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# Infrared Spectra of Aluminum Salt Solutions

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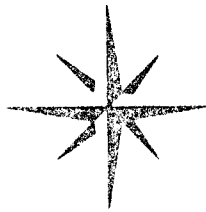
Department of Chemistry  
The American University  
Washington, D.C. 20016

By:  
J.F. McIntyre, R.T. Foley and B.F. Brown  
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| Aluminum salt solution activate metallic aluminum surfaces at different rates. The objective of this investigation was to attempt to establish whether or not structural differences at the molecular level could account for the chemical reactivity. The infrared spectra of various concentrations of aluminum chloride, aluminum nitrate, aluminum perchlorate, and aluminum sulfate were measured. The spectra included several general features: |                       |                                                             |

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- (1) a broadening of the OH stretching band of water,
- (2) a splitting of the OH stretch of water into several absorption bands,
- (3) the emergence of a new absorption band at  $2400\text{ cm}^{-1}$  (related to dimer formation),
- (4) occasional splitting of the OH bending mode of water.
- (5) no direct evidence of anion-cation covalent bonding.

In general, there was no differences at the molecular level between these aluminum salt solutions that would account for differences in chemical reactivity.

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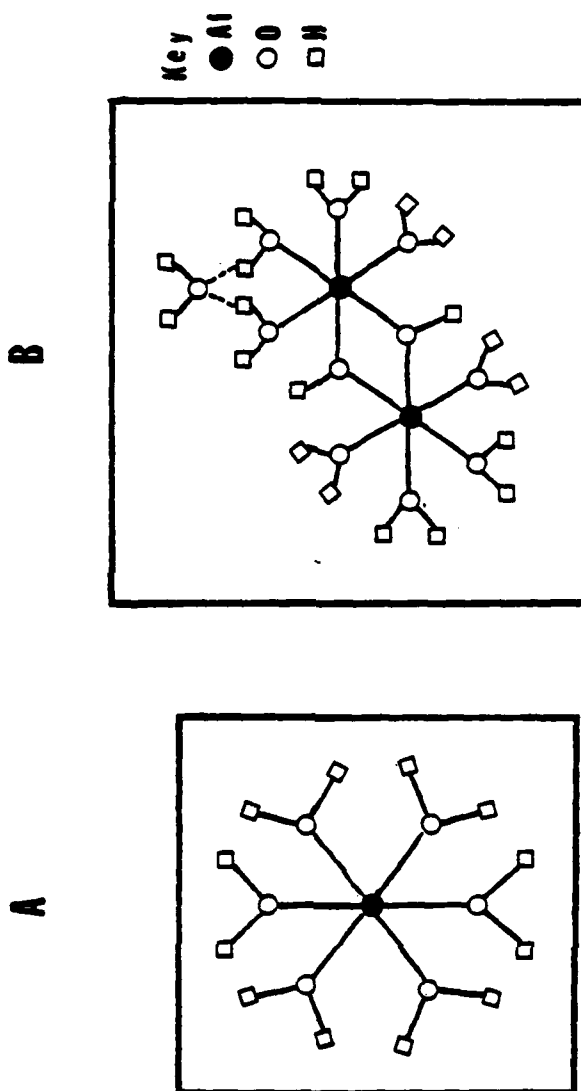
## INFRARED SPECTRA OF ALUMINUM SALT SOLUTIONS

J.F. McIntyre, R.T. Foley and B.F. Brown  
Department of Chemistry  
The American University  
Washington, D.C. 20016

Aluminum salt solutions activate metallic aluminum surfaces at drastically different rates (1). Solutions of aluminum nitrate, iodide, bromide, and chloride react rapidly—aluminum sulfate at a low rate. All of these salts hydrolyze in aqueous solution such that 0.2M solutions have pH's in the range of 2.5 to 3.5. It has been shown that the pH of the solution, per se, is not the determining factor in the activity of the aluminum salt solution (1).

The objective of this investigation was to attempt to establish whether or not structural differences at the molecular level could account for the chemical reactivity. This would involve assessing the effect of the anion on the structure of the aqueous aluminum salt solution.

The composition of hydrolyzed aluminum solutions has been studied extensively. These studies have been reviewed by Baes and Mesmer (2). Smith (3) characterizes the form of aluminum as  $Al^a$ ,  $Al^b$ , and  $Al^c$ , the form predominating dependent on the pH.  $Al^a$  consists of monomeric species such as  $Al^{+++}$ ,  $Al(OH)^{++}$ ,  $Al(OH)_2^+$ , and  $Al(OH)_4^-$ .  $Al^b$  is a polynuclear compound containing 20-100 aluminum atoms.  $Al^c$  are large  $Al(OH)_3$  particles. The solutions of interest here have pH's in the range of 1.1 to 3.6. From what has been reported in the literature and confirmed by an analysis of the hydrolysis reaction the species  $Al(H_2O)_6^{+++}$ ,  $Al(H_2O)_5OH^{++}$ ,  $Al(H_2O)_4(OH)_2^+$ , and perhaps the dimer,  $Al_2(OH)_2(H_2O)_8^{+4}$ , would be expected in these solutions. The existence of these species would in turn suggest the structures schematically given in figure 1.



**A** SCHEMATIC STRUCTURE OF  $\text{Al}(\text{H}_2\text{O})_6^{3+}$   
**B** SCHEMATIC STRUCTURE OF  $\text{Al}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$

FIGURE 1 (from Fripiat<sup>5</sup>)

Infrared spectroscopy has been successfully used to clarify the structure of aluminum salt solutions. Riesgraf and May (4) used a Fourier transform spectrometer to examine solutions of aluminum chloride and aluminum hydroxide chloride solutions. Fripiat, et al. (5) used the attenuated total reflectance technique to measure absorptions due to  $\text{AlBr}_3$ ,  $\text{AlCl}_3$ , and  $\text{Al}(\text{NO}_3)_3$ . Both of these investigations were concerned with solutions of higher pH which would lead to the formation of polymers. The present investigation was limited to solutions of low pH with the corresponding structures.

#### EXPERIMENTAL

The aqueous aluminum salt solutions in this investigation were prepared with reagent grade materials. The solutions of four salts were examined: aluminum chloride, aluminum perchlorate, aluminum nitrate, and aluminum sulfate. These four salts are highly soluble. A concentrated stock solution was prepared and less concentrated solutions were made by successive dilutions. The concentration of the stock solution was determined by performing an EDTA analytical titration, as described by Welcher (6).

Perkin-Elmer double-beam spectrophotometers model number 727 and 397 were used. Special IR cells manufactured by the Eastman Kodak Company, IR-TRAN-2 cells, were used to hold the samples. The cells are transparent between 4000 and  $750\text{ cm}^{-1}$  and show a strong absorption at  $650\text{ cm}^{-1}$ . A thin-film was prepared by placing one to five drops of sample (one drop is equivalent to  $2.5\text{ }\mu\text{l}$ ) between two IR-TRAN-2 cells and pressing the cells together.

Three scans were generally run for each salt: The first scan contained just the aluminum salt sample with no reference; the second scan required an  $\text{H}_2\text{O}$  reference; and the final scan used a sodium salt reference. The strong absorption bands of water (see figure 2) were partially compensated for by using a reference solution. The reference solution was prepared by placing one to three drops more than the number of drops used for the aluminum salt sample. A partial elimination is seen in the OH stretching region,  $3900\text{--}3200\text{ cm}^{-1}$ ; i.e., about 100% transmittance is observed. The OH bending absorption of water was usually eliminated at  $1650\text{ cm}^{-1}$ ; however, occasionally it appeared with less intensity than found in the noncompensated spectrum of the aluminum salt solution. This can be eliminated if the scan is stopped at approximately  $2000\text{ cm}^{-1}$  and additional reference solution added. Presumably the absence of absorption in these areas is due to non-interacting  $\text{H}_2\text{O}$  molecules; that is, absorption can be attributed to the bulk solvent. Absorptions located adjacent to the eliminated absorption bands are assigned to aluminum-water interactions, such as Al-O-H stretching or Al-OH-Al bending.

## RESULTS

### Aluminum Chloride Solutions

The spectra of solutions 0.1107M, 0.27M, and 1.107M in  $\text{AlCl}_3$  were taken with an  $\text{H}_2\text{O}$  reference and NaCl solution references. The absorption bands for these solutions are tabulated in Table I.

Although the spectra of these aluminum salt solutions are dominated by the absorption bands of water, a partial compensation was made by using either a water or a sodium salt reference. Inspection of figure 3,

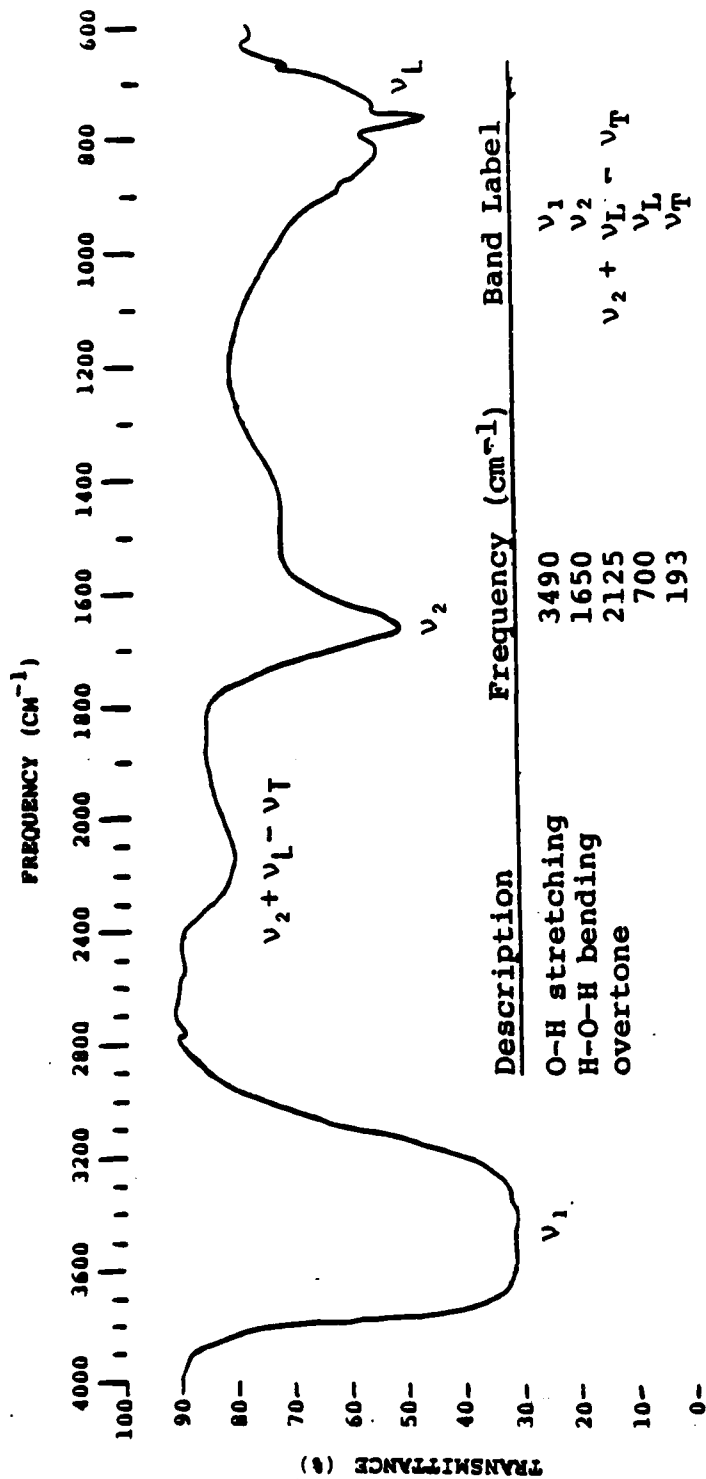


FIGURE 2  
IR SPECTRUM OF WATER

TABLE I  
AlCl<sub>3</sub> ABSORPTION

| EXPERIMENT | CONCENTRATION       | REFERENCE        | DESCRIPTION | FREQUENCY<br>(CM <sup>-1</sup> ) | ASSIGNMENT                                                                                                                                                                                        |
|------------|---------------------|------------------|-------------|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 5A         | 0.1107 M<br>pH=3.15 | H <sub>2</sub> O | SB          | 3550                             | Al-OH-Al stret.<br>mixed with OH<br>stret. of H <sub>2</sub> O.                                                                                                                                   |
|            |                     |                  | S           | 3325                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 3220                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 2650                             | H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O                                                                                                                                  |
|            |                     |                  | WB          | 2150                             |                                                                                                                                                                                                   |
|            |                     |                  | S           | 1650                             |                                                                                                                                                                                                   |
| 5B         | 0.1107 M            | H <sub>2</sub> O | M           | 820                              |                                                                                                                                                                                                   |
|            |                     |                  | S           | 3220                             | Al-OH-Al stretching<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O                                                                                  |
|            |                     |                  | W           | 2400                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 2100                             |                                                                                                                                                                                                   |
| 5C         | 0.1107 M            | H <sub>2</sub> O | S           | 1650                             |                                                                                                                                                                                                   |
|            |                     |                  | WB          | 820                              |                                                                                                                                                                                                   |
|            |                     |                  | WB          | 2900                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>H <sub>2</sub> O overtone band                                                          |
|            |                     |                  | MB          | 2500                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 2050                             |                                                                                                                                                                                                   |
|            |                     |                  | WB          | 1450                             | Al-O-H or Al-OH-Al<br>deformation.                                                                                                                                                                |
|            |                     |                  | WB          | 1200                             |                                                                                                                                                                                                   |
|            |                     |                  | WB          | 1000                             |                                                                                                                                                                                                   |
| 6          | 0.277 M<br>pH=2.80  | H <sub>2</sub> O | WB          | 2900                             | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O |
|            |                     |                  | S           | 3500                             |                                                                                                                                                                                                   |
|            |                     |                  | S           | 3125                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 2525                             | Al-O-H or Al-OH-Al<br>deformation                                                                                                                                                                 |
|            |                     |                  | W           | 2100                             |                                                                                                                                                                                                   |
|            |                     |                  | S           | 1650                             |                                                                                                                                                                                                   |
| 7          | 0.277 M             | H <sub>2</sub> O | S           | 820                              |                                                                                                                                                                                                   |
|            |                     |                  | M           | 2900                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.                                                                                                                                                |
|            |                     |                  | W           | 2300                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 1780                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 1525                             | Al-O-H or Al-OH-Al<br>deformation                                                                                                                                                                 |
| 8          | 1.107 M<br>pH=1.95  | NaCl             | M           | 940                              |                                                                                                                                                                                                   |
|            |                     |                  | S           | 2950                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.                                                                                            |
|            |                     |                  | W           | 2550                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 1710                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 1600                             | Al-O-H or Al-OH-Al<br>deformation                                                                                                                                                                 |
|            |                     |                  | M           | 950                              |                                                                                                                                                                                                   |
| 9A         | 1.107 M             | H <sub>2</sub> O | S           | 3000                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.                                                                                            |
|            |                     |                  | M           | 2550                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 2400                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 1980                             | Al-O-Al unsym. stret.                                                                                                                                                                             |
|            |                     |                  | W           | 1720                             |                                                                                                                                                                                                   |
|            |                     |                  | M           | 1600                             |                                                                                                                                                                                                   |
| 9B         | 1.107 M             | H <sub>2</sub> O | M           | 810                              |                                                                                                                                                                                                   |
|            |                     |                  | S           | 3050                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.                                                                                            |
|            |                     |                  | W           | 2550                             |                                                                                                                                                                                                   |
|            |                     |                  | W           | 2400                             |                                                                                                                                                                                                   |
|            |                     |                  | S           | 1650                             | Al-O-Al unsym. stret.<br>OH bending of H <sub>2</sub> O                                                                                                                                           |
|            |                     |                  | M           | 810                              |                                                                                                                                                                                                   |

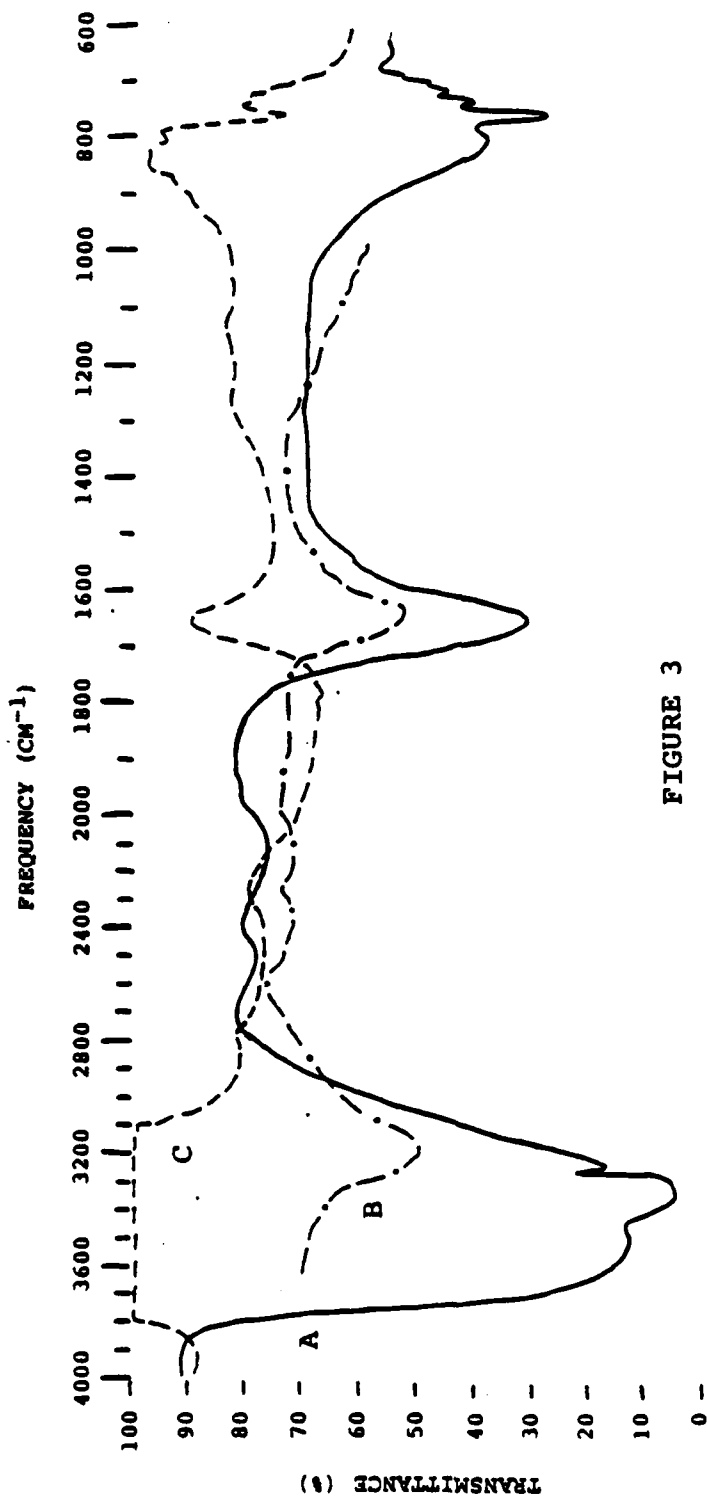


FIGURE 3  
IR SPECTRA OF 0.1107M AlCl<sub>3</sub>

- H<sub>2</sub>O REFERENCE  
A- 2.5μl sample  
- 3.75μl reference  
B- 2.5μl sample  
- 6.75μl reference  
C- 2.5μl sample  
- 10.0μl reference

the absorption spectra of 0.1107M  $\text{AlCl}_3$ , will show that the strong absorption bands of water found at  $3800\text{--}3100\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  in curve A are absent in curve C when recorded with an  $\text{H}_2\text{O}$  reference. Inspection of curve A will reveal that several types of OH stretching are found in the  $3800\text{--}3100\text{ cm}^{-1}$  range. These absorption bands are found at  $3550$ ,  $3325$ , and  $3220\text{ cm}^{-1}$ . Curve B shows an enlargement of the absorption at  $3220\text{ cm}^{-1}$ . The absorption at  $3550\text{ cm}^{-1}$  is more likely due to the OH stretching of the bulk water. The absorption at  $3325\text{ cm}^{-1}$  can be attributed to the OH stretching of water coordinated to aluminum in polymeric species, and the lower frequency absorption may be a result of OH stretching in hydrogen bonded water. Inspection of curve C shows the three types of stretching proposed by Fripiat, et al. (5) discussed below.

The present work shows a band between  $1950\text{--}1800\text{ cm}^{-1}$ . This band has been interpreted by Riesgraf and May (4) as an artifact of the combination band of water at  $2100\text{ cm}^{-1}$  when a water reference is used. However, a band in this region is sometimes found when the  $2100\text{ cm}^{-1}$  band is present; this usually appears near  $1840\text{ cm}^{-1}$ . A band is not always observed in this region which suggests that it may very well be a result of the water compensation process.

An absorption band found at  $2400\text{ cm}^{-1}$  appears consistently in all of the aluminum salt solution spectra; however, this absorption band is not documented in the literature. Initial interpretation attempted to assign this absorption to a combination band; however, the observed absorptions do not add or subtract in a manner which gives rise to this band at  $2400\text{ cm}^{-1}$ . Present assignment is attributed to Al-O-Al unsymmetrical stretching. This assignment is supported by the fact that  $\text{Al}_2\text{O}_3$  in the solid form and

saturated solutions show absorption at  $2400\text{ cm}^{-1}$  (see figure 4). This band is observed in solutions of  $1.107\text{M AlCl}_3$  at a pH of 1.85. When the pH of a solution  $0.213\text{M}$  in  $\text{AlCl}_3$  is lowered to a pH of 0.8 with  $\text{HCl}$ , the band is not observed. For this reason the appearance of this band has been used as a test for dimers in solution.

The absorption spectrum of  $0.277\text{M AlCl}_3$  (experiment 7) reveals an interesting feature near the eliminated  $1650\text{ cm}^{-1}$  absorption band of water. This spectrum gives absorptions at  $1780$  and  $1525\text{ cm}^{-1}$ , the absorption near  $1780\text{ cm}^{-1}$  is probably due to the combination band of water at  $2100\text{ cm}^{-1}$ ; however, there is no explanation for the band found at  $1525\text{ cm}^{-1}$ . This lower frequency absorption may be a result of OH bending in water coordinated to aluminum, which, because of the strong absorption of water at  $1650\text{ cm}^{-1}$ , is not likely to be seen. The  $\text{Al-O-H}$  and  $\text{Al-OH-Al}$  deformation at  $940\text{ cm}^{-1}$  is also present in this spectrum.

The unsymmetrical and symmetrical stretch of OH coordinated to aluminum is strongly evident in spectra produced by a solution  $1.107\text{M}$  in  $\text{AlCl}_3$  and compensated with a  $3.0\text{M NaCl}$  reference (see figure 5). These absorptions are found at  $3000$  and  $2550\text{ cm}^{-1}$ . Again, there is a splitting of the water absorption band at  $1650\text{ cm}^{-1}$ ; absorptions are found at  $1710$  and  $1600\text{ cm}^{-1}$ . Figure 6, the spectra of  $1.107\text{M AlCl}_3$ , also reveals the major absorptions of aluminum salt solutions; however, a new band emerges at  $2400\text{ cm}^{-1}$  which is presently attributed to the unsymmetrical stretch of  $\text{Al-O-Al}$ .

#### Aluminum Nitrate Solutions

The spectra of aluminum nitrate solutions,  $0.116\text{M}$ ,  $0.290\text{M}$ , and  $1.159\text{M}$ , were recorded and the significant absorptions are given in Table II. All

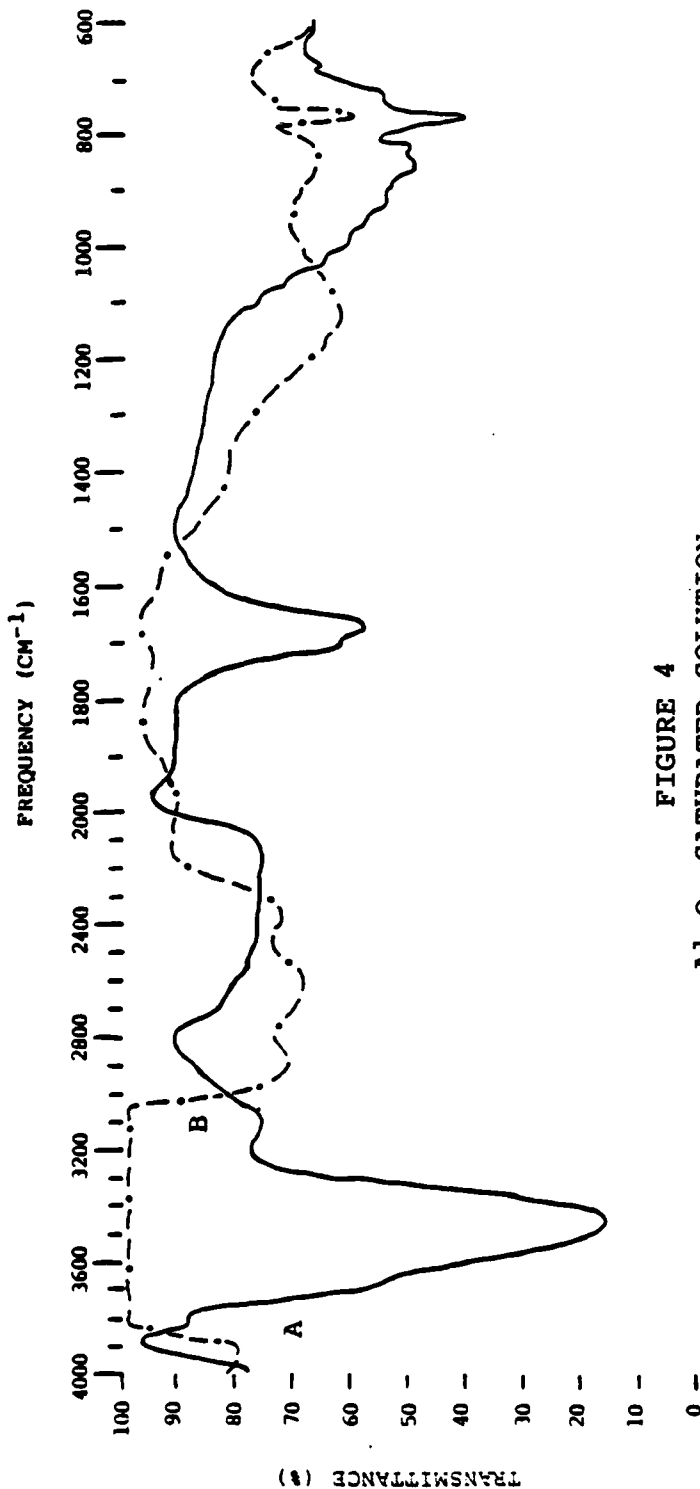


FIGURE 4  
 $\text{Al}_2\text{O}_3$  SATURATED SOLUTION  
 $\text{H}_2\text{O}$  REFERENCE  
 A- 3.12 $\mu\text{l}$  sample  
   - 8.75 $\mu\text{l}$  reference  
 B- 5.0 $\mu\text{l}$  sample  
   - 10.0 $\mu\text{l}$  reference

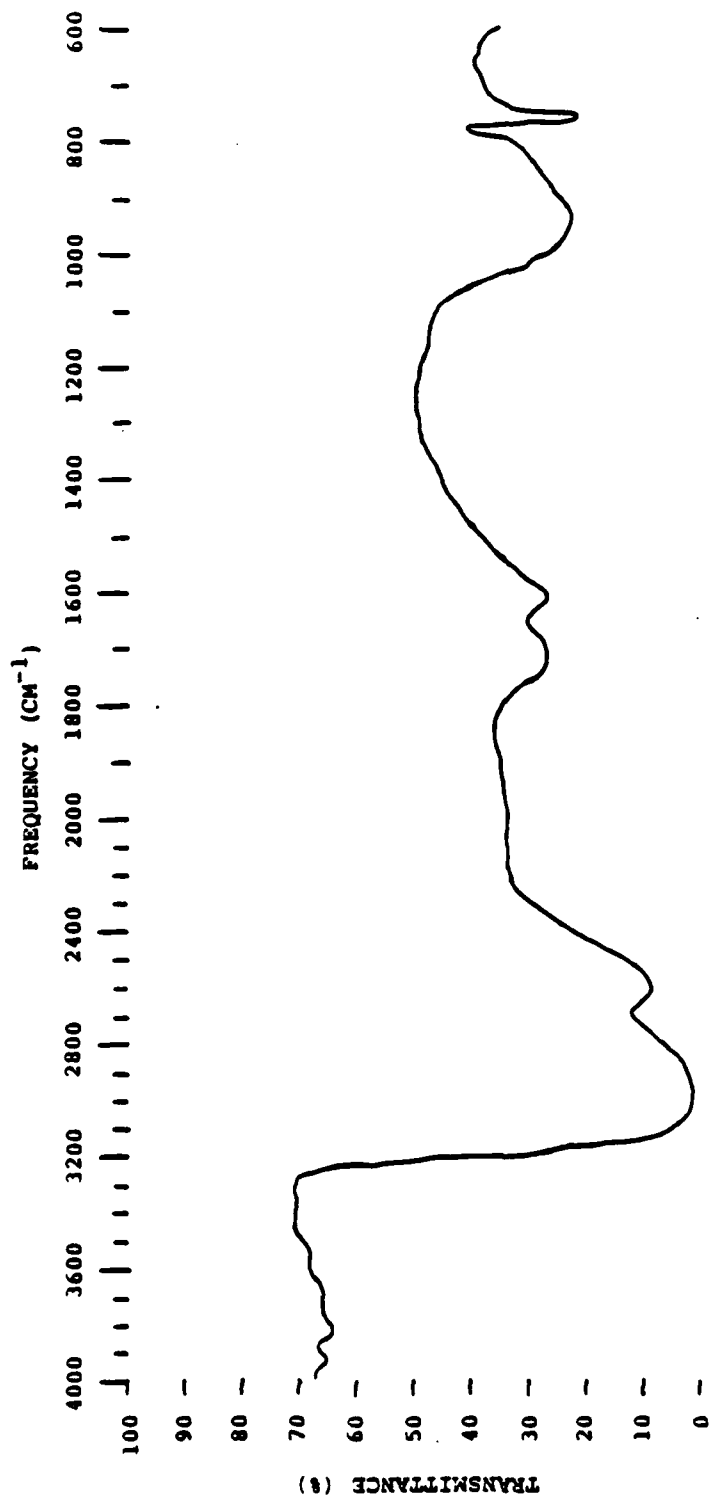


FIGURE 5  
IR SPECTRUM OF 1.107M AlCl<sub>3</sub>  
3.0M NaCl REFERENCE  
- 5.0μl sample  
- 7.5μl reference

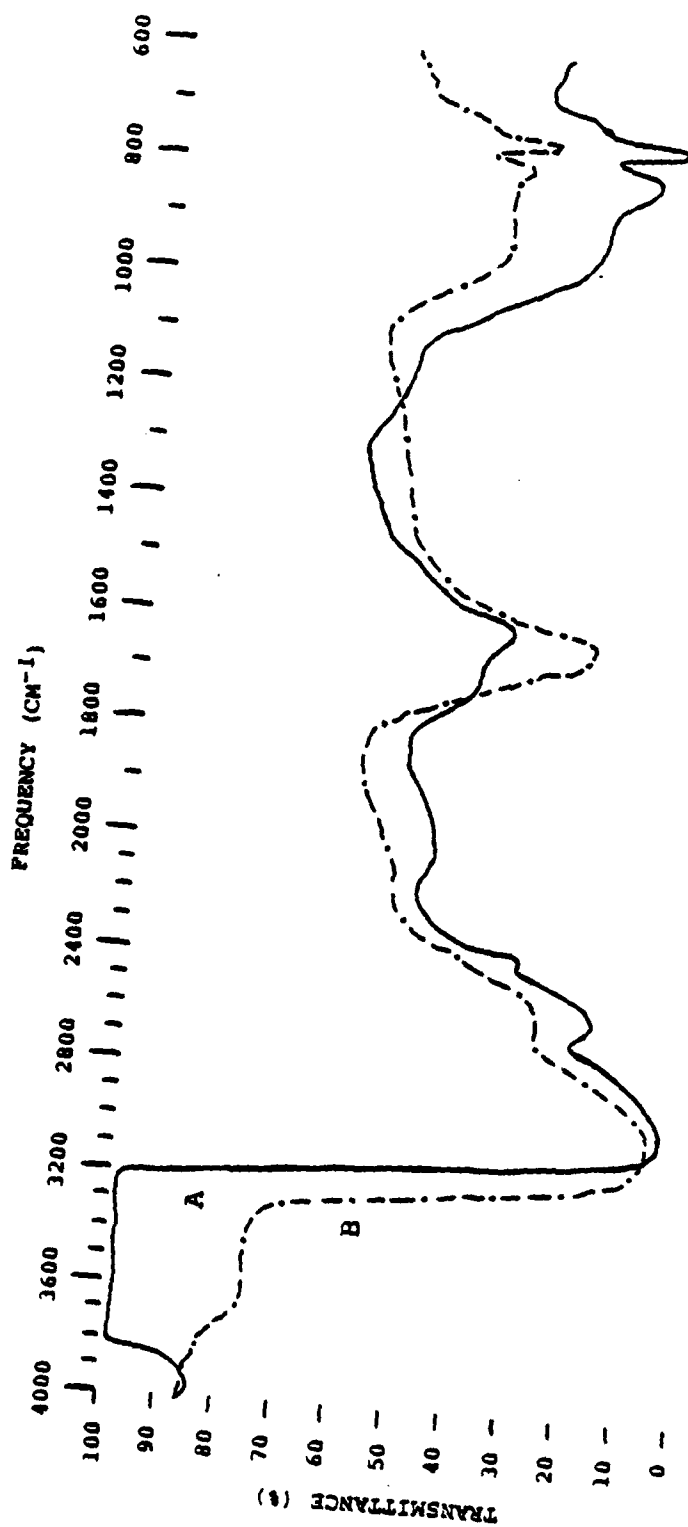


FIGURE 6  
IR SPECTRA OF 1.107M AlCl3  
H<sub>2</sub>O REFERENCE  
A- 5.0 $\mu$ l sample  
- 8.75 $\mu$ l reference  
B- 5.0 $\mu$ l sample  
- 12.5 $\mu$ l reference

TABLE II  
Al(NO<sub>3</sub>)<sub>3</sub> ABSORPTION

| EXPERIMENT | CONCENTRATION      | REFERENCE                   | DESCRIPTION | FREQUENCY (CM <sup>-1</sup> ) | ASSIGNMENT                                      |
|------------|--------------------|-----------------------------|-------------|-------------------------------|-------------------------------------------------|
| 14         | 0.116 M<br>pH=3.0  | 0.30 M<br>NaNO <sub>3</sub> | W           | 2900                          | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | M           | 2500                          | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | M           | 2000                          | H <sub>2</sub> O overtone band                  |
|            |                    |                             | M           | 1480                          |                                                 |
|            |                    |                             | W           | 1000                          | Al-O-H or Al-OH-Al deformation                  |
| 11         | 0.290 M<br>pH=2.60 | H <sub>2</sub> O            | MB          | 3500                          | Al-OH-Al stretching                             |
|            |                    |                             | S           | 3150                          | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | W           | 2400                          | Al-O-Al unsym. stret.                           |
|            |                    |                             | W           | 2075                          | H <sub>2</sub> O overtone band                  |
|            |                    |                             | W           | 1860                          |                                                 |
|            |                    |                             | S           | 1650                          | OH bending of H <sub>2</sub> O                  |
|            |                    |                             | S           | 1375                          | NO <sub>3</sub> <sup>-</sup>                    |
|            |                    |                             | W           | 1260                          |                                                 |
| 12         | 1.159 M<br>pH~1.70 | H <sub>2</sub> O            | SB          | 3050                          | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | W           | 2550                          | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | W           | 2400                          | Al-O-Al unsym. stret.                           |
|            |                    |                             | M           | 1890                          |                                                 |
|            |                    |                             | MB          | 1550                          |                                                 |
|            |                    |                             | W           | 1330                          | NO <sub>3</sub> <sup>-</sup>                    |
|            |                    |                             | M           | 960                           | Al-O-H or Al-OH-Al deformation                  |
|            |                    |                             |             |                               |                                                 |
| 13A        | 1.159 M            | H <sub>2</sub> O            | SB          | 3300                          | Al-OH-Al stretching                             |
|            |                    |                             | M           | 2570                          | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | W           | 2400                          | Al-O-Al unsym. stret.                           |
|            |                    |                             | S           | 1650                          | OH bending of H <sub>2</sub> O                  |
|            |                    |                             | W           | 1425                          |                                                 |
|            |                    |                             | MB          | 1360                          | NO <sub>3</sub> <sup>-</sup>                    |
|            |                    |                             | S           | 940                           | Al-O-H or Al-OH-Al deformation                  |
|            |                    |                             | M           | 820                           |                                                 |
| 13B        | 1.159 M            | 3.0 M<br>NaNO <sub>3</sub>  | S           | 3000                          | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | M           | 2550                          | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | W           | 2400                          | Al-O-Al unsym. stret.                           |
|            |                    |                             | MB          | 1820                          |                                                 |
|            |                    |                             | MB          | 1510                          |                                                 |
|            |                    |                             | M           | 1320                          | NO <sub>3</sub> <sup>-</sup>                    |
|            |                    |                             | S           | 950                           | Al-OH-Al deformation                            |

spectra give absorptions at approximately  $3000$  and  $2550\text{ cm}^{-1}$ , which are attributed to the unsymmetrical and symmetrical stretch of OH in water coordinated to aluminum. In the more highly concentrated solutions the newly assigned Al-O-Al unsymmetrical stretch at  $2400\text{ cm}^{-1}$ , and the splitting of the OH bending band of water at  $1650\text{ cm}^{-1}$ , is evident.

Most of the spectra in this study were recorded with an  $\text{H}_2\text{O}$  reference, but several experiments in the aluminum nitrate series used a  $\text{NaNO}_3$  solution reference. Figure 7 is typical. Close inspection will reveal that in addition to the eliminated water absorption bands, the principal  $\text{NO}_3^-$  absorption band at  $1370\text{ cm}^{-1}$  was also eliminated. As a result of using a  $\text{NaNO}_3$  reference, two new bands are found adjacent to the missing  $\text{NO}_3^-$  band. These newly observable bands are probably a result of the reference compensation process and not the emergence of new  $\text{NO}_3^-$  absorption bands; i.e.,  $\text{NO}_3^-$  complexed with aluminum or water. This conclusion is supported by the fact that no additional bands appear near the  $1370\text{ cm}^{-1}$  band in the spectra using a water reference. A covalently bound nitrate ion results in absorption at about  $1500$  and  $1275\text{ cm}^{-1}$ , the appearance of new bands different from the independently absorbing ion at  $1370\text{ cm}^{-1}$  (7).

#### Aluminum Perchlorate Solutions

Aluminum perchlorate solutions,  $0.110\text{M}$ ,  $0.285\text{M}$ , and  $1.140\text{M}$  in concentration, were studied with an  $\text{H}_2\text{O}$  reference and also with the corresponding  $\text{NaClO}_4$  solution reference. The significant features of these spectra are recorded in Table III. The frequency of the unsymmetrical stretch of OH in water coordinated to aluminum is shifted to lower frequencies in most cases (see figure 8). This observed frequency shift does not appear to be a function of concentration nor the nature of the reference solution. In

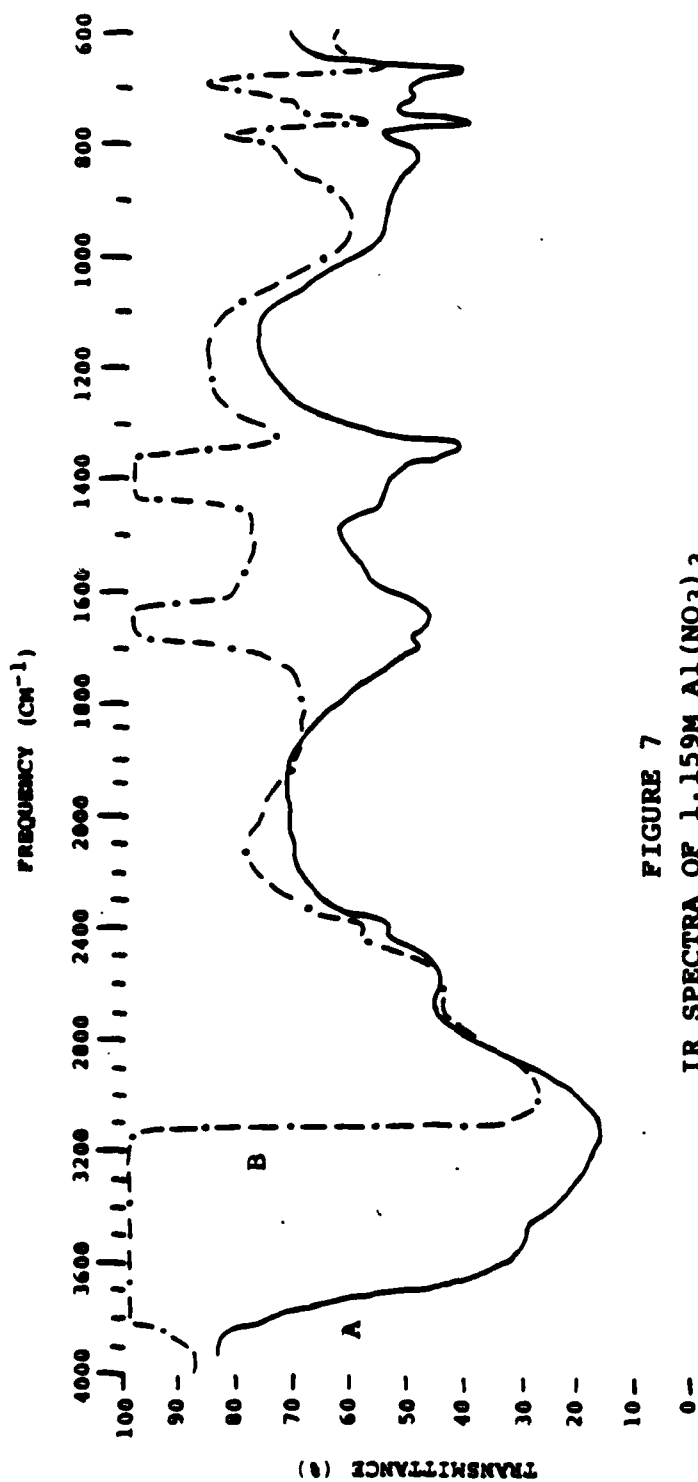


FIGURE 7

TABLE III  
Al(ClO<sub>4</sub>)<sub>3</sub> ABSORPTION

| EXPERIMENT | CONCENTRATION      | REFERENCE        | DESCRIPTION | FREQUENCY (CM <sup>-1</sup> ) | ASSIGNMENT                                                                                                                                                                                                                                                                                       |
|------------|--------------------|------------------|-------------|-------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 15A        | 0.295 M<br>pH=2.95 | H <sub>2</sub> O | M           | 2800                          | sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>ClO <sub>4</sub> <sup>-</sup>                                                                                                                                                                                       |
|            |                    |                  | M           | 2600                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2350                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | MB          | 1820                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | M           | 1120                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 820                           |                                                                                                                                                                                                                                                                                                  |
| 15B        | 0.285 M            | H <sub>2</sub> O | S           | 2950                          | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup>                                                             |
|            |                    |                  | W           | 2550                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2390                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2050                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 1650                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 1110                          |                                                                                                                                                                                                                                                                                                  |
| 16A        | 1.140 M<br>pH=1.15 | H <sub>2</sub> O | M           | 820                           | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>ClO <sub>4</sub> <sup>-</sup><br>Al-O-H or Al-OH-Al<br>deformation                                                                                                              |
|            |                    |                  | S           | 2920                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2650                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2420                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2060                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | MB          | 1840                          |                                                                                                                                                                                                                                                                                                  |
| 16B        | 1.140 M            | H <sub>2</sub> O | S           | 1120                          | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup><br>Al-O-H or Al-OH-Al<br>deformation |
|            |                    |                  | MB          | 940                           |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 3500                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 3025                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2600                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2400                          |                                                                                                                                                                                                                                                                                                  |
| 17         | 0.111 M<br>pH=3.10 | H <sub>2</sub> O | W           | 2050                          | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup>                                      |
|            |                    |                  | W           | 1650                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 1120                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | S           | 940                           |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 820                           |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | M           | 3550                          |                                                                                                                                                                                                                                                                                                  |
| 18A        | 0.285 M<br>pH=2.85 | H <sub>2</sub> O | M           | 3340                          | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup>                                      |
|            |                    |                  | M           | 3140                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | M           | 2900                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2600                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2400                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2000                          |                                                                                                                                                                                                                                                                                                  |
| 18A        | 0.285 M<br>pH=2.85 | H <sub>2</sub> O | W           | 1820                          | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup>                                      |
|            |                    |                  | S           | 1650                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | M           | 1110                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 920                           |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2900                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2610                          |                                                                                                                                                                                                                                                                                                  |
| 18A        | 0.285 M<br>pH=2.85 | H <sub>2</sub> O | W           | 1900                          | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>H <sub>2</sub> O overtone band<br>OH bending of H <sub>2</sub> O<br>ClO <sub>4</sub> <sup>-</sup>                                      |
|            |                    |                  | S           | 1120                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 820                           |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2900                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 2610                          |                                                                                                                                                                                                                                                                                                  |
|            |                    |                  | W           | 1900                          |                                                                                                                                                                                                                                                                                                  |

TABLE III (continued)

| EXPERIMENT | CONCENTRATION      | REFERENCE                   | DESCRIPTION | FREQUENCY<br>(CM <sup>-1</sup> ) | ASSIGNMENT                                      |
|------------|--------------------|-----------------------------|-------------|----------------------------------|-------------------------------------------------|
| 18B        | 0.285 M<br>pH=2.85 | H <sub>2</sub> O            | M           | 2910                             | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | W           | 2600                             | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | W           | 2400                             | Al-O-Al unsym. stret.                           |
|            |                    |                             | W           | 1900                             |                                                 |
|            |                    |                             | S           | 1650                             | OH bending of H <sub>2</sub> O                  |
|            |                    |                             | S           | 1100                             | ClO <sub>4</sub> <sup>-</sup>                   |
| 19         | 1.140 M<br>pH~1.15 | 3.0 M<br>NaClO <sub>4</sub> | M           | 810                              |                                                 |
|            |                    |                             | S           | 3050                             | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | W           | 2580                             | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | W           | 2410                             | Al-O-Al unsym. stret.                           |
|            |                    |                             | W           | 2000                             | H <sub>2</sub> O overtone band                  |
|            |                    |                             | W           | 1730                             |                                                 |
| 20A        | 1.140 M            | H <sub>2</sub> O            | W           | 1600                             |                                                 |
|            |                    |                             | W           | 1210                             |                                                 |
|            |                    |                             | M           | 940                              | Al-O-H or Al-OH-Al deformation                  |
|            |                    |                             | S           | 2800                             | sym. stret. of H <sub>2</sub> O coord. to Al.   |
|            |                    |                             | M           | 2580                             | Al-O-Al unsym. stret.                           |
|            |                    |                             | W           | 2380                             |                                                 |
| 20B        | 1.140 M            | H <sub>2</sub> O            | M           | 1980                             |                                                 |
|            |                    |                             | WB          | 1710                             |                                                 |
|            |                    |                             | M           | 1600                             |                                                 |
|            |                    |                             | SB          | 1000                             | Al-O-H or Al-OH-Al deformation                  |
|            |                    |                             | SB          | 3600                             | unsym. stret. of H <sub>2</sub> O coord. to Al. |
|            |                    |                             | S           | 3100                             | sym. stret. of H <sub>2</sub> O coord. to Al.   |
| 20B        | 1.140 M            | H <sub>2</sub> O            | M           | 2580                             | Al-O-Al unsym. stret.                           |
|            |                    |                             | W           | 2400                             | H <sub>2</sub> O overtone band                  |
|            |                    |                             | W           | 2050                             | OH bending of H <sub>2</sub> O                  |
|            |                    |                             | S           | 1650                             | ClO <sub>4</sub> <sup>-</sup>                   |
|            |                    |                             | S           | 1100                             |                                                 |
|            |                    |                             | W           | 940                              | Al-O-H or Al-OH-Al deformation                  |
| 20B        | 1.140 M            | H <sub>2</sub> O            | S           | 820                              |                                                 |
|            |                    |                             | S           | 820                              |                                                 |

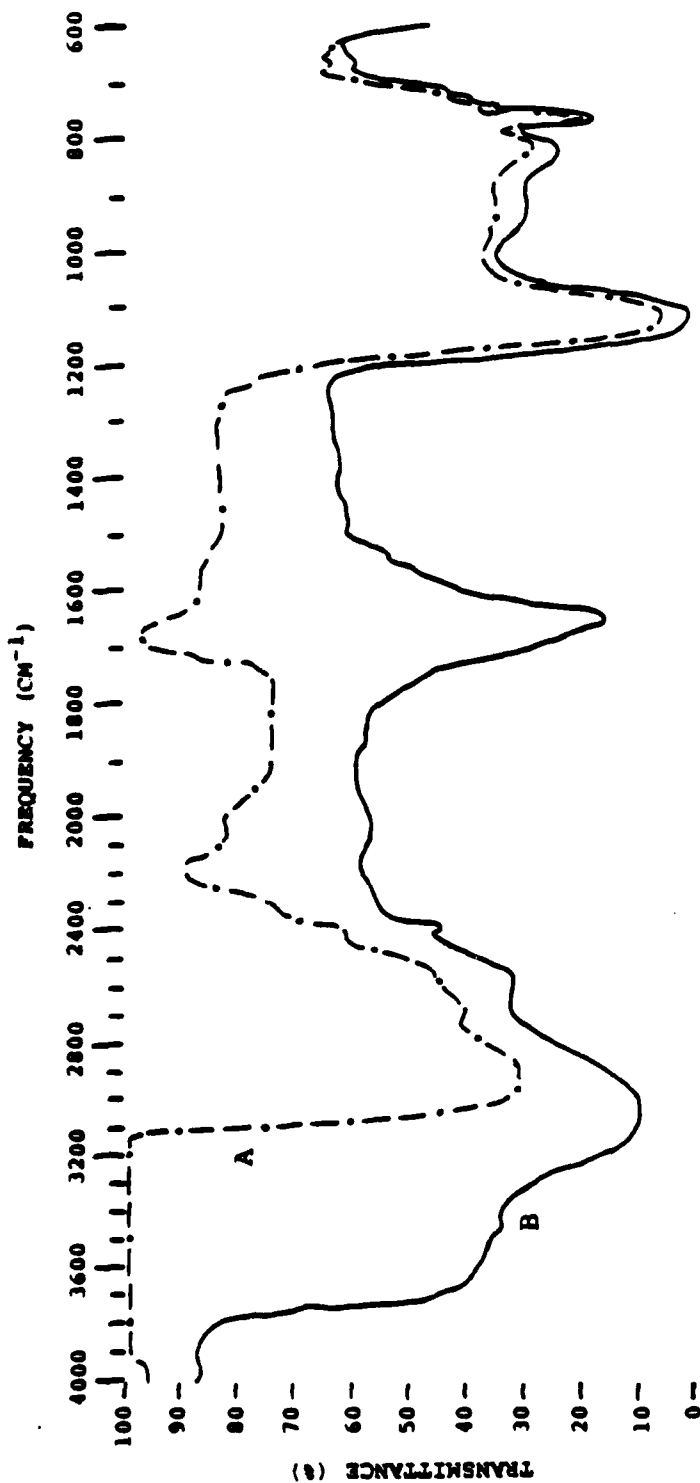


FIGURE 8  
IR SPECTRA OF 1.140M  $\text{Al}(\text{ClO}_4)_3$   
H<sub>2</sub>O REFERENCE

some cases, as in experiments 16B, 19, and 20B, the frequency is shifted to slightly higher values. This may or may not be a function of anion-cation interaction; however, the absence of additional absorption bands near the  $\text{ClO}_4^-$  band,  $1120\text{ cm}^{-1}$ , suggests that  $\text{ClO}_4^-$  is not significantly coordinating with aluminum.

The symmetrical stretch of OH in water coordinated to aluminum is found in the  $2550\text{--}2600\text{ cm}^{-1}$  range. Again, there is little evidence for anion-cation interaction. The absorption band found at  $2400\text{ cm}^{-1}$  is present in most of the spectra. The Al-O-H or Al-OH-Al deformation band is present in most of the spectra between  $940$  and  $1000\text{ cm}^{-1}$ . A close inspection of figure 9 will reveal that the  $\text{ClO}_4^-$  absorption is eliminated at  $1120\text{ cm}^{-1}$  and a strong Al-O-H or Al-OH-Al absorption band is observable.

Experiment 17 shows a definite splitting of the OH stretching band of water between  $3800\text{--}3000\text{ cm}^{-1}$ . Three distinct absorption bands are present at  $3550$ ,  $3340$ , and  $3140\text{ cm}^{-1}$ . The higher frequency band is due to the OH stretch in water and the two lower frequencies are most likely a result of Al-OH-Al stretching in polymeric species.

Experiments 19 and 20 revealed a splitting of the OH bending band as previously observed in aluminum nitrate and chloride solutions.

#### Aluminum Sulfate Solutions

The absorptions in the spectra from aluminum sulfate solutions  $0.036\text{M}$ ,  $0.125\text{M}$ , and  $1.110\text{M}$  are tabulated in Table IV. These spectra are quite similar to the absorptions found in aluminum chloride, nitrate, and perchlorate solutions. The unsymmetrical and symmetrical stretches of OH in water coordinated to aluminum are found at the usual frequencies. The band located at  $2400\text{ cm}^{-1}$  is present and the difficulty in observing the deformation band near  $940\text{ cm}^{-1}$  is also apparent.

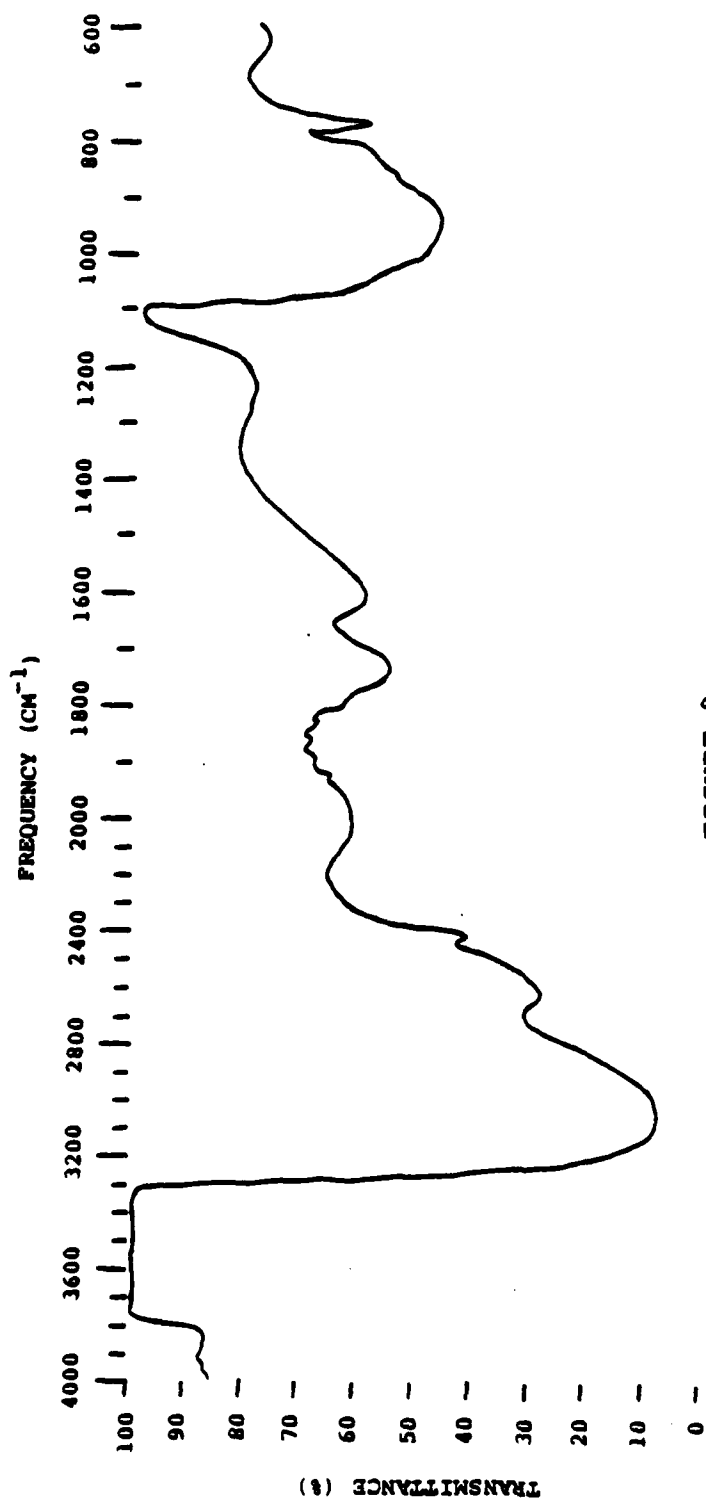


FIGURE 9  
IR SPECTRUM OF 1.140M  $\text{Al}(\text{ClO}_4)_3$   
3.0M  $\text{NaClO}_4$  REFERENCE  
- 6.25μl sample  
- 6.25μl reference

TABLE IV  
Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ABSORPTION

| EXPERIMENT | CONCENTRATION      | REFERENCE        | DESCRIPTION    | FREQUENCY<br>(CM <sup>-1</sup> ) | ASSIGNMENT                                                                                                                                                                                                                                                     |
|------------|--------------------|------------------|----------------|----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 21A        | 0.125 M<br>pH=3.30 | H <sub>2</sub> O | M              | 2850                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>SO <sub>4</sub> <sup>2-</sup>                                                                                               |
|            |                    |                  | M              | 2600                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 2425                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 1800                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1120                             |                                                                                                                                                                                                                                                                |
| 21B        | 0.125 M            | H <sub>2</sub> O | M              | 2950                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>OH bending of H <sub>2</sub> O<br>SO <sub>4</sub> <sup>2-</sup>                                                                                                                                          |
|            |                    |                  | W              | 2625                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 1650                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1110                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 820                              |                                                                                                                                                                                                                                                                |
| 21C        | 0.125 M            | H <sub>2</sub> O | SB             | 3250                             | Al-OH-Al stretching<br>Al-O-Al unsym. stret.<br>OH bending of H <sub>2</sub> O<br>SO <sub>4</sub> <sup>2-</sup>                                                                                                                                                |
|            |                    |                  | W              | 2400                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 1650                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1120                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 820                              |                                                                                                                                                                                                                                                                |
| 22A        | 1.110 M<br>pH=2.20 | H <sub>2</sub> O | MB             | 3550                             | Al-OH-Al stretching<br>unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>OH bending of H <sub>2</sub> O<br>SO <sub>4</sub> <sup>2-</sup><br>Al-O-H or Al-OH-Al<br>deformation |
|            |                    |                  | S              | 3000                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 2550                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W <sub>s</sub> | 2400                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W <sub>s</sub> | 1540                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1650                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1100                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 980                              |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 820                              |                                                                                                                                                                                                                                                                |
| 22B        | 1.110 M            | H <sub>2</sub> O | S              | 3000                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-Al unsym. stret.<br>OH bending of H <sub>2</sub> O<br>SO <sub>4</sub> <sup>2-</sup><br>Al-O-H or Al-OH-Al<br>deformation                        |
|            |                    |                  | W              | 2550                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 2400                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1650                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1100                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | W              | 980                              |                                                                                                                                                                                                                                                                |
| 22C        | 1.110 M            | H <sub>2</sub> O | MB             | 1580                             | appears as a shoulder<br>on curve A.                                                                                                                                                                                                                           |
| 23         | 0.036 M<br>pH=3.60 | H <sub>2</sub> O | W              | 2900                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>Al-O-H or Al-OH-Al<br>deformation                                                                                                                    |
|            |                    |                  | M              | 2550                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 1820                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 1520                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | WB             | 1000                             |                                                                                                                                                                                                                                                                |
| 24         | 0.125 M            | H <sub>2</sub> O | W              | 2850                             | unsym. stret. of<br>H <sub>2</sub> O coord. to Al.<br>sym. stret. of H <sub>2</sub> O<br>coord. to Al.<br>OH bending of H <sub>2</sub> O<br>SO <sub>4</sub> <sup>2-</sup>                                                                                      |
|            |                    |                  | W              | 2500                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1650                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | S              | 1120                             |                                                                                                                                                                                                                                                                |
|            |                    |                  | M              | 830                              |                                                                                                                                                                                                                                                                |

Inspection of figure 10 reveals an interesting feature: The OH bending band at  $1650\text{ cm}^{-1}$  is split and a new band emerges at  $1580\text{ cm}^{-1}$ . This band at  $1580\text{ cm}^{-1}$  is also found in the spectra of aluminum chloride, nitrate, and perchlorate and appears distinctly in curve C of figure 9. This scan was started at  $1710\text{ cm}^{-1}$  and completed at  $1200\text{ cm}^{-1}$ , an excess of  $\text{H}_2\text{O}$  reference is added prior to this scan. The absorption at  $1580\text{ cm}^{-1}$  appears as a shoulder in curves A and B, but shows up as a definite absorption in curve C. This may be a result of OH bending in water coordinated to aluminum as previously assigned.

#### DISCUSSION OF RESULTS

The absorption spectra of aluminum salt solutions include several general features:

- (1) A broadening of the OH stretching band of water.
- (2) A splitting of the OH stretch of water into several absorption bands.
- (3) The emergence of a new absorption band at  $2400\text{ cm}^{-1}$ .
- (4) Occasional splitting of the OH bending mode of water.
- (5) No direct evidence of anion-cation interactions.

The ability to eliminate portions of the water absorption spectrum proved to be quite valuable, particularly in the OH stretching region of water. The observed splitting in this region is a direct result of various types of OH present in the aluminum solutions; i.e.,  $\text{H}_2\text{O}$  coordinated to aluminum, OH stretching in polymeric species.

The occasional splitting of the OH bending mode of water is presently attributed to OH bending in water coordinated to aluminum, especially at

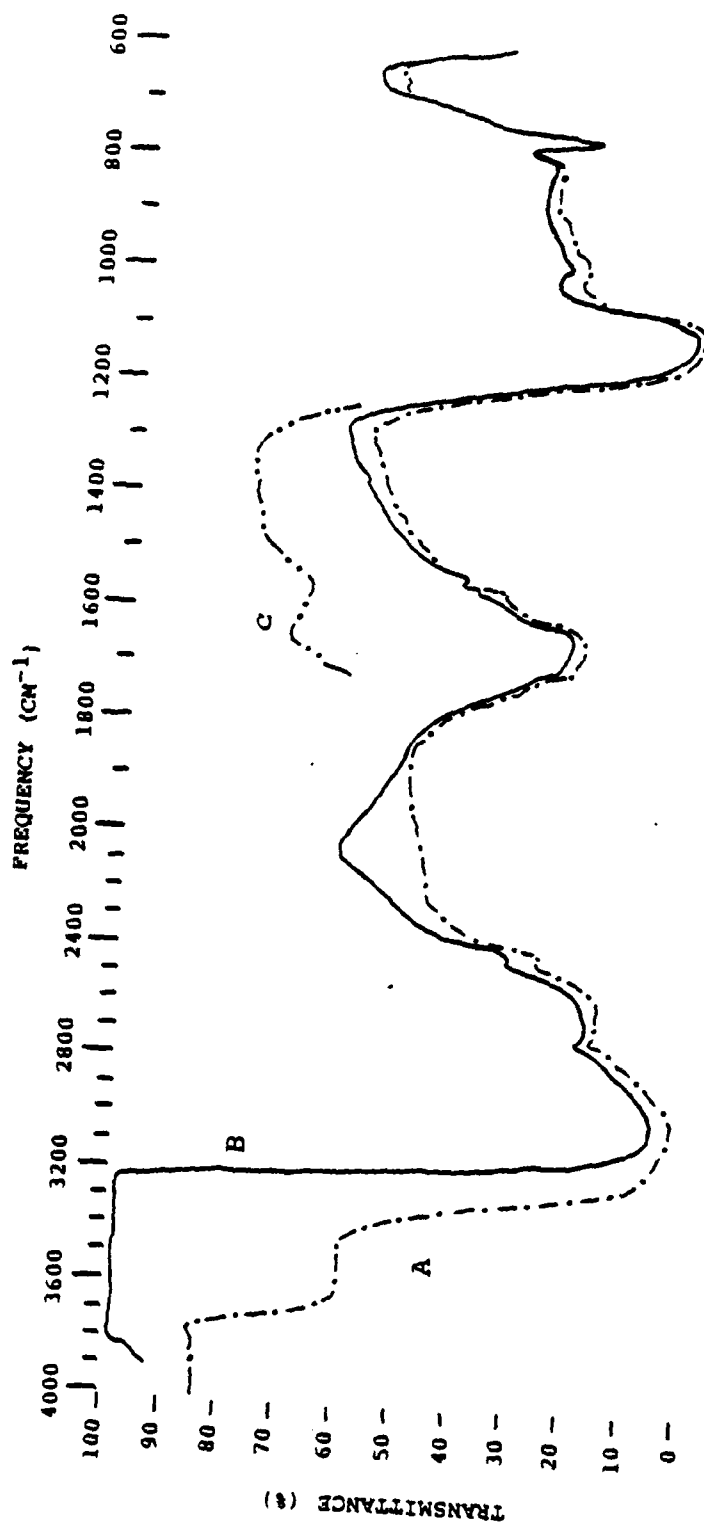


FIGURE 10  
IR SPECTRA OF 1.110M  $\text{Al}_2(\text{SO}_4)_3$   
H<sub>2</sub>O REFERENCE  
A- 1.87 $\mu\text{l}$  sample  
- 10.0 $\mu\text{l}$  reference  
B- 1.87 $\mu\text{l}$  sample  
- 12.5 $\mu\text{l}$  reference  
C- 1.25 $\mu\text{l}$  sample  
- >12.5 $\mu\text{l}$  reference

1580  $\text{cm}^{-1}$ . This interpretation for the moment is tentative and further investigation is needed.

Analysis of the absorption spectra for each aluminum salt indicates that little difference is observed between the individual salts. Thus, it may be concluded that anion effects are seemingly absent in the observed spectra. It is well known that at low pH values the aluminum salts are completely dissociated. The possibility of long-lived complexes existing in aqueous solutions where  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ , and  $\text{Cl}^-$  are covalently coordinated to aluminum is not likely. When these anions are covalently coordinated to a metal a lowering of the anion's symmetry occurs and the appearance of additional absorption bands is observed (7). The infrared spectra of aluminum nitrate and perchlorate reveal that the major absorption bands of water are eliminated and the unsymmetrical and symmetrical OH stretch of water coordinated to aluminum can be seen at 2900 and 2500  $\text{cm}^{-1}$ . In addition, a weak absorption is found at 1000  $\text{cm}^{-1}$  which is a result of Al-O-H or Al-OH-Al deformation. The absorption of OH stretching in water coordinated to aluminum can be readily seen in several spectra at 3100 and 2500  $\text{cm}^{-1}$ .

While the experimental evidence would not support the proposition that covalently-bonded Al anion complexes exist, the existence of ion pairing or triple ions is not ruled out, in fact, other lines of experimental evidence would indicate that the anions are associated in some fashion with aluminum ions.

These aluminum salt solutions have relatively low pH's. The literature indicates that the predominant structures should be monomeric species such as  $\text{Al}^{+++}$  and  $\text{AlOH}^{++}$ . Several of the bands suggest the existence of such

species as  $\text{Al}_2(\text{OH})_2^{+2}$ , or structures that would include Al-O-Al or Al-OH-Al, stretchings. Further, these are indicated at pH's lower than one would expect from literature studies, e.g., at about pH of 1.4. Depending on the concentration of the four salts, bands at 3100-3200, 3000, 2500, 2400, 1950-1800, and  $960\text{ cm}^{-1}$  were observed. These are in general agreement with the results of Riesgraff and May (4) who observed almost similar bands and gave the assignments listed in Table V.

Fripiat, et al. (5) observed absorptions at 3480, 2965, and  $2530\text{ cm}^{-1}$  for aluminum bromide, nitrate, and chloride solutions. Their assignments are as follows: The band at  $3480\text{ cm}^{-1}$  is assigned to the stretch of OH bound to two aluminum atoms, the  $2965\text{ cm}^{-1}$  band is attributed to the stretch of OH in water coordinated to aluminum, and the lower frequency band,  $2530\text{ cm}^{-1}$ , is assigned to the OH stretch of water in the second coordination sphere.

It is significant that in both studies the band at  $3400\text{ cm}^{-1}$  is considered to signify the existence of the structure Al-O-Al, which would be a test for the dimer.



### CONCLUSION

These spectra do provide information on the structure of these aluminum salt solutions which will be of value in the interpretation of results on their chemical reactivity. The evidence for the formation of dimers at relatively low pH's was not expected.

There was no unique feature in any of the four salt solutions. This is surprising because complexes such as  $\text{AlSO}_4^+$  are considered to involve the displacement of inner sphere coordinated water (8).

TABLE V \*  
Spectrum of 40%  $\text{AlCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}$

| STRUCTURE AND TYPE OF ABSORPTION                                | FREQUENCY ( $\text{cm}^{-1}$ ) |
|-----------------------------------------------------------------|--------------------------------|
| stretch of OH bound to aluminum                                 | 3400                           |
| antisymmetric stretch of OH                                     | 3000                           |
| in $\text{H}_2\text{O}$ bound to aluminum                       |                                |
| symmetric stretch of OH in                                      | 2550                           |
| $\text{H}_2\text{O}$ bound to aluminum                          |                                |
| deformation of Al-O-H in $\text{Al}(\text{H}_2\text{O})_6^{3+}$ | 970                            |
| Unassigned (possibly artifact of the                            | 1950                           |
| subtraction due to $2110 \text{ cm}^{-1}$ band of               |                                |
| water).                                                         |                                |
| unassigned (possibly vibration in                               | 600                            |
| $\text{Al}_2(\text{H}_2\text{O})_6^{3+}$ )                      |                                |

\* (from Riesgraf and May<sup>4</sup>)

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#### REFERENCES

1. K. Sotoudeh, T.H. Nguyen, R.T. Foley and B.F. Brown, CORROSION, in press.
2. C.F. Baes and R.E. Mesmer, "The Hydrolysis of Cations," John Wiley & Sons, New York (1976).
3. R.W. Smith, "The State of Al(III) in Aqueous Solution and Adsorption of Hydrolysis Products on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>," Dissertation, Stanford University, June 1969.
4. D.A. Riesgraf and M.L. May, Applied Spectroscopy, 32(4), 362 (1978).
5. J.J. Fripiat, F. Van Cauwelaert and H. Bosmans, J. Phys. Chem., 69(7), 2458 (1965).
6. F.J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, Van Nostand, Princeton, NJ (1958).
7. J.R. Ferraro, "Interpretation of the Infrared Spectra of Inorganic Molecules," presented at the Infrared Spectroscopy Institute, Canisius College, Buffalo, NY (August 1961).
8. J. Miceli and J. Stuehr, J. Am. Chem. Soc., 90, 6967 (1968).