Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hayden, Phillip L. and Rubin, Alan J.(1986) 'Determination of Monomeric and Polynuclear Aluminum(III) Species and Hydrolysis Constants', Separation Science and Technology, 21: 10, 1009 — 1024
To link to this Article: DOI: 10.1080/01496398608058393
URL: http://dx.doi.org/10.1080/01496398608058393

SEPARATION SCIENCE AND TECHNOLOGY, **21**(10), pp. 1009-1024, 1986

Determination of Monomeric and Polynuclear Aluminum(III) Species and Hydrolysis Constants

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Abstract

Aqueous reactions of aluminum(III) were investigated in acidic aluminum solutions at fixed ionic strength and below the pH of precipitation. Computer analysis of potentiometric data for three concentrations (0.1, 0.5, and 1 m*M* Al) indicated that the experimental results could be explained by assuming only two principal hydrolyzed species, $AlOH^{2+}$ and $Al_8(OH)_{20}^{4+}$. No other combination of aluminum complexes appeared to fit the data as did these species. The equilibrium constant for the monohydroxy ion was very close to values determined by other methods. The refined values of the formation constants for $^*pK_1$ and $p\beta_{8,20}$ were 5.55 and 68.7, respectively, at an ionic strength of 0.15, and 5.11 and 64.1, respectively, at zero ionic strength.

INTRODUCTION

The compounds of aluminum are extremely important in commerce and medicine as well as to engineers and scientists interested in soil chemistry and to those involved in the treatment of water and wastes. Treatment applications include the use of aluminum salts as aids in flotation and dewatering sludges, for precipitating phosphates, and in chemical coagulation which involves the separation of hydrosols. Unlike the slightly more acidic salts of iron(III) whose solution chemistry is very well known, aluminum(III) is difficult to study and thus its aqueous chemistry has not been fully resolved.

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0149-6395/86/2110-1009$3.50/0

The extremely complex nature of the aqueous chemistry of aluminum salts is reflected both in the past and present literature. The hydrolytic reactions have been studied by many investigators of various disciplines for many purposes using quite different techniques. Although there is much agreement, there are also several areas of considerable disagreement, principally the structure and charge of the polynuclear species. Secondary questions include the presence or relative importance of the $Al(OH)_2^+$ and $Al(OH)_3(aq)$ species and the matter of equilibrium. Two observations are clear from the current literature. First, the systems of interest do not exist at equilibrium. It might be safe to say that aluminum at equilibrium is not of importance in separation chemistry. Second, the nature of the species formed, particularly the polynuclear ions and the precipitates, depends greatly on temperature, rate of mixing of the reagents, the age and composition of the solution, and other physical and chemical factors; that is, on the history of the solution. Thus, one would expect the reporting of different and sometimes conflicting results. It is important in any such study that a systematic approach be used and that the experimental procedure be carefully documented.

When aluminum salts are dissolved in water in the absence of complexing anions, the free metal ion Al^{3+} hydrates, coordinating six water molecules in an octahedral orientation, and reacts to form various hydrolytic species. The first step in hydrolysis had been assumed by many to proceed in the following manner:

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5OH^{2+} + H^+ \qquad (1)$$

and the thermodynamic equilibrium constant for this reaction is

$$*K_1^T = \{AlOH^{2+}\}\{H^+\}/\{Al^{3+}\} \qquad (2)$$

where $\{AlOH^{2+}\}$ and $\{Al^{3+}\}$ are the activities of $Al(H_2O)_5OH^{2+}$ and $Al(H_2O)^{3+}$, respectively; the waters of hydration are omitted for simplicity. This reaction has been studied primarily by dissolving pure aluminum salts in water and diluting to various concentrations. Using either potentiometric and/or conductimetric techniques, the concentrations of the reacting species were determined and the constant calculated. As summarized in Table 1, there appears to be good agreement on the value of $*K_1$ at zero ionic strength of approximately 10^{-5} (*1–8*). The second step in monomeric hydrolysis, which involves formation of the dihydroxoaluminum(III) species $Al(OH)_2^+$, is not so well documented.

There are numerous investigators who have not been able to interpret their data by assuming simple monomeric aluminum hydrolysis alone.

TABLE 1
Summary of Formation Constants for $AlOH^{2+}$

Source	$p^*K_1^T$	Temperature (°C)
Bronsted and Volquartz (1928) (*1*)	4.89	15
Hartford (1942) (*2*)	4.96	25
Schofield and Taylor (1954) (*3*)	4.98	25
Ito and Yui (1954) (*4*)	5.10	25
Kubota (1956) (*5*)	5.03	25
Frink and Peech (1963) (*6*)	5.02	25
Raupach (1963) (*7*)	5.00	25
Hem and Roberson (1967) (*8*)	4.75	25

Since 1908, when Bjerrum first detected polynuclear chromium(III) complexes (*9*), many other metals have been shown to form polymeric species. Over the years the principal group of investigators who have studied metal ion hydrolysis have been Sillén and coworkers in Sweden (e.g., Ref. *10*). They have developed mathematical and graphical techniques which have now been computerized to analyze the complex metal hydrolysis equilibria and calculate equilibrium constants. Most of their studies have been conducted with aqueous solutions at 25°C and at constant ionic strength (3 *M* $NaClO_4$). They have interpreted their data primarily by assuming either a single polynuclear complex or a series of polynuclears with a basic "core" and various numbers of attached "links." One of the more extensive potentiometric investigations into the aqueous chemistry of aluminum(III) was conducted by Brosset (*11*), a member of this group. He originally analyzed the data by assuming an infinite series of complexes of the form $Al[(OH)_3Al]_n^{3+}$ in the acid range and $[Al(OH)_3]_nOH^-$ in the alkaline range. Later, Brosset et al. (*12*) reviewed the same data and concluded with reservations that a single complex with hexameric structure, $Al_6(OH)_{15}^{3+}$, was the principal species in acid solutions and the aluminate ion in alkaline solutions. They did not rule out other conceivable complexes, but since the hexamer was similar in structure to crystalline gibbsite, it was a logical product of aluminum hydrolysis. In a later paper Biedermann (*13*) described a study of aluminum(III) hydrolysis conducted at 50°C to accelerate the aqueous reactions. His results indicated a septamer, $Al_7(OH)_{17}^{4+}$, and a large polycation, $Al_{13}(OH)_{34}^{5+}$. However, he also concluded that there was a high degree of uncertainty in the data.

Both Kubota (*5*) and Faucherre (*14*) have postulated the formation of a dimer, $Al_2(OH)_2^{4+}$, in acid solutions. Faucherre suggested that the dimer formed at aluminum concentrations greater than 0.01 *M* whereas below 0.005 *M* only monomeric species are present. Aveston (*15*), using both equilibrium ultracentrifugation and potentiometric techniques, examined aluminum perchlorate solutions. Analysis of the potentiometric data with a computer program employing a least-squares approach indicated both a dimer and a large polycation, $Al_{13}(OH)_{32}^{7+}$. Using equilibrium constants refined by computer techniques, a degree of polymerization was calculated which agreed with ultracentrifugation results. Others who have reported various Al_{13} species include Akitt and Farthing (*16*), Bottero, Partyka, and Fiessinger (*17*), and, most recently, Parthasarathy and Buffle (*18*).

Using a completely different approach, Matijević and coworkers (*19–21*) also studied aluminum(III) hydrolysis. The concentration of various metal ionic species just required to coagulate and restabilize sols was correlated to the change and hence to its extent of hydrolysis or complexation. By analyzing the boundaries between concentration regions of coagulation and restabilization, the ratio of ligand to metal ion was deduced. Using criteria such as these, the octameric $Al_8(OH)_{20}^{4+}$ was suggested as the principal hydrolyzed species. Rubin and Kovac (*22*) have also been able to explain the slopes and intercepts of coagulation boundaries using the octameric ion as the model.

For a more complete discussion of the aqueous chemistry of Al(III) and a review of the literature, see Hayden and Rubin (*23*), Baes and Mesmer (*24*), Bottero et al. (*25*), and Dempsey et al. (*26*).

The purpose of the present work was to investigate aluminum(III) hydrolysis in acidic solutions below the pH of precipitation. Specifically, we wished to test for the presence of several monomeric species and to identify and determine the formation constant of polynuclear species. A systematic experimental approach was used and the procedure involved the numerical analysis of serial potentiometric titration data by a computer technique.

COMPUTER PROGRAM

The computer has been used extensively by many investigators to solve solution equilibria problems. Most approaches have utilized an iterative approximation method to determine equilibrium constants which can be resolved from various forms of input data. The use of the computer presupposes that the results obtained are compatible with the chemistry of the system and that all parameters which may affect the system have been carefully controlled. For example, the concentration of the reactants must be accurately known, and because both temperature and ionic strength affect pH measurements, these parameters must be controlled and held constant. In effect, the results are not better than the experimental data and mathematical approach.

The computer program SCOGS (stability constants of generalized species) is one of several programs formulated by Perrin, Sharma, and Sayce (*27–31*) which calculates practical or mixed formation constants of complexes with up to two metals and two ligands, provided the extent of complexation is pH dependent. The program is based on a mathematical treatment described by Wentworth (*32, 33*) and consists of a least-squares adjustment to a nonlinear equation. The techniques and results have been reported by Perrin, Sharma, and Sayce primarily for nickel and copper complexes with ligands such as ethylenediamine, histamine, and serine. The original SCOGS program was modified for the present study in order to examine large polynuclear species which aluminum(III) has been postulated to form.

The input data for the program, as used here, consists of the molar concentrations of aluminum nitrate, nitric acid, and sodium hydroxide; the pK_w of water at this particular ionic strength and temperature, 14.01; the activity coefficient for hydrogen ion calculated by the Davies equation, 0.75; the number and type of proposed complexes, that is, the number of aluminums, p, and hydroxides, q, per complex; and an estimate of the logarithm of the formation constant, $\beta_{p,q}$. The volume in milliliters, V_B, of base added and the pH for each data point are also read in. The formation constant must be defined to represent the following hydrolysis reaction and mass action expression

$$p\mathrm{Al}^{3+} + q\mathrm{H_2O} \rightleftharpoons \mathrm{Al}_p(\mathrm{OH})_q^{(3p-q)+} + q\mathrm{H}^+ \tag{3}$$

$$\beta_{p,q} = [\mathrm{Al}_p(\mathrm{OH})_q^{(3p-q)+}]\{\mathrm{H}^+\}^q/[\mathrm{Al}^{3+}]^p \tag{4}$$

Using the input data, the program sets up two mass balance equations for the metal and ligand concentrations (in this case, aluminum and hydroxide). The total aluminum concentration, which is the sum of the free metal ion and hydrolyzed aluminum concentrations, is represented by

$$[\mathrm{Al(III)}]_{\mathrm{TOT}} = [\mathrm{Al}^{3+}] + \sum^{p}\sum^{q} p[\mathrm{Al}_p(\mathrm{OH})_q^{(3p-q)+}] \tag{5}$$

Solving Eq. (4) for $[\mathrm{Al}_p(\mathrm{OH})_q^{(3p-q)+}]$ and substituting into Eq. (5), the following expression is obtained:

$$[\mathrm{Al(III)}]_{\mathrm{TOT}} = [\mathrm{Al}^{3+}] + \sum^{p}\sum^{q} p_{p.q}[\mathrm{Al}^{3+}]^{p}\{\mathrm{H}^{+}\}^{-q} \tag{6}$$

A similar expression can be written for the total hydroxide activity

$$\{\mathrm{OH}^{-}\}_{\mathrm{TOT}} = \{\mathrm{OH}^{-}\}_{\mathrm{FREE}} + \sum^{p}\sum^{q} q\beta_{p,q}[\mathrm{Al}^{3+}]^{p}\{\mathrm{H}^{+}\}^{-q} \tag{7}$$

Equations (6) and (7) are the two basic expressions used by the program to refine values for formation constants of the postulated aluminum complexes. Since the total applied aluminum concentration $[\mathrm{Al(III)}]_{\mathrm{TOT}}$ is known, and by fixing the formation constant $\beta_{p,q}$, the free metal ion concentration $[\mathrm{Al}^{3+}]$ can be determined at each data point by the Newton-Raphson approximation. Once the concentration of $[\mathrm{Al}^{3+}]$ is fixed, this value is substituted into Eq. (7) and the total hydroxide ion concentration is calculated. From this value the analytical hydroxide ion concentration is then calculated using the activity coefficient. This quantity is then used to obtain V_B(calc), which is then compared with the experimental V_B, and their difference, the residual, is determined. As the program progresses through each data point, the least-squares equations are built up and these are solved by matrix inversion to obtain the shifts in the constants. The program proceeds until the sum of the squares of the residuals is at a minimum. The improved formation constants are then calculated and printed along with their standard deviations. The standard deviation in V_B, $S(V_B)$, is also printed out for that particular value of the constant. This cycle is repeated a number of times. Usually five cycles are enough to obtain the best fit to the input data.

EXPERIMENTAL

A serial titration technique was employed to investigate the hydrolysis of aluminum(III). A series of samples was prepared in 4-oz plastic bottles which had been rinsed in 1:1 nitric acid, scrubbed with Alconox detergent, rinsed several times with distilled water, and allowed to air dry. Aliquot portions of freshly prepared and standardized reagent grade aluminum nitrate, sodium nitrate, and nitric acid were transferred to the plastic bottles. The aluminum concentrations studied were 0.1, 0.5, and 1.0 m*M*, above pH 3 and below the pH where precipitation was first detected using a Brice Phoenix model 1000 Light Scattering Photometer. Nitric acid was added to the samples to lower the pH so that only the free metal ion was present initially and to minimize adsorption of aluminum onto the surfaces of the glassware during preparation. Sodium nitrate was added to adjust the final ionic strength to 0.15. Exact amounts of sodium hydroxide were added with a 2-mL microburet while the samples were swirled to insure mixing. The samples were placed in an Eberbach shaker-bath thermostatted at 25°C and shaken at 80 rpm. The samples were removed periodically with the final pH measured after 3 months. While the pH of the samples was being measured, nitrogen gas was bubbled into the solution after passing through a series of scrubber bottles containing pyrogallol to remove oxygen, saturated lime solution to remove carbon dioxide, and distilled water. Bubbling of the nitrogen through the samples insured mixing of the solutions and exclusion of carbon dioxide. Light-scattering measurements were made to check for the presence of precipitate, and only the clear samples were retained for analysis. Approximately 25 samples were prepared at each of three concentrations along with a series of duplicates at 1.0 m*M*.

RESULTS

Several statistics calculated by SCOGS were considered in order to determine the nature of the hydrolyzed species or combination of complexes present in acid solutions. The printout of this program consists of the refined value of $p\beta_{p,q}$ and its standard deviation along with the standard deviation of the difference between V_B(calc) and V_B. The pH, experimental V_B, residual, total metal concentration (adjusted for dilution), and concentration of each complex were also printed for each data point. Judging from results published by Perrin et al. (*28*), SCOGS is capable of refining formation constants with standard deviations of 0.05 or less. The standard deviation of V_B should be approximately the same as the accuracy of the microburet, which for this work was 0.01 mL. However, the accuracy of the pH measurements in dilute aluminum solutions is limiting. The Sargent model DR pH meter is reported by the manufacturer to be accurate within 0.01 pH units, limited principally by the accuracy of the buffers. The incremental volume of sodium hydroxide required to change the pH by 0.01 pH units was calculated to be 0.045 mL, which is much larger than the accuracy of the microburet. Therefore, a more reasonable standard deviation in V_B would be 0.045 for the aluminum system.

In addition to the statistics which indicated a certain fit to the experimental data, the results of SCOGS were also plotted so that the various hydrolyzed aluminum complexes under consideration could be compared. Combined hydroxides per aluminum (ligand numbers, $\bar{n}$) were calculated both from the experimental data and using the formation constants refined by SCOGS. Six separate and general hydrolysis schemes were postulated and tested in order to determine the soluble hydrolyzed aluminum(III) complex or complexes in acid solutions below the pH at which the formation of a condensed phase just occurs. These were

Scheme 1: Al^{3+}, $AlOH^{2+}$

Scheme 2: Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$

Scheme 3: Al^{3+}, $AlOH^{2+}$, $Al(OH)_3(aq)$

Scheme 4: Al^{3+}, $AlOH^{2+}$, $Al_p(OH)_q^{(3p-q)+}$

Scheme 5: Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al_p(OH)_q^{(3p-q)+}$

Scheme 6: Al^{3+}, $Al_p(OH)_q^{(3p-q)+}$

The different ratios of aluminum to hydroxide per complex examined were 2:2, 2:5, 3:4, 3:7, 4:10, 5:12, 6:12, 6:15, 7:17, 8:20, 9:23.

The existence of $AlOH^{2+}$ is generally acknowledged so the first step, Scheme 1, was to determine the formation constant $*K_1$ for this species at the three concentrations examined. Once a value for the formation constant was refined, data points at higher pH were added and the existence of $Al(OH)_2^+$ was tested. This combination was done both by refining values for $*K_1$ and $*K_2$ simultaneously and then holding $*K_1$ constant and refining a value for $*K_2$. The results of these calculations are listed in Table 2. The small standard deviations in V_B of 0.043, 0.037, and 0.068 for the three concentrations compared to an ideal value of 0.045 indicate a good fit to the experimental data and suggest that $AlOH^{2+}$ is probably the principal hydrolyzed aluminum species in the most acid solutions. To calculate formation constants for other aluminum complexes, an average value of 5.50 was used for $p{*K_1}$. This represents a working value since it may be adjusted once the other species have been determined. The dihydroxo complex $Al(OH)_2^+$ was tested by holding constant the value of $p{*K_1}$. The results listed in Table 2 indicate that the dihydroxy ion is not an important species because the standard deviations varied from 0.330 to 0.424 which are almost an order of magnitude larger than the ideal of 0.045. Figure 1, which compares calculated with experimental ligand numbers, also indicates a large divergence.

Hydrolysis Schemes 3 and 4 were tested in a similar fashion. Scheme 3 was tested by refining a constant for $Al(OH)_3(aq)$ while holding $p{*K_1}$

TABLE 2
Summary of Data for Hydrolysis Schemes 1 and 2
Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$

$[Al]_{TOTAL}$	log $^*K_1$ (S_1)	log $^*K_2$ (S_2)	Range of V_B	S_{V_B}
1.0×10^{-3}	−5.61 (0.098)		0.4–1.0	(0.043)
5.0×10^{-4}	−5.38 (0.112)		0.6–1.1	(0.037)
1.0×10^{-4}	−5.51 (0.098)		0.3–1.0	(0.068)
1.0×10^{-3}	−5.50[a]	−9.04 (0.083)	1.0–2.6	(0.330)
5.0×10^{-4}	−5.50[a]	−9.28 (0.118)	0.9–3.0	(0.430)
1.0×10^{-4}	−5.50[a]	−9.88 (0.098)	1.0–2.6	(0.324)

[a] This value was held constant and not refined.

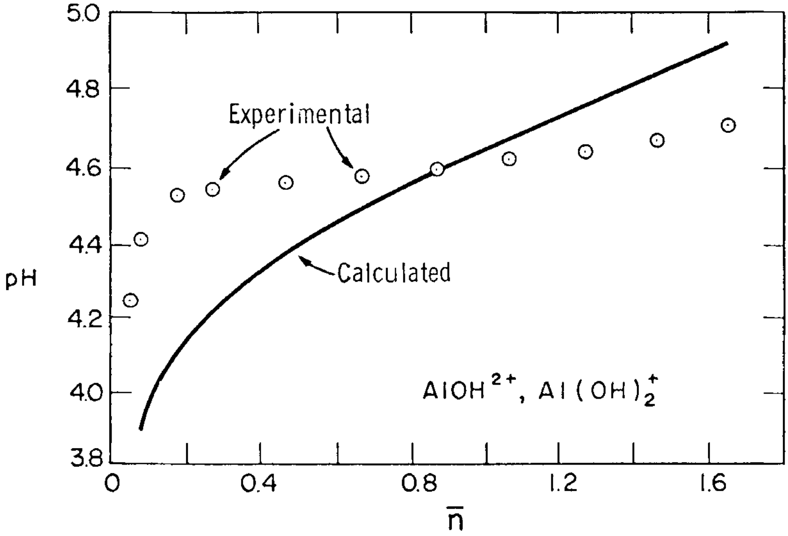

FIG. 1. Comparison of experimental and calculated ligand numbers for hydrolysis Scheme 2. 5.0×10^{-4} M $Al(NO_3)_3$, 0.15 M $NaNO_3$.

constant at 5.50. The high standard deviation in V_B, for example, 0.242 for the 0.5 m*M* aluminum solutions, indicated that $Al(OH)_3(aq)$, like $Al(OH)_2^+$, if existent at all, is unimportant in dilute aluminum(III) solutions under acid conditions.

The Scheme 4 series was also run while holding the value of p^*K_1 constant and testing each of the individual polynuclear aluminum species which have been postulated in the literature and that would appear logical in the absence of the precipitated phase. The results for 0.5 m*M* aluminum nitrate are given in Table 3. The results for five of the polynuclear species tested are also summarized in Fig. 2. Both the divergence between the experimental ligand numbers (open circles) and calculated ligand numbers (solid lines) using constants refined by SCOGS, and the standard deviation in V_B are criteria which indicate a degree of fit to the experimental data for that particular complex.

Hydrolysis Scheme 5 was similar to Scheme 4 except that the $Al(OH)_2^+$ ion was added. The value of p^*K_1 was held constant while p^*K_2 and $p\beta_{p,q}$ were varied one at a time while holding the other constant. All the polynuclear species listed in Table 3 were considered and tested. Generally the results were conclusive in that no combination of $AlOH^{2+}$, $Al(OH)_2^+$, and a polynuclear complex would fit the experimental data. If $\beta_{p,q}$ were held constant and $^*K_1$ varied, the value of the formation constant for $Al(OH)_2^+$ was so small that if it existed in solution, its concentration would be less than 1 to 2% of the total applied aluminum concentration. If this were true, the presence or absence of this species would not significantly affect the pH of the solution and therefore would be undetectable by this technique.

Aluminum hydrolysis excluding monomeric species, that is, considering only free Al^{3+} and polynuclear complexes, was tested last. Generally the results at the higher pH values are almost identical to Scheme 4, where the various polymeric complexes were tested in the presence of $AlOH^{2+}$. Although the standard deviation in V_B indicated a good fit to the experimental data, when the results were plotted as shown in Fig. 3 for $Al_8(OH)_{20}^{4+}$, it was obvious that another ionic species must be considered to explain the data at low pH. Although the calculated ligand numbers at the higher pH were almost identical to the experimental values, there was a slight divergence in acid solutions at $\bar{n}$ less than 0.2.

Reviewing the several hydrolysis schemes postulated, the only reasonable fits to the experimental data were obtained by considering the hexamer, septamer, or octamer in combination with Al^{3+} and $AlOH^{2+}$. The results of the final evaluation are listed in Table 4. Basically, the final evaluation consisted of first holding p^*K_1 constant at 5.50 and refining a value for $p\beta_{p,q}$. Then $p\beta_{p,q}$ was held constant at the refined value and p^*K_1

TABLE 3

Summary of Data for Hydrolysis Scheme 4

Al^{3+}, $AlOH^{2+}$, $Al_p(OH)_q^{(3p-q)+}$

5.0×10^{-4} *M* $[Al(III)]_{TOT}$

p	q	z	$p\beta_{p,q}$	$S_{p,q}$	S_{V_B}
2	2	+4	4.98	0.791	0.648
2	5	+1	20.07	0.073	0.209
3	4	+5	11.17	0.485	0.543
3	7	+2	25.84	0.100	0.207
4	10	+2	36.39	0.069	0.115
5	12	+3	42.11	0.086	0.118
6	12	+6	38.34	0.212	0.220
6	15	+3	52.55	0.060	0.074
7	17	+4	58.73	0.076	0.081
8	20	+4	68.64	0.053	0.051

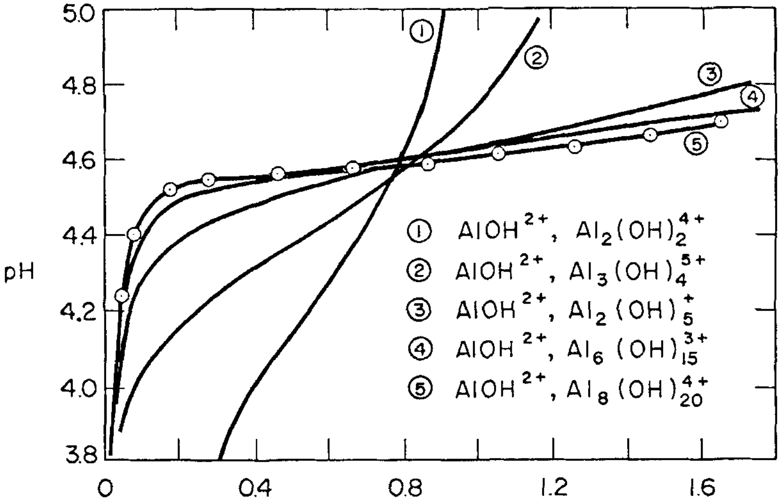

FIG. 2. Comparison of experimental and calculated ligand numbers for hydrolysis Scheme 4. 5.0×10^{-4} *M* $Al(NO_3)_3$, 0.15 *M* $NaNO_3$.

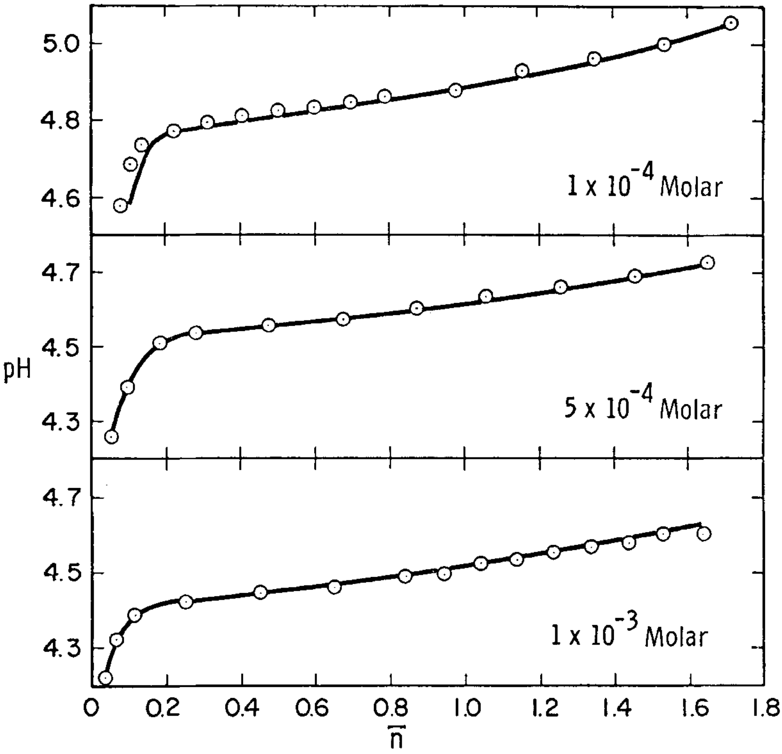

FIG. 3. Calculated ligand numbers for $AlOH^{2+}$ and $Al_8(OH)_{20}^{2+}$ using formation constants refined by SCOGS. Aluminum nitrate solutions. 0.15 M $NaNO_3$.

TABLE 4
Final Analysis—Aluminum(III) Hydrolysis

Total Al concentration M	p^*K_1 (S_1)	p	q	$p\beta_{p,q}$ ($S_{p,q}$)	S_{V_B}
1.0×10^{-4}	5.50[a]	6	15	52.99 (0.039)	0.050
	5.55 (0.069)	6	15	52.99[a]	0.049
	5.50[a]	7	17	58.54 (0.035)	0.041
	5.63 (0.065)	7	17	58.54[a]	0.040
	5.50[a]	8	20	68.85 (0.047)	0.048
	5.49 (0.055)	8	20	68.85[a]	0.048
5.0×10^{-4}	5.50[a]	6	15	52.55 (0.060)	0.074
	5.84 (0.297)	6	15	52.55[a]	0.065
	5.50[a]	7	17	58.23 (0.076)	0.081
	5.71 (0.265)	7	17	58.23[a]	0.077
	5.50[a]	8	20	68.64 (0.052)	0.051
	5.61 (0.124)	8	20	68.64[a]	0.048
1.0×10^{-3}	5.50[a]	6	15	52.31 (0.037)	0.055
	5.63 (0.163)	6	15	52.31[a]	0.053
	5.50[a]	7	17	58.05 (0.050)	0.064
	5.61 (0.185)	7	17	58.05[a]	0.062
	5.50[a]	8	20	68.46 (0.029)	0.034
	5.55 (0.105)	8	20	68.46[a]	0.033
Averages	5.67 (0.176)	6	15	52.45 (0.045)	0.056
	5.65 (0.171)	7	17	58.27 (0.053)	0.060
	5.55 (0.094)	8	20	68.65 (0.048)	0.043

[a] This value was held constant and not refined.

was determined. To determine the most statistically significant fit to the experimental data, the standard deviations of the formation constants and V_B were compared for the three polynuclear species under consideration. Although the standard deviations calculated for the septamer were slightly smaller than those for the octamer at the lowest aluminum concentration considered, 0.1 m*M*, the standard deviations calculated for 0.5 m*M* and 1.0 m*M* were significantly lower for the octamer. The standard deviations in $p\beta_{8,20}$ for the three concentrations were 0.047, 0.052, and 0.029. The standard deviations in V_B were 0.048, 0.048, and 0.033, well within experimental limits of the ideal of 0.045. The standard deviations in p^*K_1 were also smaller when calculated in combination with the octamer. Although polynuclear complexes larger than the octamer could not be tested directly using SCOGS because matrix calculations involved numbers larger than the IBM 360/75 could handle, larger polymeric species were evaluated by trial-and-error methods. For example, $Al_9(OH)_{23}^{4+}$ was tested by assuming different values for $p\beta_{9,23}$ and ligand numbers were calculated as a function of pH. The calculated ligand numbers were then graphically compared with the experimental values. The best value used for $p\beta_{9,23}$ was 78.75 but this species did not fit the data as well as the octamer.

After considering all the data, it was apparent that the principal soluble hydrolyzed aluminum(III) complexes which would be present in acid solutions *below the pH of precipitation* are the monohydroxo-aluminum(III) species, $AlOH^{2+}$, and the octameric ion, $Al_8(OH)_{20}^{4+}$. The formation constants for these two complexes refined at each aluminum concentration were averaged and the final values were 5.55 for p^*K_1 and 68.7 for $p\beta_{8,20}$ at an ionic strength of 0.15.

Figure 3 shows the comparison between experimental ligand numbers (open circles) and calculated ligand numbers (solid lines) using the formation constants listed above for $AlOH^{2+}$ and $Al_8(OH)_{20}^{4+}$ at each of the three aluminum concentrations which were studied. The good fit between the calculated and experimental data, especially for 0.5 m*M* aluminum nitrate solutions, supports the conclusion that the principal hydrolyzed aluminum(III) complexes in acid solutions are the monohydroxo species and the octameric ion.

CONCLUSION

Several points must be considered in comparing the results of this investigation involving computer analysis of potentiometric data with other aluminum(III) studies. The critical parameters such as temperature, ionic strength, mixing, and aging were all controlled, but equally as important, the exact pH of precipitation was determined by light scattering at each aluminum(III) concentration. Previous investigators have not done the latter. The pH of precipitation for each concentration must be known since mass balance equations are not valid above this value since the activity of the solid phase is defined or assumed to be unity. Potentiometric analysis of solutions in which precipitation has occurred would lead to the postulation of unjustified hydrolytic species. For example, Biedermann (*13*) and Aveston (*15*) reported large polymeric species $Al_{13}(OH)_{34}^{5+}$ and $Al_{13}(OH)_{32}^{7+}$, respectively. Both analyzed acid aluminum solutions up to OH/Al ratios of approximately 2.5. The results of this and other work indicate that the presence of precipitate was detected at OH/Al ratios between 0.8 and 2.0 depending on temperature and time of aging. In the presence of precipitate, experimental $\bar{n}$-pH curves flatten out considerably at OH/Al ratios greater than 2.0. Because the shape of these curves is dependent on the number of metal ions per complex and OH/Al ratios, potentiometric analysis of solutions with OH/Al ratios greater than 2.0 indicate a large polymeric complex, which in fact could be a combination of the octamer and aluminum hydroxide. If Biedermann (*13*) had not included data with the higher OH/Al ratios, the results would have been very similar because he did postulate a septamer $Al_7(OH)_{17}^{4+}$, a species very close to the octamer. The hexamer $Al_6(OH)_{15}^{3+}$ postulated by Brosset et al. (*12*) as a result of a potentiometric study also correlates fairly well with the octamer.

The results of this work also indicate that $AlOH^{2+}$ must be considered in a hydrolysis scheme and, as indicated in Table 1, the monohydroxoaluminum ion is well documented in the literature. Converting p^*K_1 (5.55 at an ionic strength of 0.15) to zero ionic strength using activity coefficients calculated by the Davies equation, a value of 5.11 is obtained which is very close to values of $p^*K_1^T$ listed in Table 1. The corresponding formation constant at zero ionic strength calculated for the octameric ion is 64.1.

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Received by editor March 3, 1986