# FORM OF ALUMINUM(III) IN DILUTE AQUEOUS SOLUTION

## FORM OF ALUMINUM(III) IN

## DILUTE AQUEOUS SOLUTION

By

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## ABSTRACT

Using a potentiometric method on  $10^{-4}$ M and  $10^{-5}$ M Al(NO<sub>3</sub>)<sub>3</sub> solutions at constant ionic strength (0.1 M KNO<sub>3</sub>) and temperature (25°C), titration curves were defined and examined with respect to three variables (total aluminum concentration, pH range, and time) in order to assess the reversibility of the aqueous system.

Increasing pH titration interval decreased reversibility while increasing time interval led to a slight increase in reversibility. Decreasing the total aluminum concentration also slightly improved reversibility. Overall, the reversibility of the system was observed to be poor.

Computer models were compared to experimental titration data in order to derive the speciation schemes which best fit the data. Polynuclear hydrolysis schemes fit the data best for the concentration levels as follows:

A1<sup>3+</sup>, A1(OH)<sub>4</sub>, and A1<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup> for  $10^{-5}$  M A1<sub>t</sub>. A1<sup>3+</sup>, A1(OH)<sub>4</sub>, and A1<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> and/or A1<sub>13</sub>(OH)<sub>32</sub><sup>7+</sup> for  $10^{-4}$  M A1<sub>t</sub>.

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#### CHAPTER 1

#### INTRODUCTION

## 1.1 INTRODUCTION

Most crustal rocks are composed of aluminosilicate minerals and quartz. Through natural weathering processes, cations such as Ca, Na, K, and Mg can be released from these minerals into the environment. In the past, aluminum has been considered retained in the solid phase at near neutral pHs, but at pHs  $\leq$  5 aluminum may be mobilized and may be toxic to organisms (Doudoroff and Katz 1953, Jones 1961, Sorenson <u>et al</u>. 1974, Schofield 1976, Burrows 1977, Baker and Schofield 1980, Driscoll et al. 1980).

An increase in precipitation acidity is linked to increased levels of gaseous forms of sulfur and nitrogen oxides which are chemically converted to strong acids in the atmosphere, then dissolve in rain or snow and fall to the earth. These atmospheric pollutants can represent an abnormal addition of acid to the landscape relative to carbonic acid and probably are inducing changes in the normal chemical weathering pattern.

The acid rain phenomenon has been reported to cause the appearance of high aluminum concentrations in low order streams in the northeastern U.S.A. (Johnson 1979, Driscoll 1980) and in Scandinavia (Gjessing et al. 1976).

The natural neutralization process can be viewed in two steps. In the first step, strong acids (hydrogen ion acidity) in precipitation are rapidly, but incompletely, neutralized by dissolution of a reactive metal oxide phase in the soil zone. The solution resulting from this process is enriched in dissolved aluminum which is itself a protolyte able to neutralize  $OH^-$  or  $H^+$ , depending upon the pH. (In other words, the original hydrogen ion acidity is converted to a mixture of hydrogen ion and aluminum acidity). In the second step, this new acidity is slowly neutralized by silicate mineral chemical weathering products (basic cations) such as calcium and sodium. Thus "the rate at which acid precipitation and secondary aluminum acidity is neutralized is ultimately set by the rate at which silicate minerals are decomposed under ambient conditions" (Johnson et al. 1981).

Details of aluminum hydrolysis are important in the dissolution of aluminosilicates, adsorption, and toxicity because hydrolysis is one of the most important aqueous phase reactions of aquo-aluminum.

#### 1.2 CHEMISTRY

Aluminum, element number 13 in the periodic table, is found in group IIIA along with Boron, Gallium, Indium, and Thallium. Aluminum has a molecular weight of 26.9815 g, an ionic radius of 0.5 Å, a valence of 3+, and is most commonly found in six fold coordination (occasionally in four fold coordination). Aluminum has one stable isotope ( $^{27}$ Al), and one natural radioisotope ( $^{26}$ Al) with a half-life of 7.4 x 10<sup>-5</sup> years.

Dissolved aluminum in groundwater, lakes, and rivers ranges in concentration from < 1 to about 400  $\mu$ g/L. In the oceans, there is less than 5  $\mu$ g/L of dissolved aluminum.

Solid aluminum chemistry (with respect to hydrolysis) is essentially aluminum hydroxide chemistry. Aluminum hydroxide has three polymorphs, namely gibbsite, bayerite, and nordstandite. There are also two amorphous oxyhydroxides of aluminum, diaspore ( $\alpha$ -A100H) and boehmite ( $\gamma$ -A100H). Aluminum is readily amphoteric, tends to polymerize, and forms complexes with other substances present in water (organics, fluoride, sulfate, and phosphate).

The form and concentration of aluminum in water is mostly dependent upon pH, the nature of substances in the receiving waters (including organics), and to a lesser degree, on the temperature and time duration of exposure to the water.

The knowledge of aluminum hydrolysis is in a state of flux. Presently, the Al<sup>3+</sup> aquo ion is the predominant ion when the pH is less than 3, and the Al(OH)<sub>4</sub> species predominates above pH 7. But between

pH 3 and 7 there are differing opinions on the hydrolysis forms.

The first hydrolysis product,  $A10H^{2+}$ , is well documented (Brønsted and Volqvartz 1928, Schofield and Taylor 1954, Kubota 1956, Frink and Peech 1962, Hem and Roberson 1967) although the pK<sub>1</sub>s (first hydrolysis constants) vary by about one order of magnitude (4.89, 4.98, 5.27, 5.02, and 4.75 respectively). The agreement worsens for other monomeric hydrolysis products.

To date there are several theories concerning aluminum hydrolysis. Several authors, Schofield and Taylor (1954), Frink and Peech (1963), Hem and Roberson (1967), and Marion <u>et al</u>. (1976) for example, propose a monomeric pathway, whereas Sillén (1959), Matijević <u>et al</u>. (1961), Patterson and Tyree (1973), and Hayden and Rubin (1974) propose that a polynuclear pathway would agree more with their data interpretation. However, there is not much agreement on any one polymeric scheme specifying the stoichiometry and stability complexes for the polynuclear complexes. The two most prominent schemes of postulated predominant polynuclear species stoichiometries are:

> 1.  $Al_6(OH)_{15}^{3+}$  and  $Al_{13}(OH)_{32}^{7+}$ 2.  $Al_8(OH)_{20}^{4+}$ .

Thus aluminum speciation studies have led to a major disagreement regarding the condition of the hydrolyzed aluminum. This controversy has arisen through the problems of slow kinetics and polymerization (for example, Turner 1976), the question of attainment of equilibrium, and to a lack of detailed knowledge on solubility controls.

#### 1.3 PURPOSE-SCOPE-CONDITIONS

This study deals with the aqueous chemistry of aluminum hydrolysis. Many studies in the past have investigated aluminum hydrolysis and speciation by considering equilibration between and in aqueous and solid phases simultaneously. But introduction of a solid phase complicates the system by introducing, for example, solid-liquid interfaces, surface reactions, and solid-liquid equilibrium. It would be better to consider aluminum solution chemistry alone before adding a solid phase. Thus, in this study on aluminum hydrolysis, only the aqueous phase will be considered.

The purpose of this study is to assess the reversibility of the aqueous aluminum system using potentiometric titration. The results of this investigation would be applied to environmental problems. Therefore the study was designed with natural environmental conditions in mind. All potentiometric experiments are run at room temperature extending over the pH range of natural waters (3 to 8). Low aluminum concentrations  $(10^{-4} - 10^{-6}M)$  are used and experiments are carried out in constant ionic medium (0.1 M KNO<sub>3</sub>). Aluminum nitrate is used to prepare the aluminum solutions. The nitrate ion is not known to react with aluminum in aqueous or solid form, thus all reactions occuring in the solutions can be ascribed to aluminum hydrolysis.

Several variables, namely time effects, pH range, and aluminum concentration, are assessed with respect to their effect on the reversibility of aluminum hydrolysis. Blank titrations, carried out in 0.1 M KNO<sub>3</sub> solution, are used for calibration and quality control.

5.

#### CHAPTER 2

#### ALUMINUM SOLUTE COMPLEXES

### 2.1 STRUCTURE

At pH levels below 3 the dissolved aluminum ion is sheathed by an octahedral shell of six strongly bound water molecules (Fig. 2-1 A), although the hydrating  $OH_2$  groups are not normally shown in formula representations. As the pH of a solution containing aluminum ions is raised, individual water molecules in the hydration shell become deprotonated. This occurs in a stepwise fashion, the first of the steps being illustrated in Figure 2-1 B. The radius of  $OH^-$ , being similar to that of the water molecule, does not greatly change the shape of the octahedron (the OH-Al bond is only slightly shorter than the other bonds). The first monomeric hydrolysis species,  $Al(OH)(H_2O)_5^{2+}$ , has been widely reported.

Monomeric ions formed by the deprotonation process have been shown to have a strong tendency to polymerize through double OH<sup>-</sup> bond formation (Fig. 2-1 C) into larger species:

(a) Deprotonation

$$A1(H_20)_6^{3+} = A10H(0H_2)_5^{2+} + H^+$$

(b) Polymerization (Dimerization)

2 AlOH(OH<sub>2</sub>) $_{5}^{2+}$  = Al<sub>2</sub>(OH)<sub>2</sub>(OH<sub>2</sub>) $_{8}^{4+}$  + 2 H<sub>2</sub>O





Figure 2-1: Schematic representations of:

С

(A)  $Al(H_2O)_6^{3+}$  - aluminum sheathed by six hydrating water molecules in an octahedral shell. (B)  $Al(OH)(H_2O)_5^{2+}$  result of the first deprotonation step of aquo-aluminum. (C)  $Al_2(OH)_2(H_2O)_8^{4+}$  - formed through polymerization or double OH<sup>-</sup> bridge formation between mononuclear ions. The fundamental structural unit of the polymers in solutions where the pH is lower than the pH at the isoelectric point (point of zero charge) is the six-coordinated aluminum ion centered in an octahedral arrangement of water molecules or hydroxyl ions giving a general formula of  $Al(H_20)_6^{3+}$  or  $Al(0H)_6^{3-}$  (being the extremes) as shown in Figure 2-2A. Two types of hydroxyl ions are present in the polymer. The first type, called structural OH<sup>-</sup>, are hydroxyl ions present in double bridges which link the aluminum ions together (Fig. 2-2B). The second type, called nonstructural OH<sup>-</sup>, are hydroxyl ions held in the polynuclear complexes by a single bond to an aluminum ion (Fig. 2-2B).

In the first step of polymerization, double OH<sup>-</sup> bridges form between adjacent aluminum ions thus forming a dimeric complex (Fig. 2-1C and equation b) represented by  $Al_2(OH)_2(OH_2)_8^{4+}$ . The formation of more hydroxyl bridges leads to larger structural units. Bridge formation is increased by increasing aluminum concentration and OH- availability, but is a slow process at 25°C.

Although four fold coordination is possible (as in substitution for silicon) aluminum is most commonly found in six fold coordination. When aluminum is in six fold coordination (octahedral units) the polymerization patterns are restricted. Each aluminum ion is only allowed to participate in one double OH bridge in the same plane (Fig. 2-3A). Polymer chains (straight and/or branched) can form by the joining of dimers through deprotonation and dehydration: (c)  $2 \operatorname{Al}_2(\operatorname{OH}_2)_8^{4+} - 2 \operatorname{H}^+ = \operatorname{Al}_4(\operatorname{OH}_6(\operatorname{OH}_2)_{12}^{6+} + 2 \operatorname{H}_20$ . The shape of the chain (branched or straight) is dependent upon the





Figure 2-2: Schematic representations of:

(A) Aquo-aluminum  $A1(H_2O)_6^{3+}$  and its deprotonated counterpart  $A1(OH)_6^{3-}$ , structural units of polymers. (B) A dimer illustrating the location of structural (S) and nonstructural (N) hydroxyl groups.





Figure 2-3: Schematic representation illustrating:

(A) Polymerization restrictions - each aluminum ion is only allowed to participate in one double OH bridge in the same plane. (B) Ring polymer resulting from such restrictions.

location of the double OH<sup>-</sup> bridges (Fig 2-4A and B). As polymers increase in size (thus lengthening the chain) the mole ratio of structural OH<sup>-</sup> to Al approaches 2 (Fig. 2-5 curve A). Above the mole ratio of 2, double chains form (Fig. 2-5 curve B).

Ring structures are also formed by OH bridging between aluminum ions (6):

(d)  $Al_6(OH)_{10}(OH_2)_{16}^{8+} - 2 H^+ = Al_6(OH)_{12}(OH_2)_{12}^{6+} + H_20$ as shown in Figure 2-3B. These rings coalesce in various ways resulting in further deprotonation and dehydration and ultimately form a planar structure, with an OH/Al ratio between 2 and 3, referred to as a sheet polymer (Fig. 2-5 curve C). When the sheets are stacked, different mineral structures are formed such as gibbsite and other aluminum hydroxides which are less soluble, but kinetically much slower crystallizing than gibbsite (Kittrick 1969). Once polymerization has begun, it will continue until a stable configuration is reached, or until some other restraint stops the process. The six membered ring is apparently the most stable configuration built from six octahedra, yet there is no reason why the polymer should stop growing there (except maybe for the effects of other ions). When the OH/Al ratio reaches 3, the net charge approaches zero and coagulation starts. Here the first solid forms appear in solution.



Figure 2-4: Schematic representation illustrating:

(A) A branched polymer and (B) A straight polymer chain as determined by the locations of double OH bridges.



Figure 2-5: Calculated mole ratio (n) of structural OH to Al for the three structural patterns:

- A Chain
- B Double Chain
- C Sheet Polymer

From Hem (1968)

## 2.2 CATION HYDROLYSIS (EQUATIONS)

Cations hydrolyze in a manner which follows the general equations outlined in Table 2-1 where M refers to the metal ion and Z equals its valence. The aluminum ion  $(A1^{3+})$ , when obeying a mononuclear hydrolysis scheme would hydrolyze in a way which can be represented by the following steps:

1. By adding the protonated ligand HOH.

A. stepwise addition

$$A1^{3+} + H_{2}0 = A10H^{2+} + H^{+}$$

$$A10H^{2+} + H_{2}0 = A1(0H)_{2}^{+} + H^{+}$$

$$A1(0H)_{2}^{+} + H_{2}0 = A1(0H)_{3}^{+} + H^{+}$$

$$A1(0H)_{3}^{+} + H_{2}0 = A1(0H)_{4}^{-} + H^{+}$$

$$B. addition to a core$$

$$A1^{3+} + H_{2}0 = A10H^{2+} + H^{+}$$

$$A1^{3+} + 2H_{2}0 = A1(0H)_{2}^{+} + 2H^{+}$$

$$A1^{3+} + 3H_{2}0 = A1(0H)_{3}^{+} + 3H^{+}$$

$$A1^{3+} + 4H_{2}0 = A1(0H)_{4}^{-} + 4H^{+}$$

$$A1^{3+} + 4H_{2}0 = A1(0H)_{4}^{-} + 4H^{+}$$

2. By adding the ligand OH.

A. stepwise addition  

$$A1^{3+} + OH^{-} = A10H^{2+}$$
  
 $A10H^{2+} + OH^{-} = A1(OH)_{2}^{+}$   
 $A1(OH)_{2}^{+} + OH^{-} = A1(OH)_{3}^{\circ}$ 

$$A1(OH)_{3}^{\circ} + OH^{-} = A1(OH)_{4}^{-}$$
  
B. addition to a core  
 $A1^{3+} + OH^{-} = A1OH^{2+}$   
 $A1^{3+} + 2OH^{-} = A1(OH)_{2}^{+}$   
 $A1^{3+} + 3OH^{-} = A1(OH)_{3}^{-}$   
 $A1^{3+} + 4OH^{-} = A1(OH)_{4}^{-}$ 

If aluminum followed a polynuclear hydrolysis scheme, dimerization could be expressed as follows:

$$2A1^{3+} + 2H_2 0 = A1_2 (OH)_2^{4+} + 2H^+$$
  
where  ${}^*\beta_{2,2} = \frac{[A1_2 (OH)_2^{4+}][H^+]^2}{[A1^{3+}]^2}$ 

or

0

$$2A1^{3+} + 2OH^{-} = A1_{2}(OH)_{2}^{4+}$$
  
where  $\beta_{2,2} = \frac{[A1_{2}(OH)_{2}^{4+}]}{[A1^{3+}]^{2}[OH^{-}]^{2}}$ 

If more hydrated aluminum joined together through OH<sup>-</sup> bridging (transforming nonstructural OH<sup>-</sup> to structural OH<sup>-</sup>) along with the processes of deprotonation (removal of H<sup>+</sup> from hydrating H<sub>2</sub>O groups) and dehydration (removal of H<sub>2</sub>O groups), other polynuclear forms can be acquired. For example, trimerization:

$$3A1^{3+} + 4H_2^{0} = A1_3^{(OH)}_4^{5+} + 4H^+$$
  
r  $3A1^{3+} + 40H^- = A1_3^{(OH)}_4^{5+}$ 

or even higher polymerization:

 $8A1^{3+} + 20 H_2^0 = A1_8^{(OH)}_{20}^{4+} + 20 H^+$ or  $8A1^{3+} + 20 OH^- = A1_8^{(OH)}_{20}^{4+}$ 

As the polymers increase in size, the mole ratio of structural OH<sup>-</sup> to aluminum ( $\overline{n}$ ) increases. When  $\overline{n}$  reaches a value of 3, microcrystalline and/or amorphous mineral structures (gibbsite) have formed. Thereafter solubility must be taken into consideration.

If a metal hydroxide is considered to be formed by the simple combination of one metal and n hydroxides, then the solubility could be explained by mononuclear methods as in the general equations in Table 2-2. But both mononuclear and polynuclear species can be found, and both kinds must be considered to calculate true solubility (see Table 2-2). In the presence of a precipitate, the free metal ion ( $M^{z+}$  or  $Al^{3+}$  in this case) concentration can be determined by the solubility product  $K_{so}$ , thus equation 4 in Table 2-2 would apply in this calculation.

Hydrolysis leads to both mononuclear and polynuclear hydroxo complexes, yet it is known that the mononuclear species prevail beyond a certain dilution called the Mononuclear Wall. This artifact can be explained through the polymerization process's concentration dependence. For example: Dimerization

2 
$$\text{MOH}^{+} = \text{M}_{2}(\text{OH})_{2}^{2+}$$
  
 $M_{T} = [M^{2+}] + [MOH^{+}] + 2[M_{2}(\text{OH})_{2}^{2+}]$   
 $*K_{2,2} = \frac{[M_{2}(\text{OH})_{2}^{2+}]}{[MOH^{+}]^{2}} = \frac{[M_{2}(\text{OH})_{2}^{2+}]}{(M_{T} - [M^{2+}] - 2[M_{2}(\text{OH})_{2}^{2+}])^{2}}$   
It is shown that  $M_{2}(\text{OH})_{2}^{2+}$  is dependent upon  $M_{T}$ . Thus the fraction of

## MONONUCLEAR HYDROLYSIS

(a) Addition of protonated ligand HOH.

$$\xrightarrow{\text{HL}} \text{ML} \xrightarrow{\text{HL}} \text{ML}_{2} \cdot \cdot \xrightarrow{\text{HL}} \text{ML}_{x}$$

$$\xrightarrow{*\beta_{2}} \xrightarrow{*\beta_{x}} \xrightarrow{*$$

(b) Addition of ligand OH<sup>-</sup>.

$$\xrightarrow{L} ML \xrightarrow{L} ML_2 \cdots \xrightarrow{L} ML_x$$

$$\xrightarrow{\beta_2} \xrightarrow{\beta_x}$$

STEP ONE:

(a) 
$$M^{z+} + H_2 0 = MOH^{(z-1)+} + H^+$$
  
Where  $*K_1 = *\beta_{1,1} = \frac{[MOH^{(z-1)+}][H^+]}{[M^{z+}]}$ 

(b) 
$$M^{z+} + OH^{-} = MOH^{(z-1)+}$$
  
Where  $K_1 = \beta_{1,1} = \frac{[MOH^{(z-1)+}]}{[M^{z+}][OH^{-}]}$ 

STEP TWO:

(a) MOH<sup>(z-1)+</sup> + H<sub>2</sub>0 = M(OH)<sub>2</sub><sup>(z-2)+</sup> + H<sup>+</sup>  
Where \*K<sub>2</sub> = 
$$\frac{[M(OH)_2^{(z-2)+}][H^+]}{[MOH^{(z-1)+}]}$$

or

$$M^{z^{+}} + 2 H_{2}^{0} = M(OH)_{2}^{(z-2)^{+}} + 2H^{+}$$
  
Where  $*\beta_{2,1} = \frac{[M(OH)_{2}^{(z-2)^{+}}][H^{+}]^{2}}{[M^{z^{+}}]}$ 

Table 2-1 continued

(b)  $MOH^{(z-1)+} + OH^{-} = M(OH)_{2}^{(z-2)+}$ Where  $K_2 = \frac{[M(OH)_2^{(z-2)+}]}{[MOH^{(z-1)+}][OH^-]}$ or  $M^{z+} + 2 OH^{-} = M(OH)_{2}^{(z-2)+}_{(z-2)+}$ Where  $\beta_{2,1} = \frac{[M(OH)_2^{-(z-2)+}]}{[M^{z+}][OH^{-}]^2}$ STEP X: (a)  $M(OH)_{x-1}$  (z-(x-1))+ +  $H_2O = M(OH)_x(z-x)+ + H^+$ Where  $*K_x = \frac{[M(OH)_x(z-x)^+][H^+]}{[M(OH)_{x-1}(z-(x-1))^+]}$ or  $M^{z+} + x H_2 0 = M(OH)_x^{(z-x)+} + x$ Where  $*\beta_{x,1} = \frac{[M(OH)_x^{(z-x)+}][H^+]^x}{[M^{z+}]}$ (b)  $M(OH)_{x-1}(z-(x-1)) + OH^{-} = M(OH)_{x}(z-x) + OH^{-} = M(OH)_$ Where  $K_x = \frac{[M(OH)_x^{(z-x)+}]}{[M(OH)_{x-1}^{(z-(x-1))+}][OH^-]}$ or  $M^{z+} + xOH^{-} = M(OH)_{x}^{(z-x)+}$ Where  $\beta_{x,1} = \frac{[M(OH)_{x}^{(z-x)+}]}{[M^{z+}][OH^{-}]^{x}}$ POLYNUCLEAR HYDROLYSIS (a) Addition of protonated ligand HOH.  $mM^{z+} + n H_2 0 = M_m (OH)_n^{(mz-n)+} + n H^+$ Where  $*\beta_{n,m} = \frac{[M_m (OH)_n^{(mz-n)+}][H^+]^n}{[M^{z+}]^n}$ (b) Addition of ligand OH.  $mM^{z+} + n OH^{-} = M_{m}(OH)_{n}^{(mz-n)+}$ Where  $\beta_{n,m} = \frac{[M_{m}(OH)_{n}^{(mz-n)+}]}{[M^{z+}]^{n} [OH^{-}]^{n}}$ 

MONONUCLEAR SPECIES

1a.  $M(OH)_{z}(s) = M^{z+} + z OH^{-}$ 1b.  $M^{z+} + z H_{2}O = M(OH)_{z}(s) + z H^{+}$ 2a.  $K_{so} = \{M^{z+}\} \{OH^{-}\}^{z}$ 2b.  $*K_{so} = \{\frac{H^{+}}{\{M^{z+}\}}^{z}\}$ 

Where  ${\rm K}^{}_{\rm SO}$  equals the thermodynamic solubility constant. MONONUCLEAR AND POLYNUCLEAR SPECIES

3a. {M}<sub>soluble</sub> = {M<sup>z+</sup>} + 
$$\Sigma \Sigma m \{M_m(OH)_n^{(mz-n)+}\}$$
  
3b. {M}<sub>soluble</sub> = {M<sup>z+</sup>} +  $\Sigma \Sigma (pB_{n,m} \{M^{z+}\} / \{H^+\}^n)$ 

Where B equals the overall formation constant for the polynuclear species.

IN THE PRESENCE OF A PRECIPITATE

4. 
$$\{M\}_{\text{soluble}} = \frac{\{H^{+}\}^n}{*K_{so}} + \sum_{\Sigma}^{m} \sum_{(pB_{n,m}\{H^{+}\}^{(mz-n)}/*K_{so}^{m})}$$

(to be used when all the hydrolyzed species and the formation constants are known.

{} refer to activities

polynuclear complexed metal decreases on dilution.

It must be remembered though, that the hydrolysis equations only show that these and other mononuclear and polynuclear forms are mathematically feasible, they do not confirm or deny the presence of any of these species in solution.

#### CHAPTER 3

#### ALUMINUM HYDROLYSIS AND SPECIATION LITERATURE REVIEW

#### 3.1 INTRODUCTION/SUMMARY

Aluminum hydrolysis has been studied for a long time. The numerous investigations reflect the interest and importance of aluminum hydrolysis and speciation, yet at the same time show the difficulties involved. The problems of slow kinetics and equilibrium attainment, occurrence of metastable species and metastable amorphous solids, and species detection and measurement are studied in different ways, yet the variability of experimental conditions between separate scientists' studies render the results very difficult to compare.

Through review of the literature it can be seen that critical parameters involved in hydrolysis investigations, namely concentration range, pH range, temperature, ionic strength, and mixing and aging conditions (time) may have a great deal of influence on the results. This must be considered when comparing the results.

Several trends can be found in the literature. One group of authors conclude that aluminum speciation occurs through monomeric hydrolysis. Another group finds a polynuclear hydrolysis scheme to agree more with their experimental results. This latter group is divided into about three subgroups (with respect to their ideas about the specific stoichiometry and stability of polynuclear complexes). The

first subgroup find their experimental results to fit a polynuclear hydrolysis scheme consisting of the  $Al_6(OH)_{15}^{3+}$  unit of gibbsite (Brosset <u>et al</u>. 1954) and the unit multiple  $Al_{13}(OH)_{32}^{7+}$  (Sillén 1959, Aveston 1965, VanCauwelaert <u>et al</u>. 1969) cations as important polymers. The second subgroup believe  $Al_8(OH)_{20}^{4+}$  (Matijević et al. 1961, Hayden and Rubin 1974) best fits their results. Subgroup three (Hsu and Bates 1964) denies the  $Al_8(OH)_{20}^{4+}$  species due to implied structural repulsion between the aluminum atoms and proposed the larger (double ring) polymer  $Al_{10}(OH)_{22}^{8+}$  to be the dominant cation in their investigations.

#### 3.2 LITERATURE REVIEW

The hydrolysis and complexation of Al<sup>3+</sup> in aqueous solutions has been studied since the beginning of the century when metal hydrolysis was considered to involve "aquo-acidity" (Pfeiffer 1907, Werner 1907):

$$M(H_2^0)_6^{3+} + H_2^0 = M(H_2^0)_5^{0}OH^{2+} + H_3^0^+$$

Later work (Hartford 1942) established that hydrogen ion concentration in solution increases as the concentration of the trivalent ion,  $A1(H_20)_6^{3+}$ , is increased.

Aluminum speciation has been investigated by numerous scientists using a variety of techniques but there is little agreement in their results. This disagreement can be seen by examination of Table 3-1 which summarizes various speciation studies. For the twenty-one references listed there is a range in  $pK_1$ , the first monomeric hydrolysis constant, of over one order of magnitude, 4.61 being the lowest reported  $pK_1$  and 5.97 being the highest. Appendix I lists details (Temperature, Al<sub>t</sub>, Ionic strength, method used) of the investigations summarized in Table 3-1. The wide variety of ranges in these parameters makes comparison of  $pK_1$  values difficult. Table 3-2 (or Appendix II for more details) shows that the values reported for the second monomeric hydrolysis constant,  $pK_2$ , are in worse agreement than the first. The successive appendices (III to VI) illustrate the poor agreement with other postulated hydrolysis products.

Table 3-3 compares the results of a few studies whose experimental conditions were apparently similar. The  $pK_1$  values for the

pK1
4.89
4.96
5.97 5.74
5.10 5.19
4.98
4.96
5.27 5.03
5.02
5.00 5.05
4.75
4.93
4.61
4.89
5.47
5.55
5.04
5.01
4.89
4.99
5.35
4.99

Table 3-1 The First Monomeric Hydrolysis Species A10H<sup>2+</sup> and Corresponding Reported Hydrolysis Constant

AUTHOR	pK2
Frink and Peech (1963)	11
Raupach (1963)	9.76
Sullivan and Singley (1968)	9.96
Turner (1968)	9.70
Nazarenko and Nevskaya (1969)	10.3
Reesman et al. (1969)	10.40
Nazarenko and Biryuk (1974)	10.65
Marion et al. (1976)	8.70
Smith and Martel (1976)	9.30
Stol et al. (1976)	10.32
Hemingway and Robie (1978)	8.67

Table 3-2 The Second Hydrolysis Species  $A1(OH)_2^+$  and the Corresponding Hydrolysis Constant  $pK_2$ .

AUTHOR	рК <sub>1</sub>	рК <sub>2</sub>	Total Soluble Al(M)	Method
Hartford (1942)	4.96		10 <sup>-3</sup>	Potentiometry
Kubota (1956)	5.03		10 <sup>-3</sup>	Potentiometry
Frink and Peech (1963)	5.02	11	$10^{-2} - 10^{-5}$	Potentiometry
Nazarenko and Biryuk (1974)	5.04	10.65	10 <sup>-2</sup>	Spectrophoto- metry
Smith and Martel (1976)	4.99	9.30		

Table 3-3 Comparison of Experimental Studies at 0 Ionic Strength and  $25^{\circ}C$ .

group are in fair agreement yet the pK<sub>2</sub> values vary by almost two orders of magnitude. Critical comparisons of the results can be made by observing the experimental conditions and results listed in the appendices.

Schofield and Taylor (1954) varied only temperature in their potentiometric experiments and notice a trend of decreasing  $pK_1$  values (5.28 to 4.98) as temperature increased (from 15° to 25°C). Sullivan and Singley (1968) vary both the ionic strength and total aluminum concentration (from  $10^{-3}$ M to  $10^{-5}$ M). They note a decrease in  $pK_2$  values when these parameters are increased simultaneously. Both Faucherre (1954) and Kubota (1956) observe an increase in  $pK_1$  when they increase the ionic strengths of their solutions. Smith and Martel (1976) see the same phenomenon in their experiments for both the first ( $pK_1$ ) and second ( $pK_2$ ) hydrolysis constants. On the other hand, when Nazarenko and Biryuk (1974) increase the ionic strength of their solutions, spectrophotometric measurements indicate a decrease in both  $pK_1$  and  $pK_2$ .

The most widely used technique in the study of aluminum hydrolysis is potentiometric determination of pH, although nuclear magnetic resonance, ultracentrifugation, light scattering, calorimetry, x-ray diffraction, and other methods have been used by a few investigators. Aluminum hydrolysis has been examined at temperatures as high as 200°C (Macdonald <u>et al</u>. 1973) and as low as 15°C (Brønsted and Volqvartz 1928, Schofield and Taylor 1954) in both concentrated  $(10^{-2}M)$ and dilute  $(10^{-5}M)$  solutions at a variety of ionic strengths (Note: it has already been shown that polynuclear complexes depend on Al<sub>+</sub>, but not
mononuclear complexes). With such a variety of variable parameters it is not surprising that there is no unanimity with the pK values.

There has evolved two different concepts of dealing with aluminum hydrolysis and speciation mechanisms:

(a) mononuclear hydrolysis.

(b) polynuclear hydrolysis.

Tables 3-4 and 3-5 list a few of the studies which consider the two different hydrolysis schemes.

Part of the problem in choosing a mechanism lies in the fact that equilibrium attainment at room temperature is slow, that is, the kinetics of polymerization (and crystallization) are slow. Another part of the problem is that most aluminum species cannot be measured or identified directly at concentrations less than  $10^{-2}$  M Al. Metastable amorphous hydroxy polymers form at pH's less than 4 (Brosset <u>et al</u>. 1954, Johansson 1960, 1962, Frink and Peech 1963, Aveston 1965, Hem and Roberson 1967, Turner 1968, Akitt <u>et al</u>. 1972) along with stable colloids or gels (Vermeulen <u>et al</u>. 1975) and unstable colloidal suspensions (Hem and Roberson 1967). Some authors believe these to be transient stages in the aggregation of Al(OH)<sub>3</sub> molecules and their precipitation (Frink and Peech 1963). Also there are a number of crystallization structures of solid aluminum oxides and hydroxides which are chemically similar but exhibit different solubilities.

Akitt <u>et al</u>. (1972) suggested that the details of the methods of study may be important in the formation of mono- and polynuclear hydrolysis species. When authors such as Brosset <u>et al</u>. (1954) and Ruff and Tyree (1958) added alkali to dilute salt solutions, polymers formed,

Table	3-4	Monomeric	Hydrolysis	Mechanisms
-------	-----	-----------	------------	------------

Brønsted and Volqvartz	1928
Hartford	1942
Ito and Yui	1953
Schofield and Taylor	1954
Gayer et al.	1958
Frink and Peech	1963
Raupach	1963
Kittrick	1966
Frink and Sawhney	1967
Hem and Roberson	1967
Hem	1968
Sullivan and Singley	1968
Grunwald and Fong	1969
Nazarenko and Nevskaya	1969
Reesman et al.	1969

Matijević and Tezak	1953
Brosset et al.	1954
Faucherre	1954
Sillén	1954
Ruff and Tyree	1958
Matijević et al.	1961
Hsu and Bates	1964
Aveston	1965
Fripiat et al.	1965
Turner	1968
Smith	1969
Schoen and Roberson	1970
Akitt et al.	1972
Chen	1973
Macdonald et al.	1973
Patterson and Tyree	1973
Hayden and Rubin	1974
Mesmer and Baes	1976
Nair and Prenzel	1978

Table 3-5 Polynuclear	Hydrolysis	Mechanisms
-----------------------	------------	------------

Brosset

whereas during acid addition or progressive dilution of pure salt solutions (Grunwald and Fong 1969, Faucherre 1954 and Schofield and Taylor 1954) only mononuclear species are found. But Baes and Mesmer (1981) attribute differences to the concentration ranges being used by various investigators. Baes and Mesmer observe the dominance of monomers in dilute (<  $10^{-3}$  M) solutions and polymers in more concentrated (>  $10^{-3}$  M) solutions. Faucherre (1954) was the first investigator to note a concentration dependence when dealing with hydroxy aluminum species. Faucherre predicted that in solutions of Al<sub>T</sub> less than 5 x  $10^{-3}$  M monomeric species will dominate, whereas when the total aluminum concentration is greater than  $10^{-3}$  M, polymers will be predominant. Vermeulen <u>et al</u>. (1975) agree with the observations of both Faucherre and Baes and Mesmer.

Sillén (1959) introduced the concept of the mononuclear wall as being a point of dilution after which monomeric species will prevail over polynuclear species. Sillén's idea is based on the concentration dependence of polynuclear complexes. The monomers differ from polymers by their dependence on pH (or  $[H^+]$ ) only. This is illustrated in Figure 3-1. In part A of Figure 3-1, the  $\bar{n}$  versus pH diagram depicts the case where only monomeric species occur. In part B the  $\bar{n}$  (OH/Al ratio) versus pH diagram shows the effect occuring when a polynuclear species is added. The separate curves of  $\bar{n}$  vs pH at various  $m_M$  values converge to produce the mononuclear wall (at lower  $m_M$  and  $\bar{n}$  values) which has the same shape as the  $\bar{n}$  vs pH curve depicting monomeric species only.

Chen (1973) suggests that the pH range of study is important to



Figure 3-1 Mononuclear Wall-  $\overline{n}$  vs pH curves.

(A). One monomer (MOH) present -  $\bar{n}$  is a function of pH only. (B). Two monomers (MOH, M(OH)<sub>2</sub>) present - the second species contributes to the lower part of the curve for one monomer complex by  $\Delta \bar{n}$ . (C). One monomer (MOH) and one polymer (M<sub>6</sub>(OH)<sub>12</sub>) - the separate curves of  $\bar{n}$  vs pH at various  $m_M$  values converge to produce the envelope called the mononuclear wall (with a shape equal to the monomer function).

the formation of mono- and polymeric species. Chen concludes that both Grunwald and Fong (1969) and Akitt <u>et al</u>. (1972) failed to observe polymers because they worked in fairly acid solutions (pH < 3). Dezelić <u>et al</u>. (1971) propose different equilibration times in various reported experiments as being important in species formation. Hem and Roberson (1967) and Brosset <u>et al</u>. (1954) also believe time to be one of the most important variables to which aluminum distribution between hydroxo complexes is sensitive.

Thus the above parameters, concentration range, pH range, equilibration time, along with temperature, ionic strength, and mixing conditions (method) have a great deal of influence on the variability of results obtained from aluminum hydrolysis and speciation studies.

From these reviews one might conclude that monomers would tend to form at low temperatures (25°C), low aluminum concentrations (< 5 x  $10^{-3}$  M), low pHs (< 7), and mixing conditions such as acid addition to dilute salt solutions or dilution of stoichiometric salt solutions, and under fast titration conditions. Polymers would be expected to form at high temperatures (40°C), high aluminum concentrations (> 5 x  $10^{-3}$  M), high pHs (> 7), and mixing conditions such as alkali addition to dilute salt solutions, and under fast titration conditions.

## 3.3 MONOMERIC EVIDENCE

The first stage of hydrolysis

$$A1(H_20)_6^{3+} + H_20 = A1(H_20)_50H^{2+} + H_30^+$$

along with it's equilibrium constant

$$*K_{1} = \frac{[A10H^{2+}] [H^{+}]}{[A1^{3+}]}$$

has been generally studied by determining the concentrations of reacting species in dilute aluminum salt solutions using potentiometric and conductometric methods. Most of the evidence for monomeric hydrolysis (first postulated by Brønsted and Volqvartz in 1928) has come from solubility studies (for example Raupach 1963, Gayer <u>et al.</u> 1958, and Reesman <u>et al.</u> 1969) where aluminum solid phases were presumably equilibrated with dissolved aluminum species in solution. The three studies collectively proposed the three species  $A10H^{2+}$ ,  $A1(0H)_{2}^{+}$ , and  $A1(0H)_{4}^{-}$ .

In 1963 Frink and Peech found monomeric equilibrium constants to increase upon soluton dilution or upon alkali addition. Frink and Peech attribute this phenomenon to the precipitation of  $Al(OH)_3$  when the degree of supersaturation of the dilute aluminum salt solution has reached critical levels. Frink and Sawhney (1967) concluded that the potentiometric titration curves of dilute aluminum salt solutions can be predicted by a simple reaction scheme involving mononuclear hydrolysis mechanisms and precipitation of  $Al(OH)_2$ .

There are many reports of the  $A10H^{2+}$  species, but in most cases

the extent of hydrolysis was measured in a series of dilutions of stoichiometric aluminum salt solutions (Mesmer and Baes 1971). But such measurements alone will not give a hydrolysis product since the aluminum concentration and the extent of hydrolysis are varied simultaneously. Kubota (1956), however, included in his experiments a measurement where the aluminum concentration  $(10^{-3} \text{ M})$  and the ionic strength (0 or  $10^{-2} \text{ M})$  were held constant in a range of pH (2 to 10). Kubota was clearly able to show AlOH<sup>2+</sup> as being a hydrolysis product. Nazarenko and Nevskaya (1969) were also able to confirm monomeric species since they used colored organic ligands in their study which competed with OH<sup>-</sup>.

#### 3.4 POLYMERIC EVIDENCE

In 1946, Marion and Thomas proposed the idea that aluminum polymerized through olation. Olation is the mechanism whereby a double OH bridge binds two aluminum ions together. Marion and Thomas also proposed that on aging of the polymers, hydrogen ions would split from the bound OH s leaving oxygen bridges behind. They called this process oxolation. Marion and Thomas used oxolation to account for the observed decrease in pH of aluminum solutions upon aging.

Brosset's (1952) extensive studies led to the proposal that the main products of aluminum hydrolysis are polynuclear complexes. He proposed that  $Al[(OH)_3Al]_n^{3+}$  series formed in solutions in the alkaline range. Brosset <u>et al</u>. (1954) reanalyzed the earlier data and changed the acid species to  $Al_6(OH)_{15}^{3+}$  plus a series of complexes following the formula  $Al[(OH)_5Al_2]_n^{(3+n)+}$ . Brosset <u>et al</u>. stated that "considerable difficulties were met with because equilibrium was attained rather slowly, especially in the region where precipitation occurred. It is however thought that the values finally given were not far from those at real equilibrium". Yet in Smith's (1969) work he explained "it appears that the data used by these authors (Brosset <u>et al</u>.) were considerably further from equilibrium than they had thought".

In 1954, one of Brosset's coworkers, Sillén, mathematically examined the formation of polynuclear complexes assuming that all the complexes were dissolved in solution. Sillén presented the "core and links" hypothesis in which  $M(OH)_t^{(z-t)+}$  groups were added stepwise to a

M<sup>2+</sup> core forming the general formulas for complexes. Sillén said that experimental data concludes that all complexes that exist in appreciable amounts have a composition correlating to a core and varying numbers of links. Figure 3-2 illustrates the idea whereby all complexes occurring correspond to points on a straight line passing through the composition of the core and with a slope depending on the composition of the link. All complexes on the line are not really required to form in solution, actually there may only be a few which occur in solution.

Matijević and his coworkers have made important contributions to knowledge about aluminum hydrolysis and speciation through their coagulation studies. Matijević and Tezak (1953) observed Al<sup>3+</sup> dominating in freshly prepared aluminum solutions and in solutions with acid added. But dimerization developed upon heating or aging these solutions. In a later study, Matijević <u>et al</u>. (1961) suggested the octamer Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> as the principal hydrolysis product in aqueous aluminum solutions based on an OH/Al ratio of 2.5 determined from neutralization curves of potentiometric titrations, and tetravalency of the product as indicated by the critical coagulation concentrations of aluminum salt solutions for negative silver iodide and silver bromide sols.

Kubota (1956), Faucherre (1954), and Aveston (1965) found evidence for the dimer  $Al_2(OH)_2^{4+}$  in acid solutions leading Faucherre to suggest that in solutions of total aluminum concentration greater than  $10^{-3}$  dimers existed, whereas in solutions of total concentration less than 5 x  $10^{-3}$  M monomers predominated.





Through equilibrium ultracentrifugation and potentiometric measurements Aveston (1965) also proposed the  $Al_{13}(OH)_{32}^{7+}$  cation. Although this cation did not agree with Brosset theory, one of Brossets coworkers, Sillén (1959), mentioned the species which has been shown to exist in some basic aluminum salt crystals (Johansson 1960, Johansson et al. 1960).

Hsu and Bates (1964) examined aluminum hydrolysis through a series of precipitation studies. Initially they proposed the ring-like structure  $Al_6(OH)_{12}^{6+}$  as being the polymer present in their solution, but they revised their species to a multiple of the ring structure,  $Al_{10}(OH)_{22}^{8+}$  due to structural repulsion implied in the smaller species.

Turner (1968) agrees with mononuclear hydrolysis and amorphous  $Al(OH)_3$  precipitation, but only until the aluminum salt solutions are  $\langle \bar{n} = 2.4$ . At  $\bar{n} > 2.4$  Turner concludes that polynuclear complexes are dominant.

Turner (1976) aged a partially neutralized (to  $\bar{n} = 2.5$ ) aluminum salt solution and found that the initial polynuclear hydroxyaluminum cation (Al<sub>pl</sub>) disappears slowly at 25°C and a new polymer (Al<sub>p2</sub>) forms. This new hydroxyaluminum cation has a few similar properties to Al<sub>pl</sub> (such as  $\bar{n} = 2.5$ ) but is found to be much less reactive with 8hydroxyquinoline. Turner reports transformation of Al<sub>pl</sub> to to Al<sub>p2</sub> to be a first order process (not Al<sub>p1</sub> polymerization or condensation) with an activation energy of 20.8 kcal/mole. In his Ph.D. work, Smith (1969, 1971) identified three types of aluminum which he labeled Al<sup>a</sup>, Al<sup>b</sup>, and Al<sup>c</sup> (Al<sup>a</sup> consisting of mononuclear hydrolysis species, Al<sup>b</sup> consisting of polynuclear material (about 20-100 Al atoms), and Al<sup>c</sup> being relatively larger solid Al(OH)<sub>3</sub> particles (colloidal size)). In Smith's aluminum solutions only n (OH/Al ratio) was varied. For each n value Smith found the concentration of Al<sup>a</sup> remains constant whereas Al<sup>b</sup> decreases and Al<sup>c</sup> increases in concentration. Smith and Hem (1972) suggested that the Al<sup>b</sup> particles which eventually become gibbsite. Smith also notes that the lower the n ratio or the slower the addition of base to aluminum solutions, the longer the equilibration time.

In 1974, an excellent series of studies were performed by Hayden and Rubin. They combined a precipitation study involving light scattering (turbidity) measurements with a potentiometric study and xray diffraction measurements. Hayden and Rubin controlled the critical parameters (temperature, ionic strength, mixing and aging) and determined the exact pH of precipitation for each aluminum concentration used  $(1.0 \times 10^{-4} M, 5.0 \times 10^{-4} M, and 1.0 \times 10^{-3} M)$ . Hayden and Rubin explained that the pH of precipitation for each concentration must be determined since mass balance equations are not valid in the pH range of precipitation because the equivalent concentration of the solid phase cannot be accounted for in the calculation. Thus, in potentiometric analyses of solutions where precipitation has occurred unjustified hydrolysis species would be postulated. Hayden and Rubin concluded that

conclusions from other studies (Aveston, Biederman) are in error due to this problem. As a result of their extensive study, Hayden and Rubin reported that the species  $Al^{3+}$ ,  $AlOH^{2+}$ ,  $Al(OH)_4^{-}$  and  $Al_8(OH)_{20}^{4+}$  best fit their experimental results.

Baes and Mesmer (1976) concluded that monomers form rapidly and reversibly; small polymers (dimers, trimers) form slowly; and larger polymers (of which at least one is stable) form even more slowly. Mesmer and Baes emphasize that precise conditions of hydrolysis (including solution composition, mixing rate, stirring rate, and temperature) determine the nature and quantity of the transient polynuclear species, collodial particles, and amorphous solids formed. The rate at which these transient forms are converted either to large polymers or to crystalline gibbsite depends on pH, temperature, amount of gibbsite already present, and other anions present.

From the results of three types of titrations (continuous titrations, relaxation titrations, and dilution tests), Stol <u>et al</u>. (1976) conclude different processes to be at work above and below  $\bar{n} = 2.5$ . They observed an increase in dimerization with ionic strength in solutions of total aluminum concentration less than 5 x 10<sup>-4</sup> M when  $0 < \bar{n} < 0.5$  and observed an increase in concentration of polymers when total aluminum concentration exceeded 5 x 10<sup>-4</sup> M and 0.5 <  $\bar{n} < 2.2$ . Stol <u>et al</u>. conclude the rate of reaction to be a first order process.

#### CHAPTER 4

# EXPERIMENTAL

4.1 PURPOSE

In this study of aluminum solute complexes, potentiometric titrations are used to assess the reversibility of the aqueous system ignoring the solid phases. Sets of acid and base titrations, using standardized solutions and a constant ionic strength medium, are carried out and the titration curves are compared for superposition. Blank titrations using the constant ionic strength medium solution are used for quality controls.

Several variables are investigated in order to characterize the nature of the aluminum solution behavior more explicitly. Potentiometric titrations which consider time effects, pH range, and total aluminum concentration are performed in order to assess the effects of these variables on the reversibility of the system.

## 4.2 METHODS AND MATERIALS

All pH measurements were made with an Orion Research 801 digital pH meter used in conjunction with a Ross electrode. Three types of Ross electrodes were used:

(a) A Ross Orion pair consisting of a Ross pH half cell, model

81-01, and a reference electrode, model 81-05.

(b) A large Ross Orion combination electrode, model 81-02.

(c) A small Ross micro pH electrode, model 81-03.

Ross electrodes provide better stability, faster response and greater accuracy than conventional electrodes with silver chloride or calomel internal systems because the Ross electrodes use a redox internal element system which has virtually zero temperature coefficient. That is, the potential difference between the elements is zero regardless of the difference in the temperature of the elements. The Ross electrode pair uses a double junction design so the potential is independent of the chloride concentration in the filling solution.

Teflon bottles (Nalgene 1600) of 75 and 125 ml sizes were used as liners for the titration vessel and for storage of aging solutions because of Teflon's inertness. A double walled water jacket was built to fit snugly around the Teflon bottles, and was attached to a thermostated water bath to obtain a constant temperature environment to be maintained during titrations.

Parafilm was used to seal the titration vessel and it's contents from the atmosphere while titrations were carried out. CO<sub>2</sub> scrubbed argon was bubbled through and blanketted over sample solutions. A

magnetic stirrer and Teflon coated stirring bars agitated the solutions while in the titration vessel.

Several 2.5 ml ultraprecision Gilmont microburets (sensitive to 0.0001 ml) were used to dispense titrants. For acid titrants, the buret tip was placed directly into the sample solution (through the parafilm). For alkaline titrants, a Teflon tube adapted with a capillary containing the base was submerged in the sample solution (through the parafilm). The alkali base in the tubing was separated from the actual glass tip of the buret by a decane barrier. Hence the base was in contact only with Teflon.

Both Teflon and glass containers (500 mL and 1 L) were used for storage of reagent solutions. All labware in contact with samples or reagent solutions was cleaned with or soaked in 2 M  $HNO_3$  and rinsed with deionized water and Millipore water before initial use.

#### REAGENTS:

#### High Purity Millipore Water-

Obtained by passing distilled water through a MilliQ Water Purification System. Used for reagent solutions, dilutions, and final rinsing when cleaning glassware.

# 0.1 M KNO3 Medium:

Prepared by dissolving 10.11 g KNO<sub>3</sub> (BDH Anal-R Chemical) in millipore water and diluting to 1 liter. Used for reagent solution preparation and dilutions.

# 1 M HNO3 Stock Solution:

Prepared by diluting 64 ml concentrated acid to one liter with ionic medium solution.

1 M KOH Stock Solution:

Prepared by dissolving 28.0547 g KOH (Fisher Scientific Co.) to 500 ml with ionic medium. Stored under Argon.

Standard Na<sub>2</sub>CO<sub>3</sub> Solution ( $\simeq 0.002 \text{ eq/kg}$ ):

Prepared by dissolving 0.1 g (dried)  $Na_2CO_3$  (Baker Chemical Co.) to 1 kg with ionic medium. Used for standardization of acid solutions.

Aluminum Stock Solution ( $\approx 10^{-2}$ M):

Prepared by dissolving 3.7513 g of dried  $A1(NO_3)_3$  (BDH Chemical Co.) to 1 1 with ionic medium solution.

HNO<sub>3</sub> Dilution (
$$\approx 10^{-2}$$
 M):

Prepared by diluting 10 ml stock to one liter with ionic medium. Used as a titrant.

HNO<sub>3</sub> Dilution (
$$\approx 10^{-3}$$
M):

Prepared by diluting 100 ml of the  $10^{-2}$  acid to one liter with ionic medium. Used as a titrant.

Prepared by diluting 5 ml stock to 500 ml with ionic medium.

Stored under Argon. Used as a titrant.

Prepared by diluting 50 ml of the  $10^{-2}$  base to 500 ml with ionic medium. Stored under Argon. Used as a titrant.

# Aluminum Dilution ( $\approx 10^{-4}$ M):

Prepared by diluting 10 ml stock solution to one liter with ionic medium solution.

# Aluminum Dilution (≈10<sup>-5</sup>M):

Prepared by diluting 100 ml of the  $10^{-4}$  M solution to one liter with ionic medium solution.

Decane:

Fisher Scientific Co. Used as a barrier between alkali base and glass burets.

4.3. STANDARDIZATION PROCEDURES

#### ACID STANDARDIZATION-

A 50 g aliquot (accurately weighed) of  $Na_2CO_3$  solution is introduced to the titration vessel. The vessel is sealed with parafilm and is brought to temperature (25°C) while being stirred at a constant rate. The initial pH is recorded and the titration is initiated. Aliquots of acid are added through a buret at three minute intervals while the pH is monitored. At least three runs are performed.

The equivalence point is determined for each run via the Gran method where  $(V_0 + V_a)10^{-pH}$  is plotted against  $V_a$ , where  $V_o$  equals the original sample volume and  $V_a$  is the volume of acid added. A linear regression on low pH values gives the equivalence point,  $V_e$ , which is then used in the equation:

$$C_{a} = \frac{\text{alkalinity (eq/1) * V}_{o}}{V_{e}}$$

where alkalinity (eq/1) is obtained from the sodium carbonate solution concentration and  $C_{a}$  is the concentration of the unknown acid.

#### BASE STANDARDIZATION-

A 2.0 g aliquot (accurately weighed) of standardized acid is diluted to 50 g (accurately weighed) with ionic medium and placed in the titration vessel. The vessel is sealed and degassed (purged with prepurified argon to remove  $CO_2$ ) at constant stirring and temperature. After degassing, the initial pH is recorded. Alkali titrant is injected into the vessel via a Teflon capillary at three minute intervals while the change in pH is monitored. The amount of base added at each interval is also recorded. Several runs are performed.

The equivalence point is determined for each run using the Gran method where  $(V_o + V_b)10^{+pH}$  is plotted against  $V_b$ .  $V_o$  is the original sample volume,  $V_b$  equals the volume of base added. A linear regression on the most linear part of the plot will give  $V_e$ , the equivalence point volume, which can then be used in the following:

$$C_b = \frac{C_a V_a}{V_a}$$

where  $C_{a}$  is the standardized acid concentration and  $C_{b}$  is the concentration of the unknown base.

#### ELECTRODE STANDARDIZATION/BLANK CHARACTERIZATION

To standardize the electrode before experimental titrations, and to characterize the  $\text{KNO}_3$  medium, a blank (media) titration is carried out.

A 50.00 g aliqout (accurately weighed) of 0.1 M  $\mathrm{KNO}_3$  is transferred to the titration vessel. The vessel is sealed with parafilm and is purged with prepurified argon to remove carbonate ions from solution while under constant stirring and temperature. Traces of  $\mathrm{CO}_2$ are removed from the argon by filtering the gas through a column containing an Ascarite drying agent.

During the titration, acid titrant additions are made by microburet. The solution is titrated at three minute intervals while the pH is monitored. As a check, alkali is injected in a back titration and the pH changes are monitored (Fig. 4-1 a is a typical media titration). To evaluate the linearity of the electrode, a Gran plot is performed on the data. For an acid titration  $(V_0 + V_a)10^{-pH}$  is plotted versus  $V_a$ , the volume of acid added (and  $V_0$  equals the original sample volume). A linear regression on the plot will indicate the electrode linearity.

To recheck the data, a Gran plot is performed on the base titration data where  $(V_s + V_b)10^{pH}$  is plotted versus  $V_b$ . In this case  $V_s$  equals the original sample volume plus the amount of acid added during the acid titration, and  $V_b$  is the amount of base added. A linear regression on this plot reevaluates the electrode linearity.

A plot of  $mv_r$  (millivolts read) versus  $pH_c$  (calculated pH) reveals a line with slope b and intercept E° (Fig. 4-1 b). This relation arises through (Nearnst equation):

 $E = E^{\circ} + b \log [H]$ 

where E = mv reading.

 $E^{\circ}$  = regression function intercept.

b = regression function slope.

and [H] =  $H^+$  concentration calculated from  $V_s$  (sample volume), titrant concentrations and volumes.

When E° and b are determined, true pH can be obtained through the relation (rearrangement of above):

 $(E - E^{\circ})/b = \log [H]$ 

The true pH calculation is used in aluminum sample solution titrations in order to compare the titrations to the 'blank' titration (see Fig. 4-2).



Figure 4-1 Graphical representation of a typical media titration. (A) pH versus equivalents of titrant added. (B) mv versus  $pH_c$  reveals slope b and intercept E° for use in the Nearnst equation.



Figure 4-2 Graphical comparison of a typical media titration (no aluminum) and a typical aluminum solution titration.

#### 4.4. EXPERIMENTAL PROCEDURES

## BASIC PROCEDURE-

For the titration of aluminum solution samples, a procedure analogous to the blank characterization procedure is followed. A 50.00 g portion (accurately weighed) of aluminum solution is placed in the titration vessel. A Teflon coated stirring bar is added, then the vessel is sealed with parafilm. A Ross electrode is introduced to the system through the parafilm. Argon is pumped through a CO<sub>2</sub> scrubbing system into the vessel. The sample is degassed for approximately one half hour at 25°C before the titration is initiated.

After the initial pH is recorded, the titration begins. An aliquot of alkali is injected into the vessel (volume recorded). After a specific time interval the pH is recorded and another aliquot is added. This procedure continues until a specified pH level is reached.

After the last pH change from base addition is recorded, acid addition begins. As before, successive additions of acid and the corresponding pH changes are monitored until the original pH of the sample solution is attained. In all cases duplicate titrations are run.

# VARIATIONS IN PROCEDURE-

Important parameters were varied in order to assess effects upon the titrations. More specifically, different concentrations of aluminum sample solutions and titrants, variations in the length of time between titrant additions, and different ranges in pH were considered.

#### I. pH Range Effects

The effect of pH range of titration on the aluminum sample titration curves is assessed by carrying out experiments over several pH ranges. In  $10^{-4}$  M aluminum solutions the titrations began around pH 4.9 and were run up to the successive pHs of 5.5, 6.0, 6.5, 7.0, and 7.5 (Fig. 4-3) after which acid titrant is added to reverse the titration until the initial pH is attained.

#### II. Time Effects

To examine the effect of time, titrant additions are made at both 2 and 10 minute intervals. Initially  $10^{-4}$  M aluminum solutions are used and titrations are run from the initial pH of 4.9 to pH 5.5 before being reversed by acid addition (Fig. 4-4 a).

Later, to see what effect time interval has on the pH range covered, experiments covering successive pH ranges are carried out (See Fig. 4-4, a,b, and c and 4-5 a and b as summarized in Fig. 4-3 a and b).

#### III. Aluminum Concentration

Since total aluminum concentration is an important factor in the composition of dissolved aluminum solute complexes (due to the mononuclear wall), aluminum concentration is examined here. To do this, all experiments are run at two aluminum concentrations  $(10^{-4} \text{ M and } 10^{-5} \text{ M})$ . Initially,  $10^{-4}$  M aluminum samples were used in the assessment of time effects, and pH range effects, thus these experiments are rerun at the lower concentration level in order to examine the concentration effect. Figures 4-6 and 4-7 show the  $10^{-5}$  M aluminum sample titrations (at two minute intervals) in the pH ranges 5.0 to 6.5.



Figure 4-3 Graphical representation of aluminum sample solution titrations. Effect of pH range on forward and reverse titration of  $10^{-4}$  M aluminum solutions. (A) 2 minute interval, (B) 10 minute interval between titrant additions.



Figure 4-4 Graphical representation of aluminum sample solution titration. Effect of time interval on forward and reverse titrations of  $10^{-4}$  M aluminum solutions. (A) to pH 5.5, (B) to pH 6.0, (C) to pH 6.5.







Figure 4-6 Graphical representation of aluminum sample solution titration. Effect of total aluminum concentration on forward and reverse titration of aluminum solutions. (A) to pH 5.5, (B) to pH 6.0. a.  $10^{-5}$ M total aluminum.

a. \_\_\_\_\_ 10 <sup>-</sup>M total aluminum. b. ----- 10 <sup>-4</sup>M total aluminum.



Figure 4-7 Graphical representation of aluminum sample solution titration. Effect of total aluminum concentration on forward and reverse titration of aluminum solutions. (C) to pH 6.5.

a.  $10^{-5}$ M total aluminum. b. -----  $10^{-4}$ M total aluminum.

#### CHAPTER 5

## **RESULTS AND DISCUSSION**

# 5.1 POTENTIOMETRIC TITRATION REVERSIBILITY STUDY

Neutralization curves for  $10^{-4}$ M and  $10^{-5}$ M Al(NO<sub>3</sub>)<sub>3</sub> solutions, titrated at 2 and 10 minute intervals, are shown in figures 4-3 to 4-7. The results of the three variables examined with respect to titration reversibility are discussed below under the appropriate headings. I. pH Range Effects

For examination of pH interval change with respect to reversibility, the eq. acid added/eq. base added ratio (A/B ratio) was considered along with graphical appearance of the titration curves. A 100% reversible titration would exhibit an A/B ratio equal to 1, and the titration curves would superimpose (as found with the blank titrations). But the ratio would deviate from 1 if the titrations were less reversible and the forward and reverse titration curves would separate.

Five pH titration intervals were examined and exhibited the A/B ratios shown in table 5-la. As the titration pH interval increased, it was accompanied by a decrease in reversibility. In all cases, when the acid back titration reached the initial pH level (4.9) a base excess of about 7.5 to  $8 \times 10^{-6}$  eq. (compared to zero for the 100% reversible blank) was observed. In other words, a certain amount of base from the forward titration had not been accounted for by acid (i.e. it was bound in an

aluminum complex and was unavailable for titration). In examination of the titration curves themselves, it can be seen that the more basic ends of the curves are closer to being superimposed then the acid ends of the titration. This observation is exemplified in table 5-lb where A/B ratios for stepwise pH increments of the titration curves are listed. As the pH of the steps rise, the A/B ratios increase towards 1. However, this may be an artifact of the titration sequence acid  $\rightarrow$  base  $\rightarrow$ acid.

II. Time Effects

Increasing the titration interval from 2 to 10 minutes resulted in curves with overall similar shapes. But the 2 minute interval curve is:

- a) slightly steeper at lower titer amounts,
- b) initiated at slightly lower pH,
- c) required a longer time to reach the buffer range (between pH 5.0 and 5.2)

The 10 minute interval curves reached the equivalence range first, with the consumption of less titer. Thus the 10 minute interval allows slightly increased reversibility in titrations up to pH levels of 7.5 (as experimentally shown in this study) over the 2 minute interval. III. Concentration Range Effects

Graphical observation of the titration curves show that the lower concentration aluminum solution  $(10^{-5} \text{M})$  titration:

a) is initiated at a higher pH level (5.2 vs 4.9),

# Table 5-1 A/B Ratios

a) 10<sup>-4</sup>M Solution, 2 minute interval

Titration pH Interval	A/B Ratio
4.9 - 5.5	0.286
4.9 - 6.0	0.244
4.9 - 6.5	0.233
4.9 - 7.0	0.192
4.9 - 7.4	0.189

b) 10 <sup>-4</sup> M Solution, 2 minute interval		
Graphical pH Interval	A/B Ratio	
5.0 - 5.5	0.260	
5.5 - 6.0	0.476	
6.0 - 6.5	0.636	
6.5 - 7.0	0.666	

7.0 - 7.5

0.722

c) 10<sup>-5</sup>M Solution, 2 minute interval

Titration pH Interval	A/B Ratio	
5.2 - 5.5	0.278	
5.2 - 6.0	0.278	
5.2 - 6.5	0.270	

d) 10<sup>-5</sup>M Solution, 2 minute interval

Graphical pH Interval	A/B Ratio
5.5 - 6.0	0.406
6.0 - 6.5	0.605

b) thus does not exhibit the initial inflection seen in the more concentrated aluminum solution titration curves.

Examination of the A/B ratios of the two concentration levels for the different titration pH intervals (table 5-la,c) reveals that reversibility increases as the aluminum concentration decreases (due to movement towards the mononuclear wall where mononuclear species are reversibly formed).

#### 5.2 REVERSIBILITY ASSESSMENT

The  $10^{-4}$ M aluminum alkali (forward) titration curves are characterized by:

a) an initial inflection (pH 4.9 to 5.0) followed by

- b) a buffer zone (pH 5.0 to 5.4) followed by
- c) a second inflection.

Examination of the acid back titrations and A/B ratios (table 5-1) indicate the reversibility of the titrations as being poor.

The  $10^{-5}$  M aluminum base titration curves:

- a) do not show the initial inflection due to titration initiation at a higher pH (5.2)
- b) exhibit the buffer zone (pH 5.4 to 5.8) and
- c) the final inflection zone.

Acid back titrations show the lower concentration aluminum solution to have a more reversible character but still to be very poorly reversible.

Varying pH range covered by the forward (and reverse) titrations of the aluminum solutions shows that even though the basic ends of the titrations graphically (and through stepwise A/B ratios) appear more superimposible than the acid ends, the reversibility decreases with increasing titration pH range.

Varying time interval between titrant additions from 2 to 10 minutes resulted in overall similarly shaped curves. The 10 minute
interval improved reversibility slightly over the smaller time interval, but the reversibility still appears poor.

The overall conclusions on the assessment of reversibility is that the titration of aluminum (under the defined conditions) is quite irreversible. In no case in this study were titration curves superimposible.

## 5.3 SPECIES DETERMINATION

Experimental aluminum neutralization curves are compared with a blank curve (fig 4-2) to determine OH/Al ratios ( $\bar{n}$ ) at various pH levels.  $\bar{n}$  vs pH curves, commonly used to examine titration data (Baes and Mesmer 1976), are constructed. Theoretical titration curve models incorporating various combinations of the species listed in table 5-2 were developed through a computer program (ASCP) and compared to the experimental curves.

These comparisons do not involve comparisons of the activity coefficients nor the pKs. Activity coefficient or hydrolysis constant changes result in a shift of the monomeric curves along the horizontal axis (Fig 5-la), but do not effect the overall shapes of the curves. However, these types of changes in polynuclear curves result in horizontal shifting accompanied by some alteration of the curve shapes. Figure 5-lb illustrates what happens to the model curves for the Al<sub>6</sub>  $(OH)_{15}^{3+}$  species plus various combinations of mononuclear species when the polynuclear pK is assumed to be 40 (compare 5-lb with 5-3a, the curves obtained when pK is 47).

Based on comparison of the experimental curves (Fig. 5-2a) with the model curves (Figs. 5-2b, 5-3, 5-4) the following conclusions are reached:

a) mononuclear model curves do not fit the experimental curves.

b) Addition of the dimer  $(Al_2(OH)_2^{4+})$  to the models does not improve the fit.

c) Addition of Al<sub>6</sub>(OH) $\frac{3^{+}}{15}$  improves the fit for the 10<sup>-5</sup>M

Table 5-2 Species	(and	pKs)	Used	in	Models
-------------------	------	------	------	----	--------

Mononuclear	Species	рК
A1 <sup>3+</sup>		
A10H <sup>+2</sup>		5.01
A1(OH)2 <sup>+</sup>		8.7
A1(OH) <sub>3</sub> °		11.64
A1(OH) <sub>4</sub>		23.7

Polynuclear Species	рК
A12(0H)2 <sup>4+</sup>	7.1
A1 <sub>6</sub> (0H) <sub>15</sub> <sup>3+</sup>	47.0
A1 <sub>8</sub> (OH) <sub>20</sub> <sup>4+</sup>	68.65
A1 <sub>13</sub> (OH) <sub>32</sub> <sup>7+</sup>	104.5

Polynuclear Models:

a.

Ъ.

1. Polymer + 
$$A1^{3+}$$
 +  $A1(OH)_4^{-}$   
2. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_4^{-}$   
3. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
4. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_2^{+}$   
5. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$   
6. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_2^{+}$   
7. Polymer +  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_2^{+}$   
Mononuclear Models:  
A1 01 =  $A1^{3+}$  +  $A1OH^{2+}$   
A1 02 =  $A1^{3+}$  +  $A1OH_2^{+}$   
A1 03 =  $A1^{3+}$  +  $A1OH_2^{+}$   
A1 04 =  $A1^{3+}$  +  $A1OH_2^{-}$   
A1 012 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$   
A1 013 =  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_2^{+}$   
A1 013 =  $A1^{3+}$  +  $A1OH^{2+}$  +  $A1(OH)_3^{\circ}$   
A1 014 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 023 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 024 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 023 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 024 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0123 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{+}$  +  $A1(OH)_2^{+}$  +  $A1(OH)_4^{-}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_4^{--}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_4^{--}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_4^{--}$   
A1 0124 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_4^{--}$   
A1 01234 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_4^{--}$   
A1 01234 =  $A1^{3+}$  +  $A1OH_2^{++}$  +  $A1(OH)_2^{++}$  +  $A1(OH)_3^{\circ}$  +  $A1(OH)_4^{--}$ 



 $A1_6(CH)_{15}^{3+}$ ). Refer to figure 5-4 for com-

concentration. The Al<sub>6</sub>(OH) $_{15}^{3+}$  + 04 model curve (see table 5-3) fits fairly well to the 10<sup>-5</sup> M experimental curve.

d) Addition of  $Al_8(OH)_{20}^{4+}$  and/or  $Al_{13}(OH)_{32}^{7+}$  gives identical curves which fit fairly well to the  $10^{-4}$  M concentration experimental curve (for the poly + 04 model curve).

It would be expected that as  $Al_t$  increased the n of the dominant polynuclear species would increase, but there seems to be no definite pattern exhibited here.

## Monomeric Models (Figure 5-2b)

Mononuclear species are not concentration dependent, thus model curves for combinations of these species are applicable to any concentration of Al<sub>t</sub>. The monomeric model curves level off at  $\bar{n}$  values determined by the most 'dominant' or influential specie(s) of the particular model. The overall order of curve influence for the mononuclear species is: \*Al(OH)<sub>3</sub>° > Al(OH)<sub>4</sub> > Al(OH)<sub>2</sub><sup>+</sup> > AlOH<sup>2+</sup>. Horizontal placement of the  $\bar{n}$  vs pH model curves is dictated by a constant incorporating the activity coefficient and hydrolysis constant for each species (Fig 5-la).

Both the  $10^{-4}$  M and  $10^{-5}$  M experimental curves are located between the areas occupied by the AlO4 and Al O(1)2(4) models (see table 5-2). The lower reaches of the experimental curves ( $\overline{n} < 1.8$ ) seem to parallel the Al O4 model's vertical trend. The  $10^{-5}$  M experimental curve is also closer to the mononuclear wall.



for (a) experimental data and (b) nono-

nuclear models.

Overall, the mononuclear models are a very poor fit to the experimental curves.

\*It is noted that in all cases, when the mononuclear species, A1(OH)<sub>3</sub>°, is included in a model it specifically dictates what happens to the model curve - no matter what other species are present (mononuclear or polynuclear). All model curves containing A1(OH)<sub>3</sub>° are nearly identical to each other and to the mononuclear curves containing A1(OH)<sub>3</sub>°. It is similar to removing A1<sub>t</sub> from solution (i.e. as total solid) since it is unchanged. Thus polynuclear models containing A1(OH)<sub>3</sub>° are not included in the figures depicting the model curves.

# Polynuclear Models (Figures 5-3, 5-4) Dimer - Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>:

At low concentrations  $(10^{-4}-10^{-5}M)$ , addition of the dimer, Al<sub>2</sub>  $(OH)_2^{4+}$ , has no effect on the monomer curves. Higher concentration ranges of Al<sub>t</sub> would be needed to show a significant dimer effect. Since there is no significant change in the model curves from the monomer model curves the dimer curves are not illustrated in the polynuclear model figures. At the  $10^{-5}M$  level, the Al 04 model curve slightly shifts horizontally, becoming only a bit closer to the experimental curve, but exhibiting no shape change. These model curves offer a very poor fit to the experimentally derived curves.

 $A1_8(OH)_{20}^{4+}$ ,  $A1_{13}(OH)_{32}^{7+}$  (Fig 5-3):

Examination of higher order polymers reveals that when  $Al_8(OH)_{20}^{4+}$  and/or  $Al_{13}(OH)_{32}^{7+}$  are present in a model (minus  $Al(OH)_3^{\circ}$ ) the resulting curves are almost identical. Since the differences are not significant, the model curves are illustrated on the same diagram (Fig 5-3).

Introduction of either (or both) of these polymers describes Al 04 model curves which are shifted far to the left of the original mononuclear model curves but which are in a horizontal locale similar to the experimental curves.

The  $10^{-4}$  M model curves are:

a) located slightly to the left of the 10<sup>-4</sup>M experimental curves,

b) show fair vertical fit until  $\overline{n}$  increases above 1.8. The  $10^{-5}$  M model curves are:

- a) located slightly to the right of the corresponding experimental curve,
- b) show similar vertical trend until  $\overline{n}$  rises above 2, but is a poor match with the experimental curve.

A1<sub>6</sub>(OH)<sup>3+</sup><sub>15</sub> (Fig. 5-4):

The Al<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup> species has a strong effect on the model curves. When it appears in a model (minus Al(OH)<sub>3</sub>°) it dictates the shape of the resulting curves, even when the other polymers  $(Al_8(OH)_{20}^{4+}, Al_{13}(OH)_{32}^{7+})$  are present. The apparent order of curve influence in the

polynuclear species is:  $Al_6(OH)_{15}^{3+} > Al_{13}(OH)_{32}^{7+} = Al_8(OH)_{20}^{4+} > Al_2(OH)_2^{4+}$ .



Figure 5-3 Graphical representation of  $\bar{n}$  vs pH curves for polynuclear models containing the two species  $Al_8(OH)_{20}^{-4+}$  and  $Al_{13}(OH)_{32}^{7+}$ .

When the  $Al_6(OH)_{15}^{3+}$  polymer is introduced into the model it causes the model curves to shift far to the left in their lower regions. The  $10^{-4}$  M model curves:

- a) lie to the left of the  $10^{-4}$  M experimental curves.
- b) (the Al 04 model) has similar vertical trends but is a very poor match to the experimental curve.

The  $10^{-5}$  M model curves:

 a) lie slightly to the left of the corresponding experimental curves.

b) (the Al 04 model) fits fairly well in vertical trend.



for polynuclear models containing the specie**s** Al<sub>5</sub>(OH)<sub>15</sub><sup>3+</sup>.

5.4 COMPARISON OF RESULTS WITH THE LITERATURE

Hayden and Rubin (1974) performed potentiometric titrations on  $10^{-3}$  to  $10^{-4}$  M Al(NO<sub>3</sub>)<sub>3</sub> solutions in 0.15 M NaNO<sub>3</sub> and analyzed their experimental data using their SCOGS computer program. Their results show that Al<sup>3+</sup>, AlOH<sup>2+</sup> (pK 5.55), Al(OH)<sub>4</sub><sup>-</sup> (pK 23.75), and Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> (pK 68.7) form the model which best describes their experimental curve. The results of potentiometric experiments and computer modelling in this aluminum speciation study are in partial agreement with Hayden and Rubin. The Al<sup>3+</sup>, Al(OH)<sub>4</sub><sup>-</sup>, and Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> species are found in both 'best fit' models for the  $10^{-4}$ M Al<sub>t</sub> levels. (Addition of AlOH<sup>2+</sup> assuming Hayden and Rubin's pK of 5.55 instead of 5.01 may shift the Al 014 model curve towards the experimental  $10^{-4}$ M curve, but literature search results show a pK<sub>1</sub> of 5.55 to be high).

Many investigators have detected the presence of a precipitate between  $\bar{n} = 0.8$  and  $\bar{n} = 2$ . They also show that  $\bar{n}$  vs pH curves tend to 'flatten out' when  $\bar{n} > 2$  from the precipitate's influence. These observations also apply to the experimental data in this study. Figure 5-2a shows the point in the titration where flakes of the precipitate were clearly visible in sample solutions. The precipitate initial influence on the experimental curves can be seen before the precipitate is visible to the naked eye, as the titration curves start to flatten out below  $\bar{n}$  of 2 for  $10^{-4}$ M Al<sub>t</sub> ( $\bar{n}$  of 2.2 for  $10^{-5}$ M Al<sub>t</sub>). Hayden and Rubin stated that analysis of solutions of  $\bar{n} > 2$  would indicate the

presence of a large polymer, but that in actuality there would be only a combination of  $Al_8(OH)_{20}^{4+}$  and solid aluminum hydroxide. When extrapolated to this study it can be understood why the experimental results do not fit well to any model curves (since they ignore solubility) when  $\bar{n} > 2$ .

### CHAPTER 6

#### PROPOSED HYDROLYSIS SCHEME

Examination of potentiometric titration data has led to the proposal of two sets of hydrolysis species for the two concentration levels studied. The more concentrated  $(10^{-4} \text{M}) \text{ Al}(\text{NO}_3)_3$  solution exhibited the presence of Al<sup>3+</sup>, Al(OH)<sub>4</sub><sup>-</sup>, and the larger polymers Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> and/or Al<sub>13</sub>(OH)<sub>32</sub><sup>7+</sup>. The  $10^{-5} \text{M}$  solution contained Al<sup>3+</sup>, Al(OH)<sub>4</sub><sup>-</sup> and the smaller polymer Al<sub>6</sub>(OH)<sub>15</sub><sup>3+</sup>.

At pH less than 3 the dissolved aluminum is in the form of the hydrated  $Al(H_20)_6^{3+}$  ion. As the pH of the aluminum solution is raised this ion becomes deprotonated. But the deprotonated form  $Al(H_20)_5 OH^{2+}$  is unstable and quickly polymerizes through dehydration to form the dimer  $Al_2(OH)_2^{4+}$ . This form too is unstable being only an intermediate step towards the larger polymeric forms. In the less concentrated solution this form is the  $Al_6(OH)_{15}^{3+}$  ion. The more concentrated aluminum solution contains  $Al_8(OH)_{20}^{4+}$  and/or  $Al_{13}(OH)_{32}^{7+}$  as the larger polymer, but  $Al_8(OH)_{20}^{4+}$  will be assumed in this case.

The polynuclear forms found under the conditions used in this study can appear as straight chain polymers, double chain polymers, or ring structures (Fig. 6-1, 6-2). Hsu and his co-workers (1964, 1966, 1967, 1977) support the presence of ring structures because of implied structural repulsion (between aluminum ions) in the more open forms. However, the precipitate observed in the present experimental solutions was amorphous as determined by x-ray diffraction giving small credence that there was little or no large scale structures in solution. One might interpret this as favoring the straight chain polymers over the double or branched chain or ring polymer forms.

The proposed hydrolysis schemes are as follows:

Step 1 Deprotonation

$$A1(H_20)_6^{3+} + OH^- = A1(H_20)_5OH^{2+} + H^+$$

Step 2	Polymerization through dehydration
	2 Al(H <sub>2</sub> 0) <sub>5</sub> OH <sup>2+</sup> = Al <sub>2</sub> (H <sub>2</sub> 0) <sub>8</sub> (OH) <sub>2</sub> <sup>4+</sup> + 2 H <sub>2</sub> 0
Step 3	For $10^{-5}$ M solution - polymerization (chain)
	$3A1_2(H_20)_8(OH)_2^{4+} + 9OH^- = A1_6(H_20)_{11}(OH)_{15}^{3+} + 13 H_20$
Step 3	For $10^{-4}$ M solution - polymerization (chain)
	$4A1_2(H_20)_8(OH)_2^{4+} + 12OH^- = A1_8(H_20)_{14}(OH)_{20}^{4+} + 18 H_20$









- a) straight chain
- b) double chain
- c) ring polymer







Figure 6-2 Possible forms of the  $Al_8(OH)_{20}^{4+}$  polymer.

- a) straight chain
- b) double chain
- c) ring polymer

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Author	Method	Ionic Strength	(M) T (M)	T°C	<sup>рК</sup> 1
Brønsted and Volqvartz (1928)	pH measurements (catalytic diazoacetic ester method)	. (0)	$10^{-2} - 10^{-4}$ a luminum perchlorate	15	4.89
Hartford (1942)	Potentiometry (glass electrode)	(0)	10 <sup>-3</sup>	25	4.96
Faucherre (1948)	Potentionetry (glass electrode)	0.6 NO3-	5 x 10 <sup>-3</sup>	20?	5.97
n	n	0.12 NO3	13	**	5.74
Ito and Yui (1954)	pH measurements and conductivity		a luminum chloride	25	5.10/5.19
Schofield and Taylor (1954)	Potentiometry (glass electrode)	10 <sup>-3</sup> KC1	10 <sup>-2</sup> -2x10 <sup>-5</sup> aluminum	25	4.98
	11	11	chloride and	21.5	5.13
11	11	18	potassium alum	20	5.15
u	<b>H</b> .	**	"	15	5.28
Kenttamaa (1956)	pH measurements and cryoscopy			25	4.96
Kubota (1956)	pH measurements (glass electrode)	10 <sup>-2</sup> NaC104	10-3	25	5.27

					2+
APPENDIX	I	The	Mononuclear	Species	A 10H2

Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	pK 1
Frink and Peech (1963)	pli titration and conductivity	(0)	10 <sup>-2</sup> - 10 <sup>-5</sup>	25	5.02
Raupsch (1963)	Thermodynamic calculations	0.03	10 <sup>-2</sup> -3x10 <sup>-5</sup>	25	4.97
п	Potentiometry	11	**	"	5.00
u	Conductivity	11			5.05
Hem and Roberson (1967)	Potentiometry (glass electrode)	10 <sup>-2</sup> NaC104	10 <sup>-4</sup> - 10 <sup>-5</sup>	25	4.75
Sullivan and Singley (1968)	Potentiometry (glass electrode)	10 <sup>-3</sup> C104	10 <sup>-3</sup> aluminum	?25	4.93
n	n	10 <sup>-14</sup> C10 <sub>14</sub>	perchlorate 10		5.29
0	n	$10^{-5} c 10_{4}^{-7}$	10 <sup>-5</sup> a.p.	**	5.16
Grunwald and Fong (1969)	Potentiometry	0.1 - 0.5	6x10 <sup>-2</sup> -7x10 <sup>-3</sup>	30	4.61
Nazarenko and Nevsk <sub>o</sub> ya (1969)	Spectrophotometry (with the competing ligands Arsenazo I and Protocatchol Violet)	10 <sup>-2</sup> NaClO <sub>4</sub>	2 x 10 <sup>-5</sup>	25	4.89
Nesmer and Baes (1971)	(agreed with but not found in their elevated temperature experiments in 1 M KCl)	1М NaClO <sub>ц</sub>		25	5.47
Parks (1972)	Literature search	(0)		25	5.01

## APPENDIX I Continued

Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	рК 1
Hoyden and Rubin (1974)	Potentiometry and light scattering	0.15 NaNO3	10 <sup>-2</sup> -5x10 <sup>-5</sup>	25	5.55
Nazarenko and Biryuk (1974)	Spectrophotometry (with the competing ligand Alizarin 3 Sulphonic Acid)	(0)	10 <sup>-2</sup>	25	5.04
18	11	0.1 NaClO <sub>4</sub>	**	11	4.90
u	10	0.3 NaC104	11	H	4.60
18	n	0.5 NaC104			4.30
n	u	1.0 NaClO <sub>4</sub>	11	11	3.60
Marion, Hendricks, Dutt, and and Fuller (1976)	Monomeric model for soluble aluminum - values from Parks	(0)		25	5.01
Stol, Van Helden, and Deðruyn (1976)	Potentiometry (homogeneous alkali injection technique)	10 <sup>-4</sup> -2.8 NaNO or NaC1 3	0.5-5x10 <sup>-5</sup> aluminum nitrate or chloride	25	4.89
Smith and Martel (1976)		(0)		25	4.99
<b>n</b> .		0.5		11	5.52
11		1.0		11	5.69
Dehek, Stol, and DeBruyn (1978)	Potentiometry	0.4	5 x 10 <sup>-2</sup>	25	5.35
May, Helmke, and Jackson (1979)	Potentiomet <b>rya</b> nd Spectrophotometry	10 <sup>-2</sup> Na NO <sub>3</sub>	2x10 <sup>-8</sup> -1.4x10 <sup>-5</sup>	25	4.99
L0	u .	(0)	14		5.03

## APPENDIX I Continued

Author	Method	Ionic Strength	а1 <sub>т</sub> (М)	T°C	pK2
Frink and Peech (1963)	Potentiometry	(0)	10 <sup>-2</sup> - 10 <sup>-5</sup>	25	11
Raupach (1963)	Potentiometry	0.03	$10^{-2} - 3 \times 10^{-5}$	25	9.76
Sullivan and Singley (1968) "	Potentiometry (glass electrode) "	$10^{-3} \text{ c10}_{\text{H}}^{-1}$ $10^{-4} \text{ c10}_{\text{H}}^{-1}$ $10^{-5} \text{ c10}_{\text{H}}^{-1}$	10 <sup>-3</sup> aluminum perchlorate 10 <sup>-1</sup> a.p. 10 <sup>-5</sup> a.p.	25 "	9.96 10.59 12.12
Turner (1968)	Theoretical treatment of Raupach's 1963 data				9.70
Nazarenko and Nevskaya (1969)	Spectrophotometry (with the competing ligands Arsenazo I and Protocatchol Violet)	0.1M NaC10 <sub>1</sub>	$2 \times 10^{-5}$	25	10.3
Reesman, Pickett, and Keller (1969)	Potentiometry (glass electrode)	0.1M NaC10 <sub>4</sub>	2.7x10 <sup>-2</sup> -3x10 <sup>-4</sup>	25	10.40
Parks (1972)	Literature Review	0.1 M		25	8.70

APPENDIX II	The Mononuclear	Species	A1(OH) , +			
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Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	<sup>рК</sup> 2	
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Nazarenko and Biryuk (1974)	Spectrophotometry (with the competing ligand Alizarin 3	(0)	10 <sup>-2</sup>	25	10.65	
n	Sulphonic Acid) H:	0.1M NaC1044	<b>11</b>	н	10.35	
11	u	0.3M NaC104	н	11	9.73	
	u	0.5M NaC 104	31	u	9.12	
u	n	1.0M NaC104	n	u	7.58	
Marion, Hendricks, Dutt, and Fuller (1976)	Monomeric model for soluble aluminum - values from Parks	(0)		25	8.70	
Smith and Martel (1976)		(0)		25	9.30	
0		0.5		11	10:40	
Stol, Van Helden, and DeBruyn (1976)	Potentiometry (homogeneous alkali injection technique)	10 <sup>-4</sup> -2.8 NaNO <sub>3</sub> or NaCl	5 x 10 <sup>-5</sup> Aluminum nitrate or chloride	25	10.32	
Hemingway and Robie (1978)				25	8.67	

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Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	<sup>рК</sup> 3
Brosset, Biederman and Sillen (1954)	Reevaluation of Brosset's earlier Hydrogen electrode data.	2M NaC10 <sub>4</sub>	a luminum perchlorate		
Sullivan and Singley (1968)	Potentiometry	10 <sup>-3</sup> c10 <sub>4</sub> -	10 <sup>-3</sup> a.p.	25	14.13
n	<b>n</b>	10 <sup>-4</sup> C10 <sub>4</sub> -	10 <sup>-4</sup> a.p.	11	15.19
10	0	10 <sup>-5</sup> C104 <sup>-</sup>	10 <sup>-5</sup> a.p.	"	23.49
lazarenko and Nevskaya (1969)	Spectrophotometry (with the competing ligands Arsenazo I and Protocatchol Violet)	0.1M NaC104-	2 x 10 <sup>-5</sup>	25	15.6
ezelic, Bilinski,and Wolf (1971)	Potentiometry (glass electrode)	0.6M NaCl	0.2-3x10 <sup>-2</sup>	20	15.32
arks (1972)	Literature Review	0.1		25	15.20
azarenko and Biryuk (1974)	Spectrophotometry (with the competing ligand Alizaran 3 Sulphonic Acid)	(0)	10 <sup>-2</sup>	25	16.75
u	n	0.1M NaC10,	10 <sup>-2</sup>	**	16.25
n .	н	0.3M NaC10,	18	11	15.25
51	H .	0.5M NaC10.	10	u	14.38
11	U	1.0M NaC101	n	"	11.84

APPENDIX	III	Contin	ued
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Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	₽ <sup>K</sup> 3
Marion, Hendricks, Dutt, and Fuller (1976)	Monomeric model for soluble aluminum - values from Parks	0.1		25	15.20
Smith and Martel (1976)		(0)		25	15.00
11		0.5		13	16.30
Stol, Van Helden, and DeBruyn (1976)	Potentiometry (homogeneous alkali injection technique)	10 <sup>-14</sup> -2.8 NaNO or NaCl 3	5 x 10 <sup>-5</sup> aluminum nitrate or chloride	25	16.28

Author	Method	Ionic Strength	Al <sub>T</sub> (M)	T°C	рК <sub>і+</sub>
LaCroix (1949)	Potentiometry	1 - 10 <sup>-2</sup>	1 - 10 <sup>-2</sup> Alcl <sub>3</sub>	20	21.47
Brosset, Biederman, and Sillen (1954)	Reevaluation of Brosset's earlier Hydrogen electrode data.	2M NaC10 <sub>4</sub>			
Szabo, Csanyi, and Kavai (1955)	Potentiometry		$4 \times 10^{-2} - 2 \times 10^{-3}$	20	23.23
Kittrick (1966)	Potentiometry (glass electrode)	1.4x10 <sup>-3</sup> 4.4x10 <sup>-3</sup>	$2.8 \times 10^{-14} - 10^{-14}$	23-25	23.29
Hem and Roberson (1967)	Potentiometry	10 <sup>-2</sup> NaC 10 <sub>1+</sub>	10 <sup>-4</sup> -10 <sup>-5</sup>	25	22.73
Sullivan and Singley (1968)	Potentiometry	10 <sup>-3</sup> C104 <sup>-</sup>	10 <sup>-3</sup> aluminum perchlorate	25	23.55
n	u	10 <sup>-4</sup> C10 <sub>4</sub> -	10 <sup>-4</sup> a.p.	н	23.30
н	11	10 <sup>-5</sup> C104	10 <sup>-5</sup> a.p.	0	31.46
Reesman; Pickett, and Keller (1969)	Potentiometry (glass electrode)	10 <sup>-2</sup> Nac 104	$3 \times 10^{-2} - 3 \times 10^{-3}$	25	23.74
Parks (1972)	Literature Review				23.30
Hayden and Rubin (1974)	Precipitation boundary analysis	0.15M NaNO3	5x10 <sup>-2</sup> -5x10 <sup>-5</sup>	25	23.75
Marion, Hendricks, Dutt, and Fuller (1976)	Monomeric model for soluble aluminum - values from Parks	$10^{-1+}$ $C10_{1+}^{-}$	10 <sup>-1</sup>	25	23.30
Hemingway and Robie (1978)				25	23.29
May, Helmke, and Jackson (1979)	Potentiometry	10 <sup>-2</sup> NaC10 <sub>1+</sub>	$1.4 \times 10^{-5}$ -	25	22.17

iometry res is a transient rs only -Potentiometry yoscopy res important only at l <sub>t</sub> -estimated tiometry tivity	0.6 0.12 (0) (0)	10 <sup>-2</sup> "	20 " 25 25	8.2. 8.00 7.55
iometry es is a transient s only -Potentiometry yoscopy es important only at l <sub>t</sub> -estimated iometry tivity	0.6 0.12 (0) (0)	10 <sup>-2</sup> "	20 " 25 25	8.2 8.00 7.5 6.22
tes is a transient is only -Potentiometry yoscopy tes important only at l <sub>t</sub> -estimated tiometry tivity	0.12 (0) (0)	" 10 <sup>-2</sup>	" 25 25	8.00 7.5 6.22
tes is a transient s only -Potentiometry yoscopy res important only at l <sub>t</sub> -estimated dometry tivity	(0)	10 <sup>-2</sup>	25	7•5 6•2
res important only at l <sub>t</sub> -estimated clometry ctivity	(0) (0)	10 <sup>-2</sup>	25	6.22
lometry tivity	(0)	10 <sup>-2</sup>	25	
			2)	6.2
entrifugation and dometry (glass dode)	1M NaClO <sub>4</sub>	0.1-3x10 <sup>-4</sup> aluminum perchlorate	25	7.07
lometry	$6 \times 10^{-2}$	6 x. 10 <sup>-2</sup>	30	6.3
	$7 \times 10^{-3}$	7 x 10 <sup>-3</sup>	н	7.5
iometry (Hydrogen ode)	1M KC1	5 x 10 <sup>-3</sup>	62.5	7.7
ionetry	0.4	5 x 10 <sup>-2</sup>	25	7.1
iometry	(0)	10 <sup>-2</sup> -10 <sup>-4</sup>	25	6.95
	<pre>ciometry ciometry (Hydrogen code) n.m.r., <sup>1</sup>H n.m.r. ciometry ciometry</pre>	clometry $6 \times 10^{-2}$ 7 x $10^{-3}$ clometry (Hydrogen 1M KC1rode)n.m.r., <sup>1</sup> H n.m.r.clometry0.4clometry(0)	clometry $6 \times 10^{-2}$ $6 \times 10^{-2}$ 7 x $10^{-3}$ 7 x $10^{-3}$ clometry (Hydrogen       1M KC1       5 x $10^{-3}$ clometry (Hydrogen       1M KC1       5 x $10^{-3}$ n.m.r., <sup>1</sup> H n.m.r.       5 x $10^{-2}$ 6 x $10^{-2}$ clometry       0.4       5 x $10^{-2}$ clometry       (0) $10^{-2} - 10^{-4}$	iometry $6 \times 10^{-2}$ $6 \times 10^{-2}$ $30$ 7 x $10^{-3}$ 7 x $10^{-3}$ "         ciometry (Hydrogen       1M KC1 $5 \times 10^{-3}$ $62.5$ rode)       1M KC1 $5 \times 10^{-3}$ $62.5$ n.m.r., <sup>1</sup> H n.m.r.       0.4 $5 \times 10^{-2}$ $25$ ciometry       (0) $10^{-2} - 10^{-4}$ $25$

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APPENDIX VI Other Poly	nuclear Species				
Author	Method	Ionic Strength	A1 <sub>T</sub> (M)	T°C	<sup>pK</sup> 4,3
Mesmer and Baes (1971)	Potentiometry (Hydrogen electrode)	1M KCl	5 x 10 <sup>-2</sup> 1	24.8	
······································					<sup>рК</sup> З,З
Fanube (1954)	Infrared				
Kaupach (1957)	Infrared				
	·	<del>811-<sup></sup> 111-181</del>			
					<sup>pr</sup> 8, <sup>1</sup>
Fripist, VanCouwelsert, and dosmons (1965)	Potentiometry	2м NaNO3	10 <sup>-2</sup>	30	
VanCauwelaert and Bosmans (1969)	Potentiometry (glass	2M NaNO3	4x10 <sup>-2</sup> -5x10 <sup>-3</sup>	30	27
n	electrode)	ر. ۱۱	4x10 <sup>-2</sup> -3x10 <sup>-4</sup>	40	25.5
					<sup>pK</sup> 15,6
Brosset, Biederman, and Sillen (1954)	Reanalysis of Brossets earlier data.	2M NaNO3	10 <sup>-2</sup>	40	47
Nair and Pronzel (1978)	liumerical treatment of literature data	(0)	10 <b>-</b> 3	25	35.9

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Author	Method	Ionic Strength	Al <sub>r</sub> (m)	T °C	<sup>pK</sup> 16,7
Fripiat, VanCauwelaert, and Bosmans (1965)	Potentiometry	2m nano <sub>3</sub>	10 <sup>-2</sup>	30	
VanCauwelaert and Bosmans (1969) "	Potentiometry (glass electode) "	2M NaNO3 "	4x10 <sup>-2</sup> -5x10 <sup>-3</sup> 4x10 <sup>-2</sup> -3x10 <sup>-4</sup>	30 40	52.7 48.5
					<sup>pK</sup> 17,7
Sillen and Martel (1971)	Potentiometry	3M NaC104		25	48.80
Nair and Prenzel (1978)	Numerical treatment of literature data.	(0)	10-3	25	36
					<sup>pK</sup> 20,8
Brosset, Biederman and Sillen (1954)	Reanalysis of Brosset's earlier data.	2M NaClO <sub>lt</sub>			
Matijevic, Mathai, Otterwill, and Kerker (1961)	Coagulation		$7 \times 10^{-6}$		
Akitt, Greenwood, Khandelwal, and Lester (1972)	27 <sub>Al n.m.r</sub> .				
layden and .ubin (1974)	Potentionetry and light scattering	0.15 NaNO <sub>3</sub>	10 <sup>-3</sup> -10 <sup>-4</sup>	25	68.65
·					рК <sub>22</sub> ,8
- Matijevic, Mathai, Otterwill, and Kerker (1961)	Coagulation	· · · · · · · · · · · · · · · · · · ·	7 x 10 <sup>-6</sup>		

## APPENDIX VI Continued

Author	Method	Ionic Strength	Al <sub>T</sub> (M)	Т∘С	<sup>pK</sup> 24,8
Matijevic, Mathai, Otterwill, and Kerker (1961)	Coagulation		7 x 10 <sup>-6</sup>	ug <del>al - 1</del> .	
					<sup>pK</sup> 22,10
Hsu (1977)	Precipitation studies		10 <sup>-3</sup>		
		······································			<sup>pK</sup> 24,10
VanCauwolpert and Bosmans (1969)	Potentiometry	2M NaNO3	4x10 <sup>-2</sup> -5x10 <sup>-3</sup>	30	
n	u	11	4x10 <sup>-2</sup> -3x10 <sup>-4</sup>	40	
					<sup>pK</sup> 32,13
Aveston (1965)	Ultracentrifugation and Potentiometry (glass electrode)	1M NaClO <sub>4</sub>	0.1-3x10 <sup>-1</sup> aluminum perchlorate	25	104.5
VanCauwelaert and Bosmans (1969)	Potentiometry	2M NaNO <sub>3</sub>	4x10 <sup>-2</sup> -5x10 <sup>-3</sup>	30	
10			$4x10^{-2}-3x10^{-1+}$	40	
Nair and Prenzel (1973)	Numerical treatment of literature data.	(0)	10-3	25	80.66

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Author	Method	Ionic Strength	Al <sub>t</sub> (M)	T°C	<sup>рК</sup> 24, 13
Rausch and Bale (1964)	• Precipitation Studies		1M A T (NO. )	<b>7</b> 0	
Akitt, Greenwood, Khandelwal, and Lester (1972)	<sup>27</sup> Al n.m.r.			70	
Mesmer and Baes (1976) Akitt and Farthing (1981)	<sup>27</sup> Al n.m.r.		0.5M A1(NO <sub>3</sub> )	3	
	,	<u></u>			<sup>pK</sup> 34,13
Sillen and Martel (1971)	Potentiometry	3M NaC10 <sub>4</sub>	<u>, , , , , , , , , , , , , , , , , , , </u>	25	97.60
Nair and Prenzel (1978)	Numerical treatment of literature data.	(0)	10-3	25	73.3

## APPENDIX VI Continued