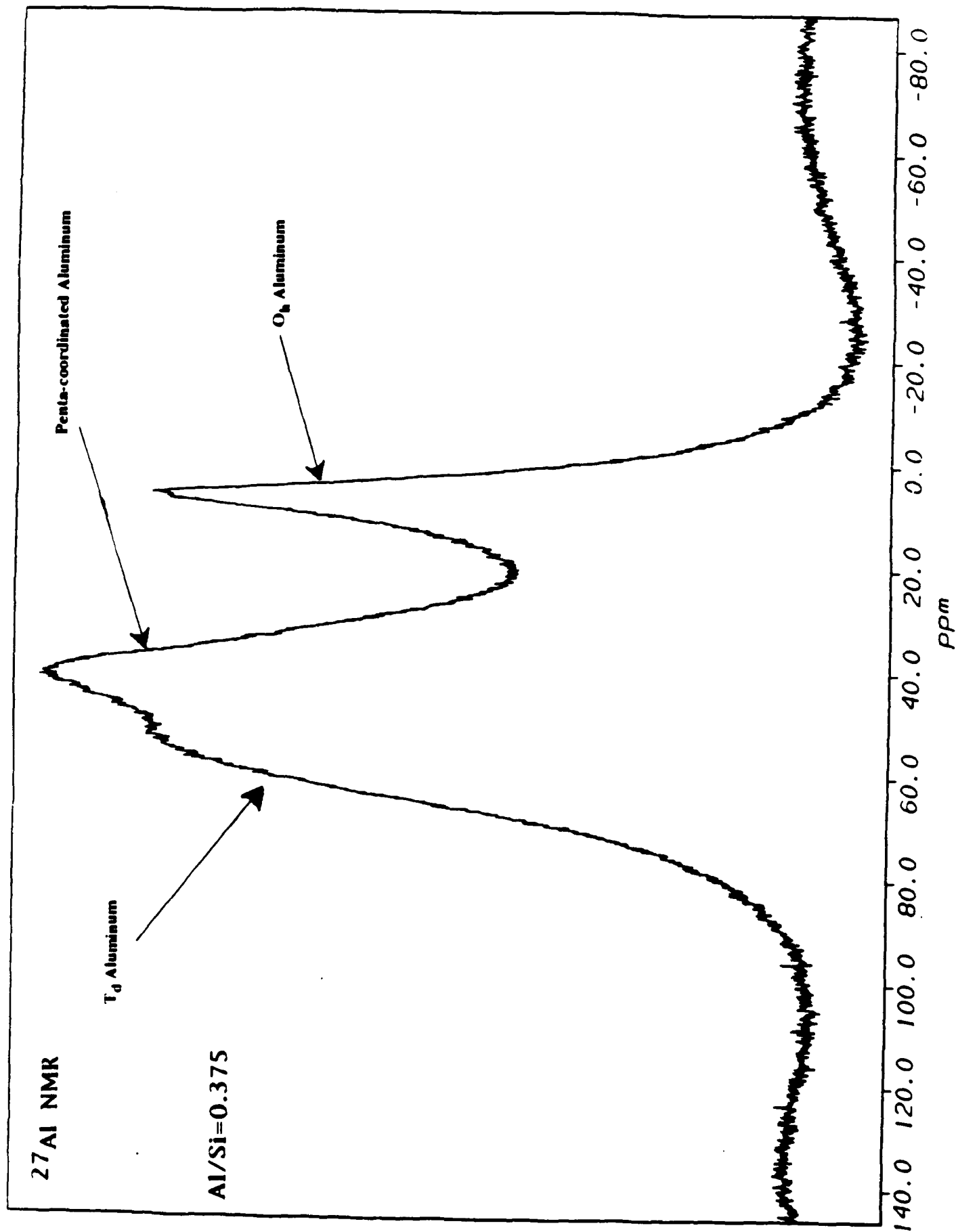


Figure 9: ^{13}C NMR (Decoupled) of Solution at B

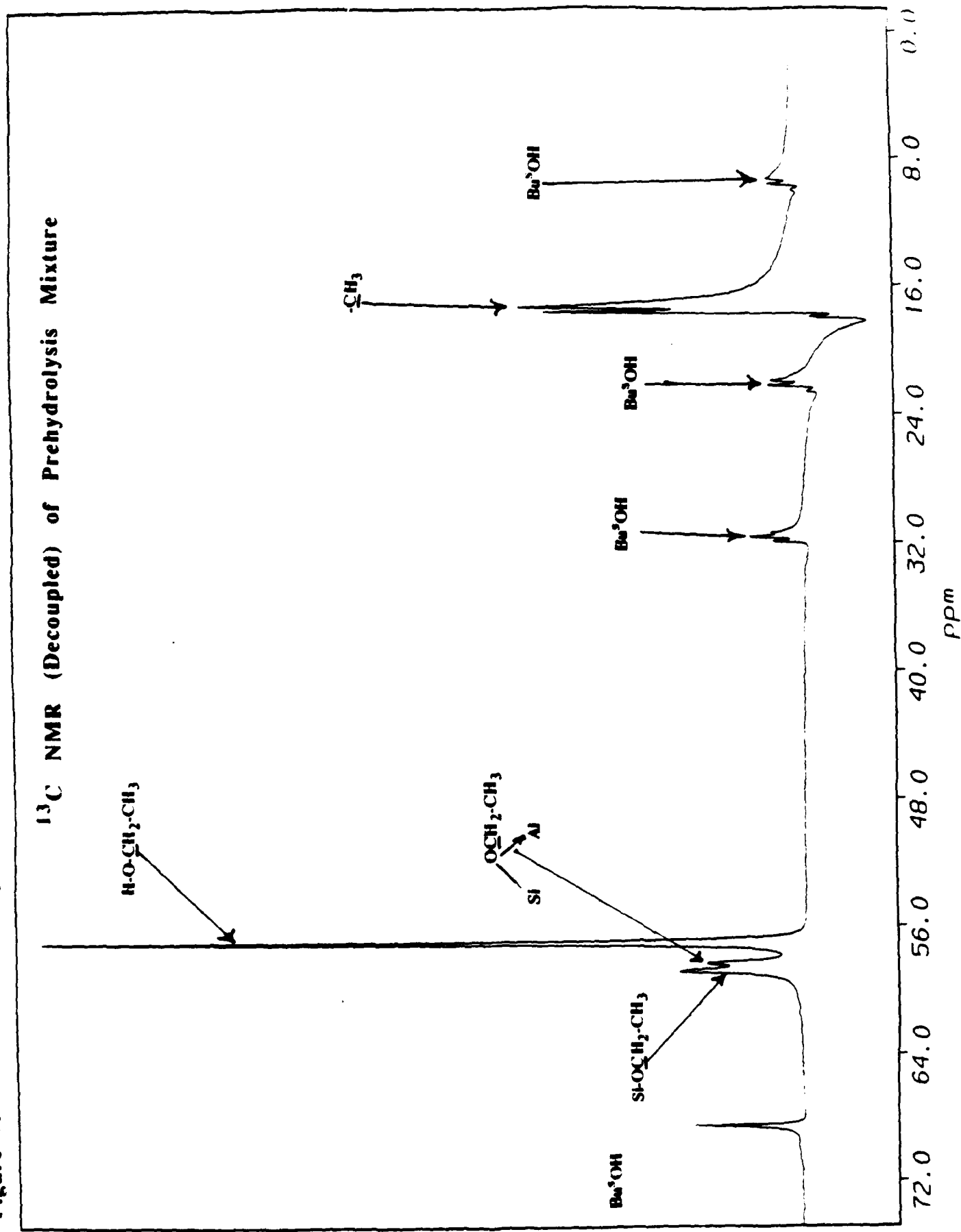


Figure 10: ^{17}O NMR of Solution at B

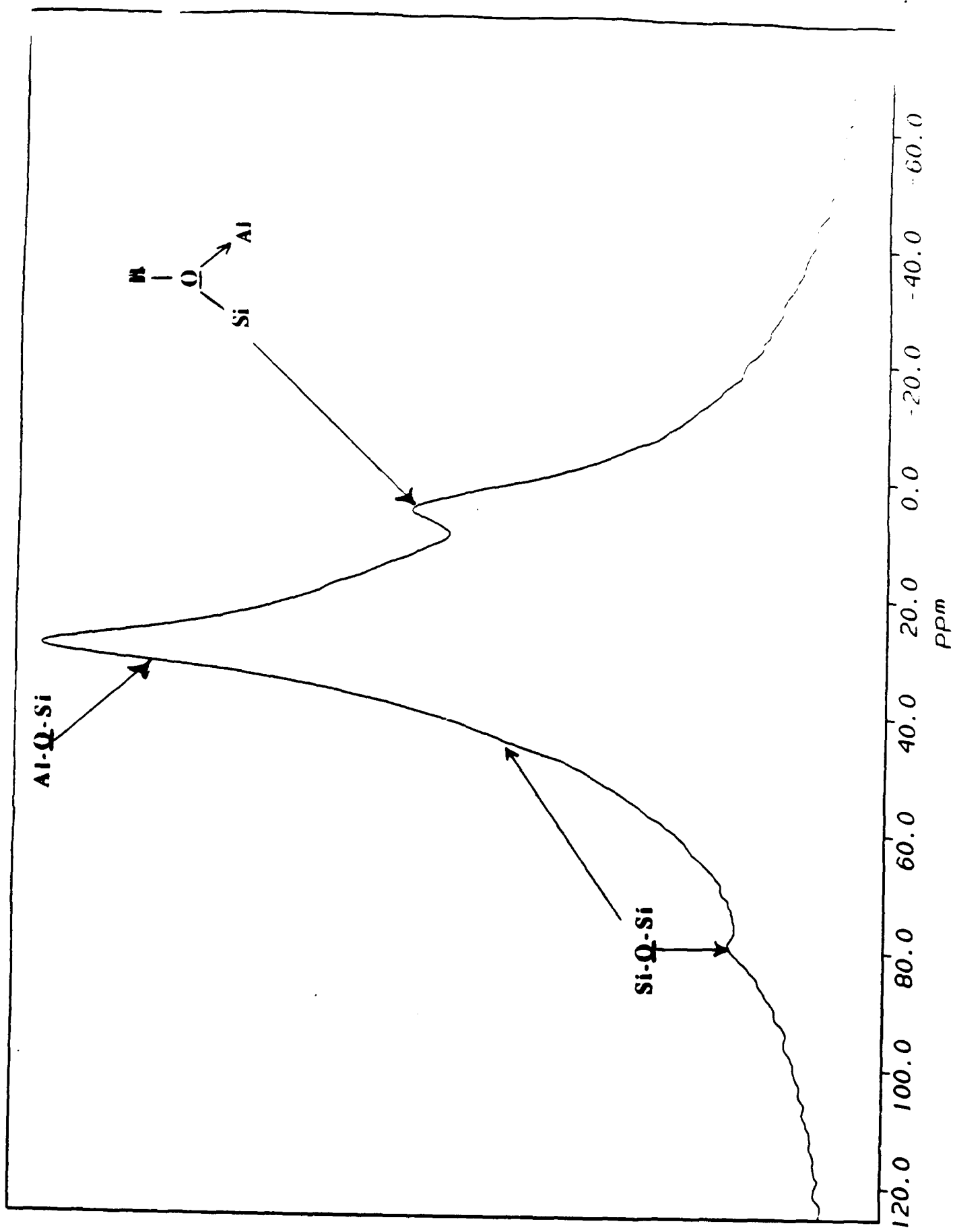


Figure 11: ^{29}Si NMR of Solution at C

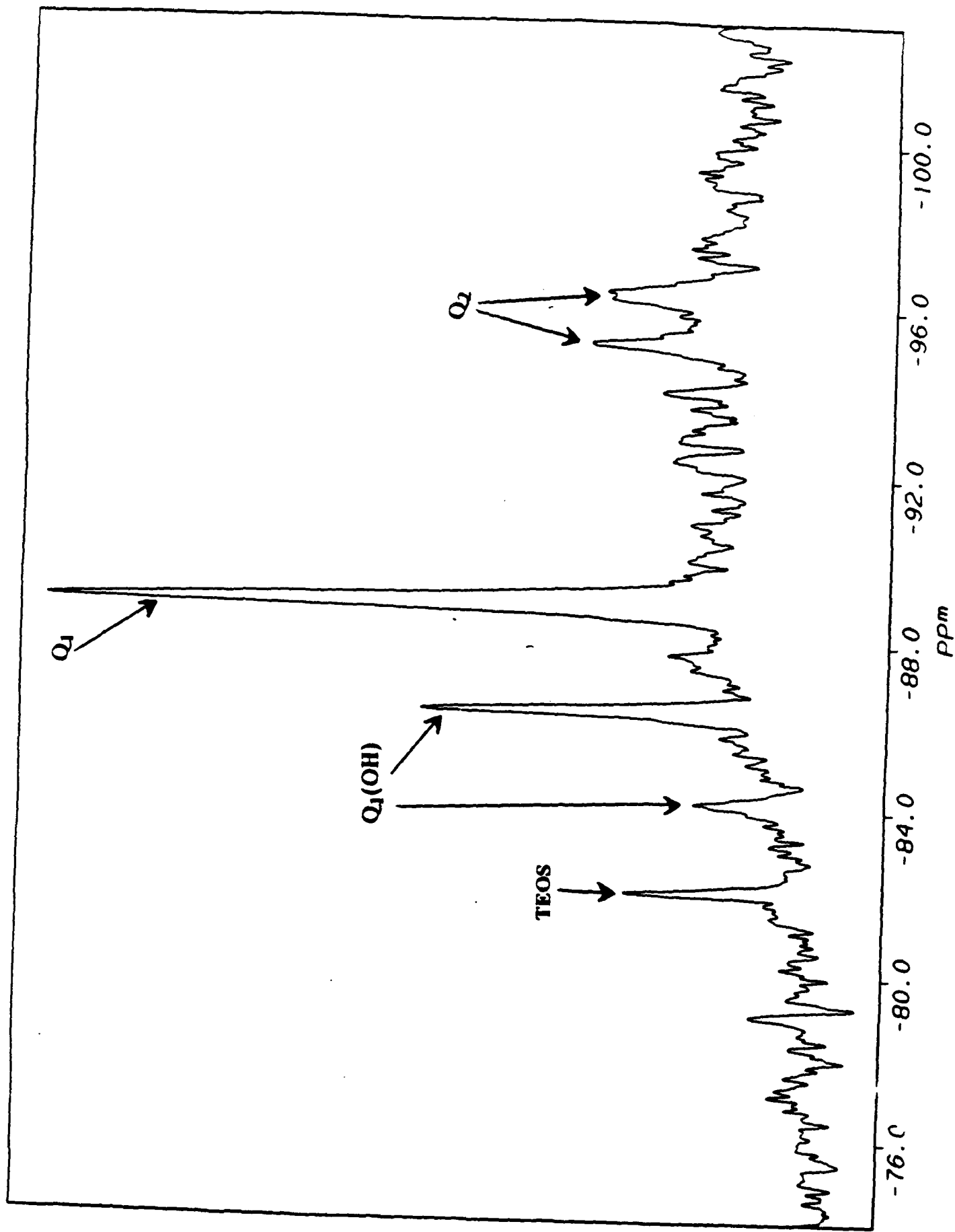


Figure 12: ^{27}Al NMR of Solution at C and To Gelation

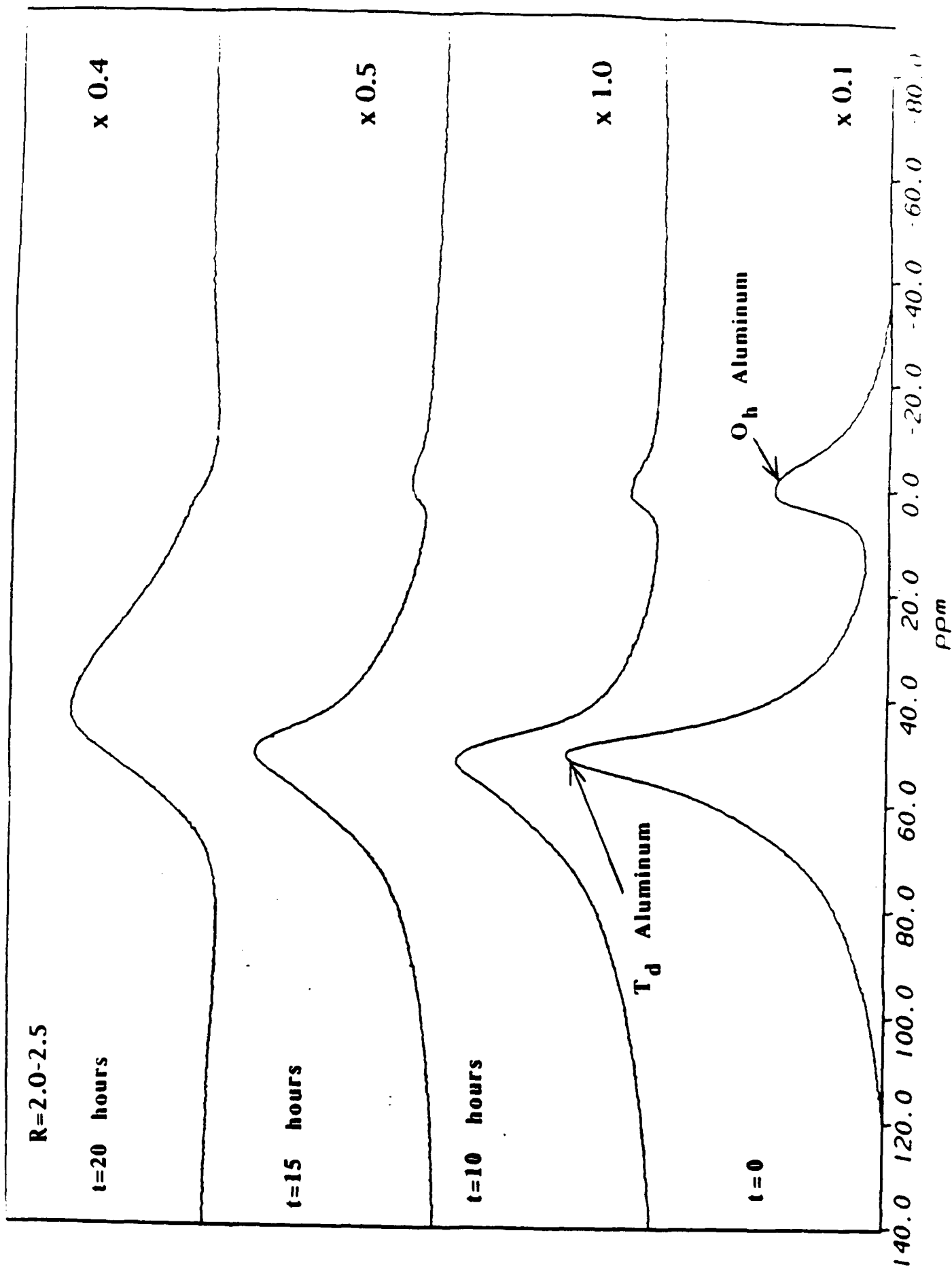


Figure 13: Comparison of ^{27}Al Liquid and MAS Spectra

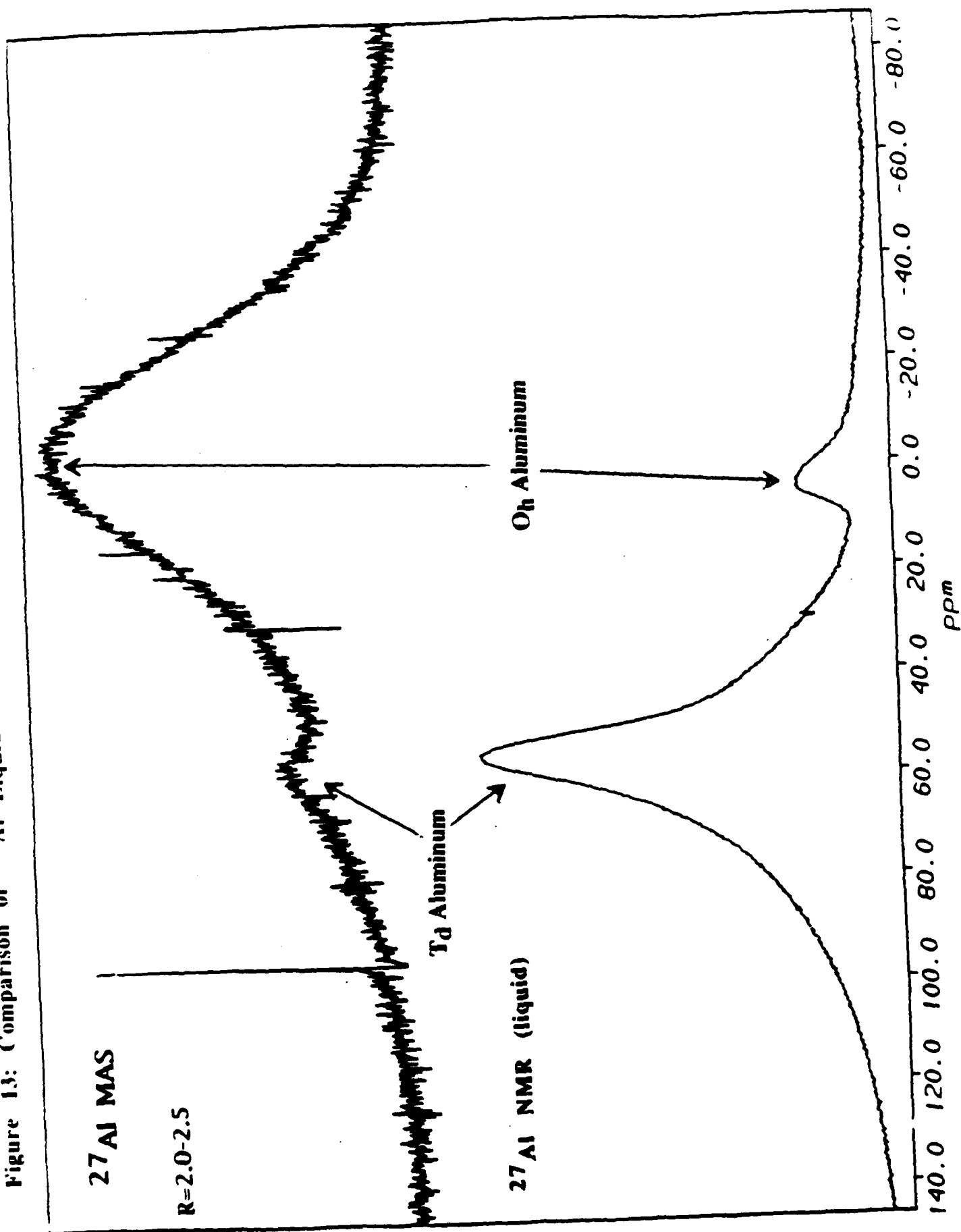


Figure 14: ^{13}C NMR (Decoupled) of Solution at C

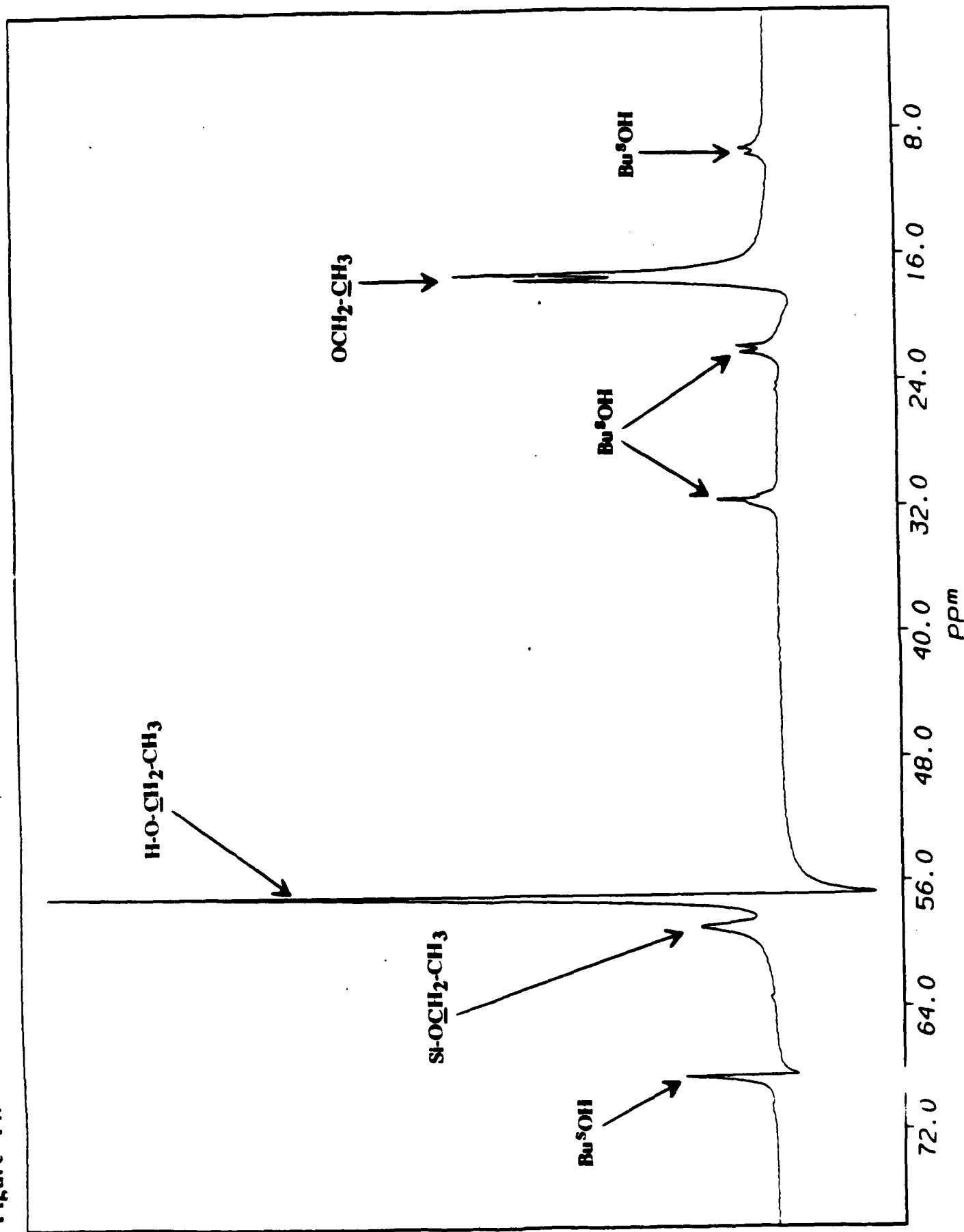


Figure 15: ^{17}O NMR of Solution at C

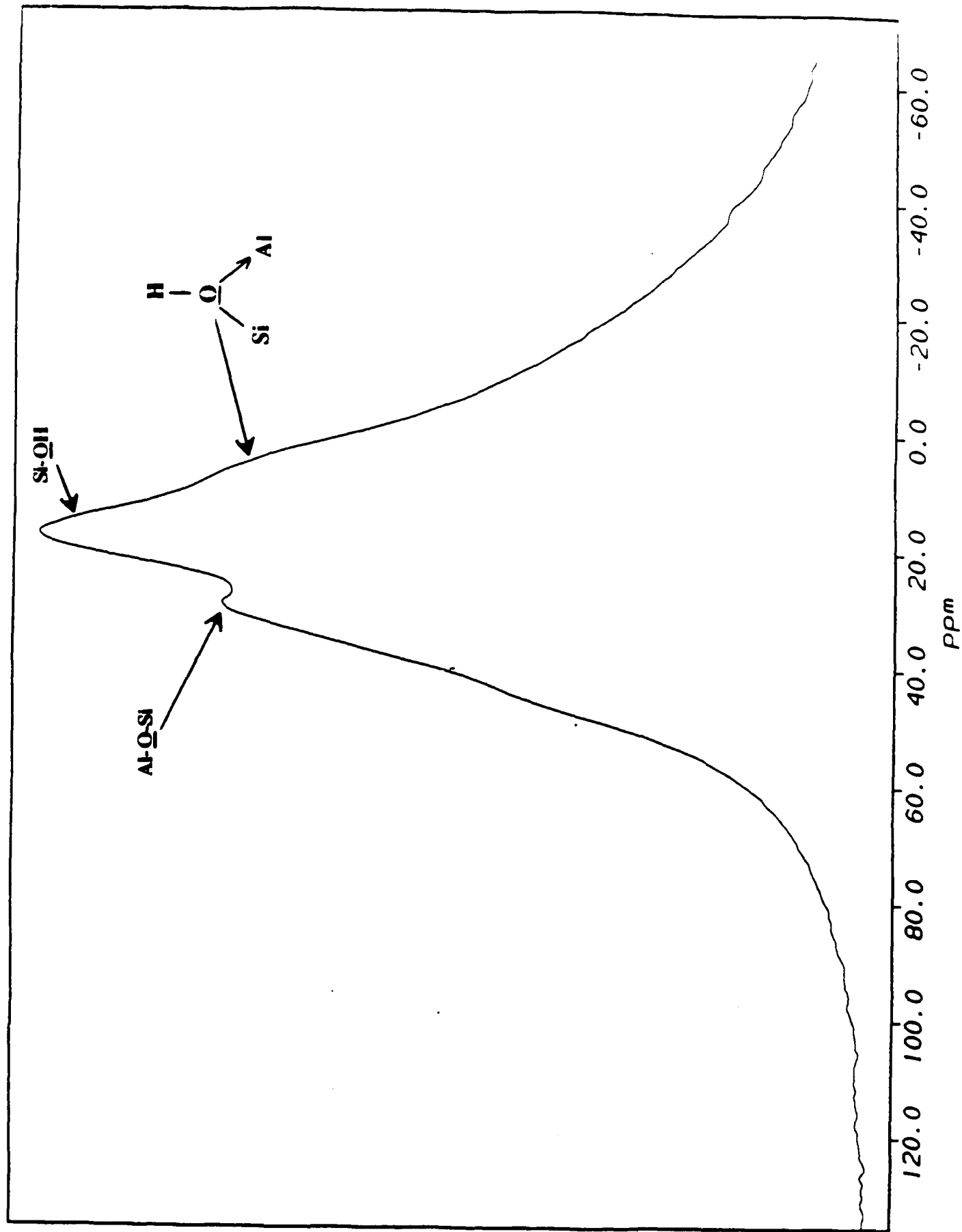


Figure 16: ^{27}Al MAS NMR of Gelled Sols

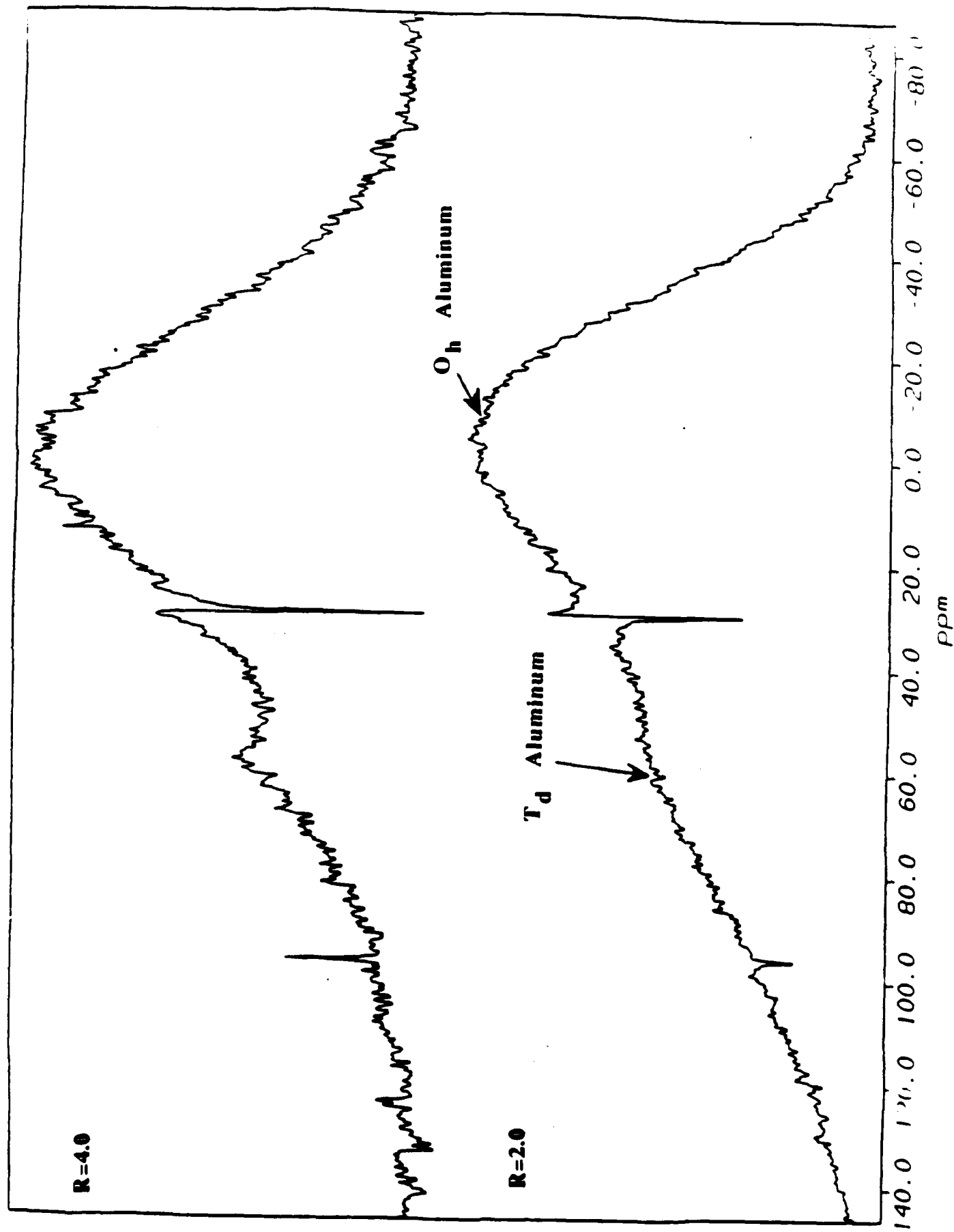


Figure 17: ^{13}C MAS NMR of Gelled Sols

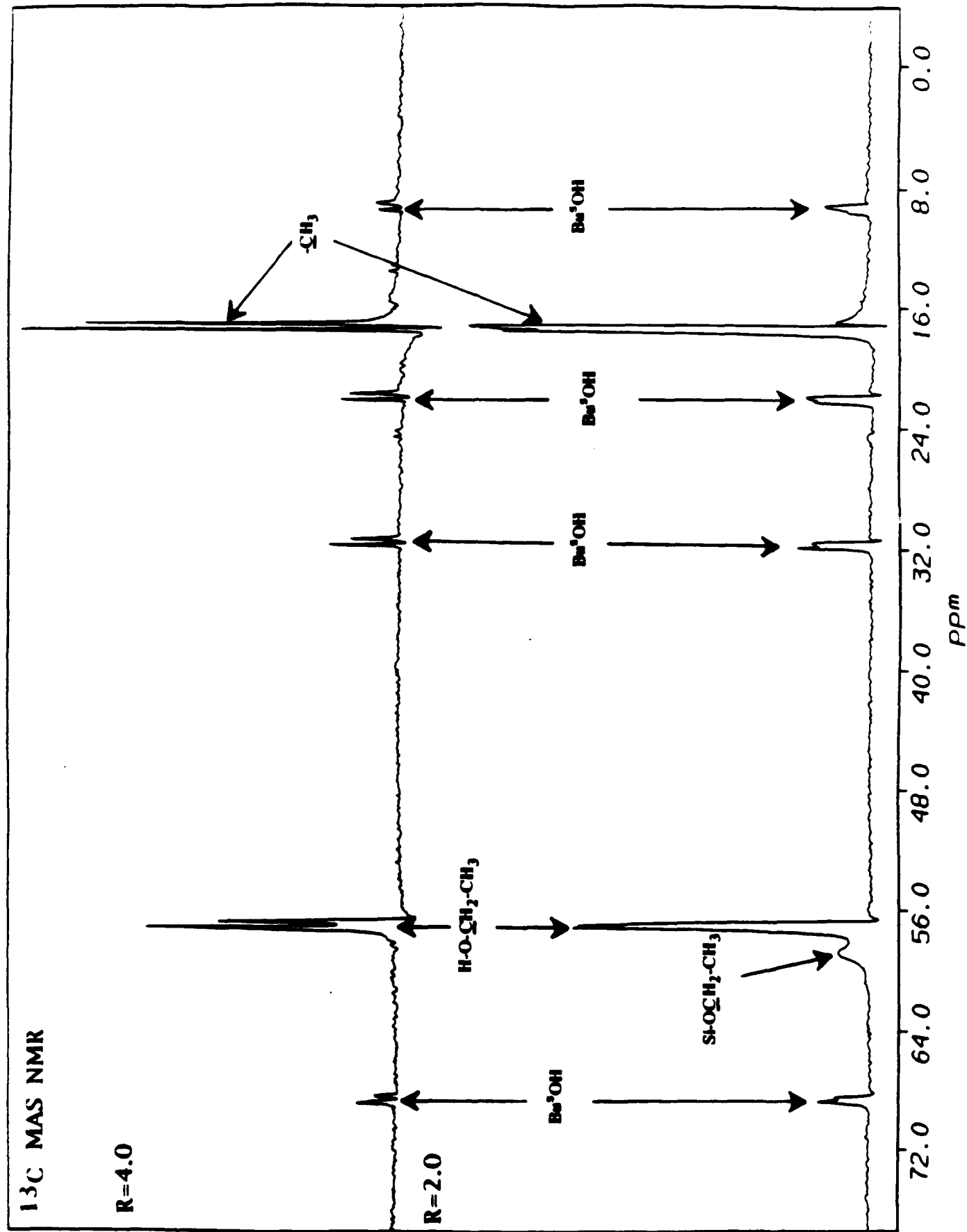


Figure 18: ^{17}O MAS NMR of Gelled Sols

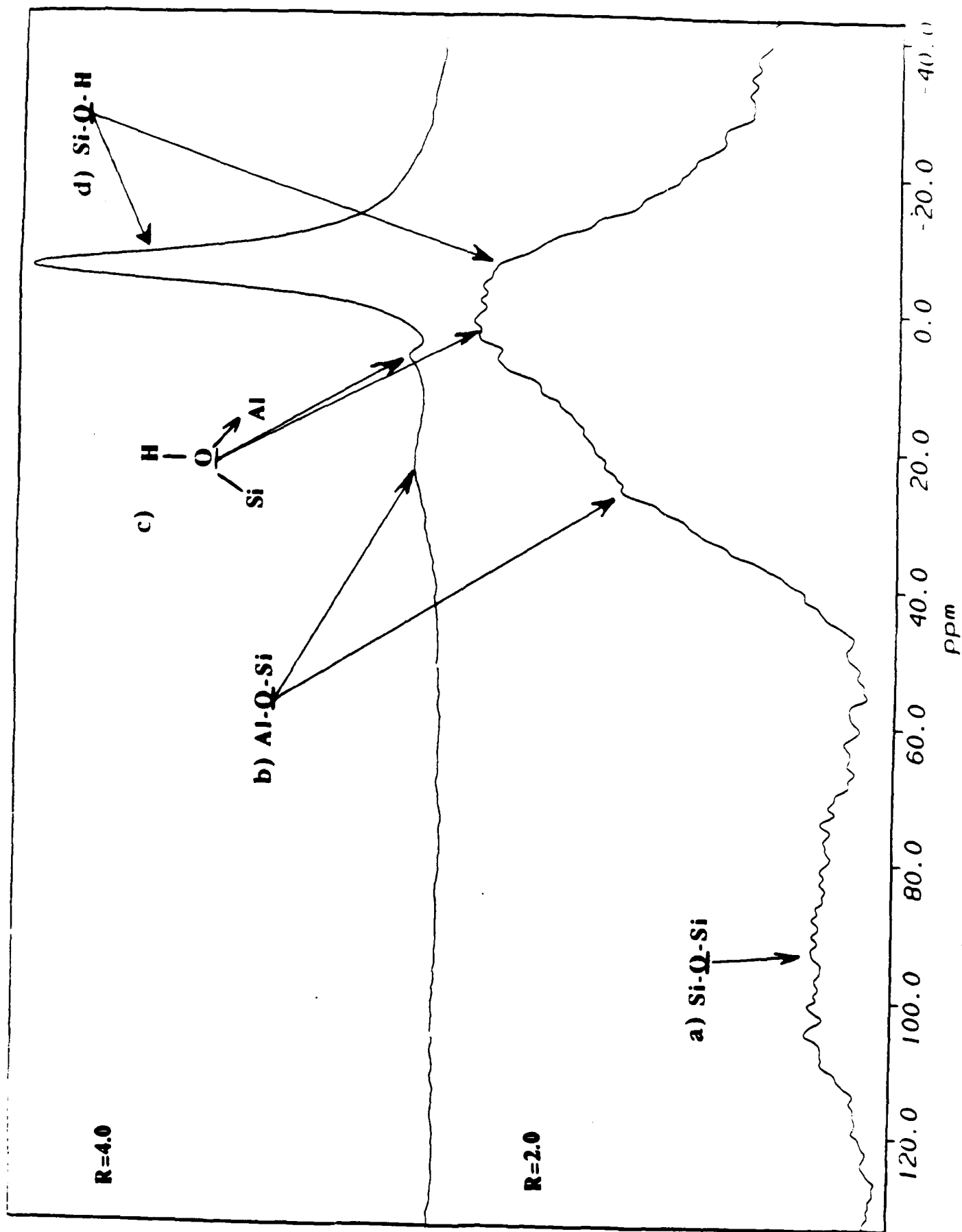
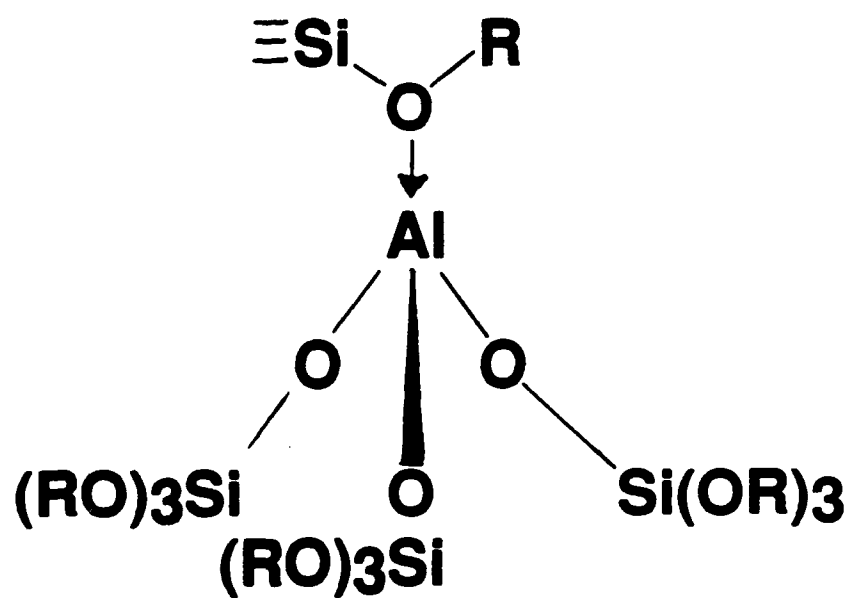


Figure 19

"Simplified" Prehydrolyzed Precursor

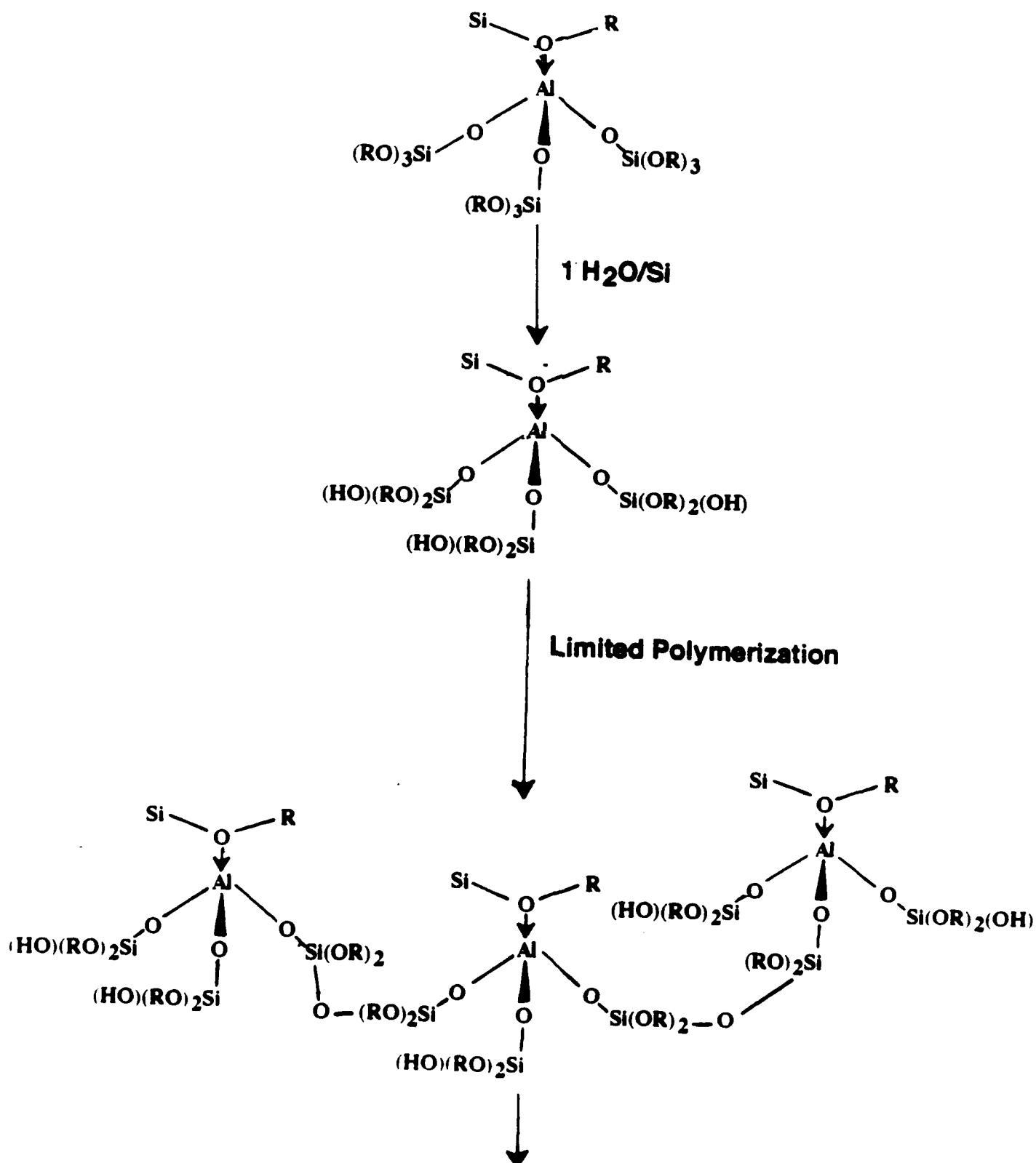


*R = H, Et, $\text{Si}(\text{OEt})_3$

Figure 20

Low Water to Silicate Ratio (R)

Water in 2nd Step = $2 - 1.2 = 0.8$



Expansion to O_h Aluminum

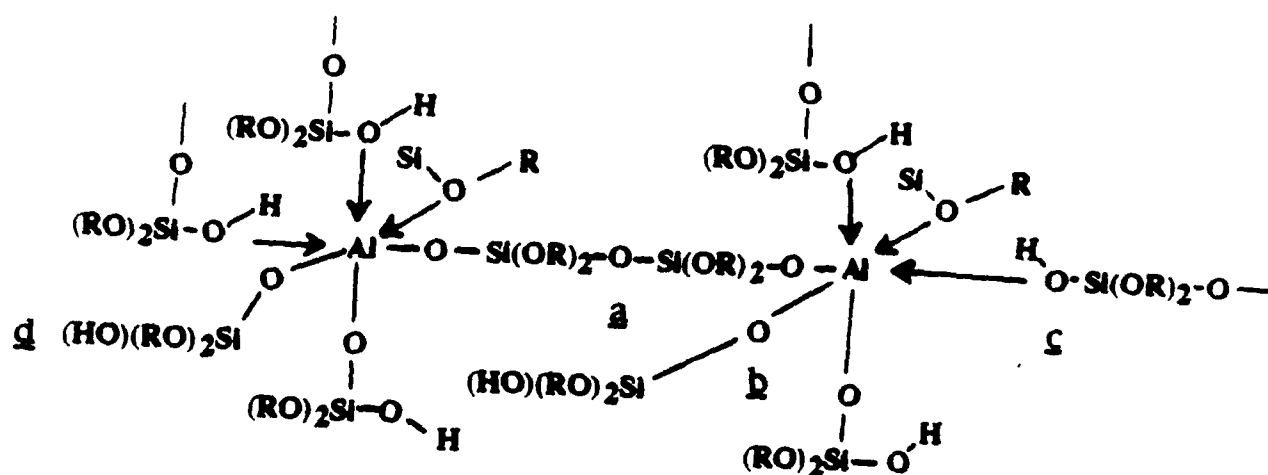


Figure 21

High Water to Silicate Ratios

Water in 2nd Step= $4.0-1.2=2.8$

