

# Hydrolysis-Precipitation Studies of Aluminum (III) Solutions

## I. Titration of Acidified Aluminum Nitrate Solutions

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Acidified aluminum nitrate solutions were titrated with alkali (NaOH or KOH) over a temperature range of 24°C to 90°C. A homogeneous distribution of added base was achieved by: (i) in situ decomposition of urea (90°C); and (ii) a novel method involving injection through a capillary submerged in the agitated salt solution.

The experimental pH curves are characterized by two plateaus (or platforms) separated by a steep jump in pH. These characteristic features were not previously observed in continuous titration experiments. This is especially true of the second platform, which begins at an OH/Al ratio larger than 2.5. Stable colloidal solutions or gels are formed on traversing this plateau. The hydrolysis-precipitation behavior was also followed by light scattering and x-ray diffraction measurements.

A qualitative picture of the neutralization process is developed.

### INTRODUCTION

The structure and composition of the surfaces of metallic oxides in contact with an aqueous environment are only poorly defined. There exists a need for a detailed characterization of the oxide/aqueous interface to account quantitatively for adsorption effects, the colloidal stability, and the catalytic properties of oxides.

We have undertaken a systematic investigation of the aluminum hydroxide system to gain an improved insight into the interaction between water (also aqueous solutions) and this important hydrated oxide material. The first step in such a study is the preparation and characterization of the solid, an aspect of research in colloid chemical studies that is often neglected. This paper reports on a new experimental technique for the systematic

study of the hydrolysis-precipitation process. A brief discussion of some qualitative observations made on the progress of the precipitation reaction and the nature of the products formed is also included.

During the last 50 yr extensive studies have been made of the hydrolysis of Al(III) ions. Considerable effort has been spent on unraveling the thermodynamic equilibria and on identifying the aluminum-bearing species in solutions with OH/Al molar ratios ranging from zero to values in excess of three. The actual precipitation step has not received much attention.

Potentiometric techniques are featured prominently in experiments designed to measure precisely the hydrolysis equilibria in aluminum salt solutions (1-4). These and other studies suggest that at very low total aluminum concentrations (about  $10^{-5}$  M) the mono-

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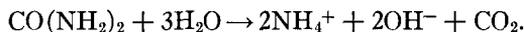
nuclear complexes  $\text{Al}(\text{OH})_2^{2+}$  and  $\text{Al}(\text{OH})_2^+$ , are present in significant amounts. The best quantitative evidence for this conclusion is furnished by the precise measurements of Kubota (5) and Nazarenko and Nevskaya (6). At increasing Al concentrations the formation of polynuclear hydroxo-complexes are called upon to explain the experimental data (2-4, 7-9). Unfortunately, no general consensus of opinion exists as to the exact identity and number of such polymeric species in solution.

A number of investigators attempted a more direct identification of the polynuclear species. These techniques include diffusion measurements (10), small-angle x-ray scattering (11), ultracentrifugation studies (2), and light scattering (12). For a particular scheme of hydrolysis to be regarded as the only possible one it is necessary to show that the experimental results are inconsistent with all other plausible schemes. This claim cannot be made by any of the investigators and the assignment of the degree of polymerization remains ambiguous. In general, a combination of monomeric, dimeric, and trimeric species with the polymeric species  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  or  $\text{Al}_{14}(\text{OH})_{34}^{8+}$  is postulated. It should also be mentioned that the extensive olation and oxolation schemes proposed by many as a precursor to the nucleation and precipitation step has been attacked by some researchers (13, 14). These authors postulate crystallite formation at an early stage in the titration of Al(III) and Fe(III) solutions with a base, rather than the polynuclear complexes of the hydrolysis schemes.

A survey of the literature also showed that the method used for mixing the aluminum salt solution with the alkali-containing solution in the hydrolysis experiments may be significant. One must avoid local hydroxyl ion concentrations appreciably larger than the overall concentration as this will result in the formation of a precipitate that is most reluctant to redissolve even though it is unstable. Therefore, our first objective was to design a vessel and develop a procedure that would eliminate such mishaps and enable us to follow continuously

the pH of solutions to which a base is slowly added.

In 1937, Willard and Tang (15) used the reaction of urea with water to precipitate  $\text{Al}^{3+}$  ions from a homogeneous solution. At temperatures above about 70°C urea reacts with water to give the overall reaction



The mechanism of this reaction was studied by Shaw and Bordeaux (16). Since the urea molecules are distributed homogeneously in the solution the  $\text{OH}^-$  ions are also generated homogeneously throughout the system and thus the occurrence of local  $\text{OH}^-$  ion concentrations markedly higher than the average value is avoided.

However, the urea method has some drawbacks:

- (i) The temperature of the solution must be above 70°C to yield a practicable reaction rate.
- (ii) The rate of  $\text{OH}^-$  generation varies with solution pH; hence, it is difficult to calculate accurately the amount of  $\text{OH}^-$  liberated as a function of time.
- (iii) Carbon dioxide released in the decomposition of urea can give rise to  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions in solution, which may influence the hydrolysis of the aluminum ions.

We have therefore developed an *injection* method that permits the homogeneous distribution of the added base solutions (sodium or potassium hydroxide). As a check of the achievement of homogeneous distribution of  $\text{OH}^-$  ions in the system by this method, the results were compared with those obtained with the urea method. Next the injection method was used to obtain titration curves at 24°, 28°, 40°, 60°, and 90°C.

## MATERIALS AND METHODS

### *Apparatus*

The experiments were carried out in two double-walled Pyrex glass vessels of similar design (i.d. about 20 cm). Important details

of the reactor are shown schematically in Fig. 1. Considerable effort has been spent on assuring vigorous mixing of the reactants. To prevent vortex formation, three vertical glass baffles are built into the inner wall of the cylindrical vessel.

Agitation is achieved by two stirrer blades attached to a shaft mounted centrally in the container (see Fig. 1). The shaft is driven by a variable speed motor, generally at a speed of 1200 rpm. The shaft in one of the reactors is constructed of stainless steel and in the other of Pyrex glass. The flow pattern created by the design of the stirrer blades is roughly indicated in the sketch of the apparatus.

It is well-known that large shear forces cannot be exerted at a gas-liquid interface. By letting drops of alkali solution into the agitated aluminum solution conditions are ripe for the creation and persistence of local concentration inhomogeneities. This likelihood may be avoided by introducing the alkali solution through a capillary tube with its tip submerged below the solution-gas interface. The large shear stresses needed for rapid mixing are then maintained by such an injection method. Diffusion of ions from the outer solution into the capillary is prevented by the relatively small diameter of the tube ( $\sim 0.1$  mm). The alkali solution in the capillary is only slightly agitated; therefore, penetration of Al solution into the capillary will set up high concentrations of hydroxyl ions at the liquid-liquid boundary. Prevention of solution penetration is achieved in the continuous injection by keeping the base solution in the capillary under a regulated nitrogen pressure of about 50 mm Hg. In the reactor vessel containing the steel shaft the alkali solution is injected from a one-liter glass cylinder via the capillary tube. In the other vessel, a peristaltic pump (Gilson 702) adds the alkaline solution to a small volume (about 50 cm<sup>3</sup>), which is kept at a pressure of 50 mm Hg and then connects to the injection capillary. All capillaries are constructed of teflon to avoid heterogeneous nucleation of insoluble aluminum compounds at their tips, as was observed with

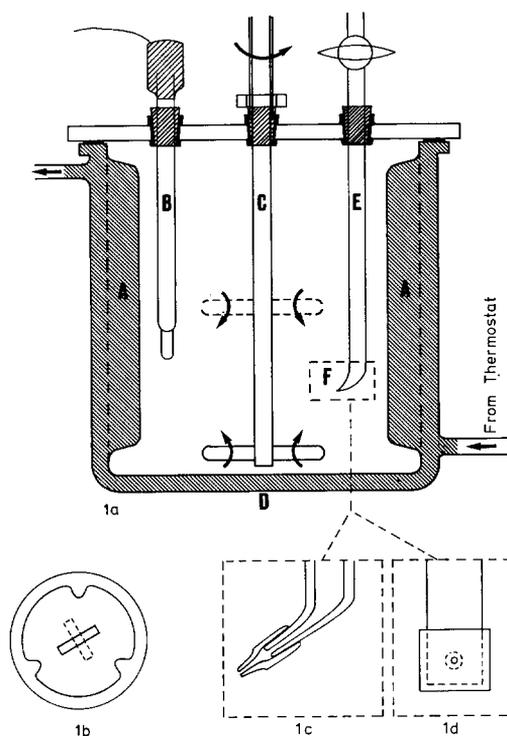


FIG. 1. Sketch of reactor used in injection experiments. (a) Diagram of reactor: A, baffles; B, electrode; C, stirrer; D, double-walled glass vessel; E, injection system; and F, injection tip (see also 1(c) and 1(d)). (b) Cross section through vessel showing baffle arrangement and stirrer blade orientation. (c) Injection capillary tip. (d) Alternative injection tip; glass tube with teflon sleeve, ejection through 0.1-mm diam hole in teflon.

glass capillaries. Injection flow rates of the order of 1 ml min<sup>-1</sup> are commonly used.

The temperature of the vessels and their contents is regulated by circulation of water from a thermostat through the space between the inner and outer walls of the reactor. The vessels are also equipped with a reflux cooler.

A glass lid provided with a number of inlets for inserting electrodes, a thermometer, and pipettes for drawing solution samples is attached snugly to the cylindrical vessel with a rubber gasket and vertical clamps.

The pH measurements are made either with a Philips pH meter (PR 94-03) or an Orion pH-mV meter (model 801) combined with an automatic electrode switch (Orion 855) and a

digital printer (Orion 851). Ingold glass electrodes (HA 401-60) are used and are calibrated at the start of each experiment with Electrofact buffer solutions (pH = 4.0 and pH = 7.0 at 20°C).

Two checks were made of the intensity of mixing in the vessels. On addition of 3 ml of a concentrated potassium permanganate solution, the reactor solution was observed to be uniformly colored in a matter of 0.1 sec. A 1.5 *M* sodium hydroxide solution was injected through a capillary tube into a stirred 0.1 *M* nitric acid solution at a relatively high flow rate of 3 ml min<sup>-1</sup>. The pH of the solution was measured simultaneously with two sets of electrodes, one situated near the point of injection and the other at a higher level. No significant difference in the pH values registered by these electrodes could be detected.

### Materials

All chemicals were of analytical or anala R grade. Twice distilled and demineralized water was used and gave identical results. Purified solid sodium or potassium hydroxide was dissolved in CO<sub>2</sub>-free water. The solutions were standardized against weighed amounts of oxalic acid. CO<sub>2</sub>-free solutions obtained by boiling and then stored under nitrogen gave results similar to solutions with the normal amounts of dissolved CO<sub>2</sub>. In all of the tests reported here aluminum nitrate was used. No obvious differences were observed in the hydrolysis studies when using sodium or potassium hydroxide.

### Experimental procedure

(a) *Urea decomposition method.* Aluminum nitrate solutions (0.50 and 0.050 *M*) were heated to 90°C. The pH of the solution was adjusted to 1.0 by addition of concentrated nitric acid. A concentrated urea solution previously heated to about 50°C (no decomposition results at this temperature) was then added. On this addition the temperature of the mixed solution dropped to about 85°C but within 15 min the desired temperature (90°C)

was again reached. After addition of urea the pH of the solution was again adjusted to 1.0. The change in pH with time was then registered on a recorder.

With aluminum concentrations of 0.5 *M* and 0.05 *M* the initial urea concentrations were 1.500 *M* and 0.225 *M*, respectively. The solution volume after mixing reached 4 l.

(b) *Alkali injection method.* Solutions containing 2.0 or 0.20 moles of aluminum nitrate in 2.75 l were brought to the desired temperature. Again the solutions were acidified to a pH of 1.0 or less by addition of concentrated nitric acid. By dilution of CO<sub>2</sub>-free stock solutions of sodium or potassium hydroxide, solutions 5.15 *M* and 0.866 *M* were prepared and used in the injection studies. After injection of 1.25 l of alkali solution the averaged total aluminum concentration in the system became either 0.5 *M* or 0.05 *M*.

To prevent clogging of the injection capillary by precipitation, at the start of the experiment the injection tube was filled with water. After the solution reached the desired temperature and its pH was adjusted to about 1.0 the capillary was lowered into the solution and the pressure above the hydroxide solution was adjusted to between 30 and 100 mm Hg. Injection of the 1.250 l of alkaline solution took about 25 hr.

### Auxiliary measurements

During the titration experiment 20-ml pipette samples were taken at predetermined time intervals or at fixed pH values. These samples were taken for investigation by light-scattering and for electrophoretic measurements. Hundred-milliliter samples provided, after filtration, solids for x-ray diffraction study. The solids were washed and then dried at 120°C.

The electrophoretic velocity of the particles was determined in a Rank Brothers apparatus. Preliminary light-scattering determinations were done in an instrument manufactured by the Société d'Instruments de Contrôle et d'Analyses (model Fica 50). The solutions were

filtered through millipore filters (50 nm) directly in the measuring cells. The cells were then centrifuged in a Beckman preparative centrifuge at 20 000 rpm.

## RESULTS

### *Urea Decomposition Method at 90°C*

The rate of change of pH of solutions with and without  $\text{Al}^{3+}$  at 90°C is shown in Fig. 2. A characteristic feature of curve A (pure 0.8 M urea solution) is the steep jump in the pH value from 2 to about 5.5 followed by a gradual approach to a constant value at 7.0. Curves B (0.5 M  $\text{Al}^{3+}$ ) and C (0.05 M  $\text{Al}^{3+}$ ) resemble the urea decomposition curve up to a pH value of approximately 2.3. The initial rise in pH is steeper for the more concentrated aluminum ion solution. In this region of the pH-time curve the  $\text{OH}^-$  ions liberated by urea decomposition are undoubtedly neutralizing the free acid present. The neutralization rate must be a function of the initial concentration of the urea, which explains the difference in curves B and C.

Binding of  $\text{OH}^-$  ions by aluminum is heralded by the appearance of an extended near-horizontal platform in curves B and C. The pH range over which this plateau extends lies roughly between pH 2 and 2.5 for curve B and between the pH values 2.5 and 3.0 for curve C. A second steep rise in pH then follows the termination of the plateau. It is in turn again succeeded by a second inclined platform. This second plateau, which rises more steeply than the first one, went unnoticed (or was undetectable) in continuous titration experiments reported by other authors (17–19). In curve B this platform begins at a pH value of 4.2 and in curve C at a slightly higher value of 4.5. A third jump in pH followed by a leveling off to a near constant value beyond pH 6, concludes the titration curve.

Up to the point where the second platform begins the solutions remain visually clear. Beyond this point the solutions slowly take on a bluish tint and display the well-known Tyndall effect. At higher pH values a white

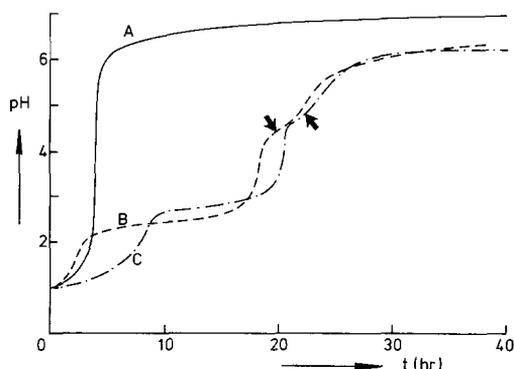


FIG. 2. pH curves for precipitation by decomposition of urea at 90°C. Curve A: Decomposition rate of urea (0.8 mole/liter) in absence of aluminum salt. Curve B: pH curve for 0.5 M aluminum nitrate; initial urea concentration 1.50 M. Curve C: pH curve for 0.05 M aluminum nitrate; initial urea concentration 0.225 M. Arrows indicate the point of visible precipitate formation.

precipitate is formed in the 0.05 M aluminum solution. A very viscous gel showing thixotropic behavior forms at higher pH values in the 0.5 M  $\text{Al}^{3+}$  solution.

### *Injection at Different Temperatures*

To determine whether the base solution added during the continuous titration is homogeneously distributed by the injection technique, injection experiments were also done at 90°C. The results obtained in these tests are compared with those of the urea decomposition method in Fig. 3. A comparison is made between the 0.05 M  $\text{Al}^{3+}$  solution with urea and a solution without urea with a starting concentration of 0.072 moles/l of aluminum nitrate. After the titration was completed, the total Al concentration would have been 0.05 M if no precipitation took place.

An exact superposition of these two curves is not possible because the time scales cannot be made to coincide. Although the decomposition of urea leads to a strictly homogeneous liberation of hydroxyl ions, the rate of generation is not constant but a function of the pH. The time scales have therefore been adjusted to give the best possible fit. The shape of the

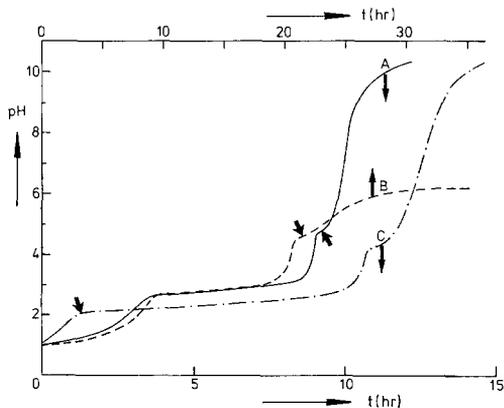


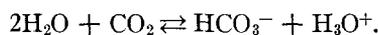
FIG. 3. Comparison of pH curves obtained with the injection and the urea decomposition method. Curve A: injection of KOH; initial aluminum nitrate concentration 0.072 *M*. Curve B: urea decomposition, aluminum nitrate concentration 0.05 *M*. Curve C: injection of KOH; initial aluminum nitrate concentration 0.72 *M*. Heavy arrows indicate the points of visible precipitate formation.

two curves is similar. The first platform is centered at about a pH of 2.8 for both curves and the beginning of the second inclined plateau is only slightly displaced from a pH of 4.5 for the urea curve to a pH of 4.7 for the injection curve. The leveling off of the urea curve at a pH around 6 is, of course, inherent in the method of generation of OH<sup>-</sup> ions and thus is not displayed by the injection curve. The appearance of a colloidal solution and the development of a precipitate in the later stages of the titration also coincide with the observations made in the urea experiment.

A third curve, an injection with KOH in a solution initially 0.725 *M* in aluminum nitrate is also included in Fig. 3. This curve agrees as to shape almost perfectly with its equivalent, curve B of Fig. 2. The gel-like behavior of the precipitate observed at higher pH values is also found here. Light-scattering experiments made with samples taken from injection and urea decomposition experiments were also found to give comparable increases in the weight-averaged molecular weights at rising pH values. We are confident that the data presented in Fig. 3 and other results not shown confirm the achievement of a near-

perfect homogeneous distribution of the injected alkali provided the rate of injection and the concentration of the reactants are not too high.

It might be argued that the existence of the second platform is related to the formation of hydrogen carbonate ions according to the reaction



However, since injection experiments with carbonate-free alkali hydroxide solutions yield similar pH curves, this possibility must be rejected. Furthermore, at room temperature the inflection point due to the above reaction should occur at a pH value of 6.33, which is higher than that observed in our studies.

A set of injection experiments was carried out at five different temperatures (24°, 28°, 40°, 60°, and 90°C). The same characteristic shape obtained at 90° was found at all the other temperatures. The development of a second plateau in the titration curve when the titration is performed continuously, slowly, and under homogeneous injection is now convincingly documented. This second plateau implies the existence of a second stage in the hydrolysis-precipitation process. The detailed composition of the continuous titration curve at 24°C is illustrated in Fig. 4.

The pH value of the solution during the titration was registered at successive intervals of 1 min with the aid of the Orion digital printer. A computer program was written to use these data for the differentiation of the pH-time curve. A plot of the differentiated curve is also given in Fig. 4. As may be seen from this figure, such a plot brings out beautifully the characteristic features of the titration curve. The first near-horizontal platform is represented by the shallow minimum of the differentiated curve. The second inclined platform transforms to a deep narrow minimum in the differentiated plot. Note that in this experiment the first appearance of a colloidal solution coincides almost exactly with the minimum point in the narrow trough.

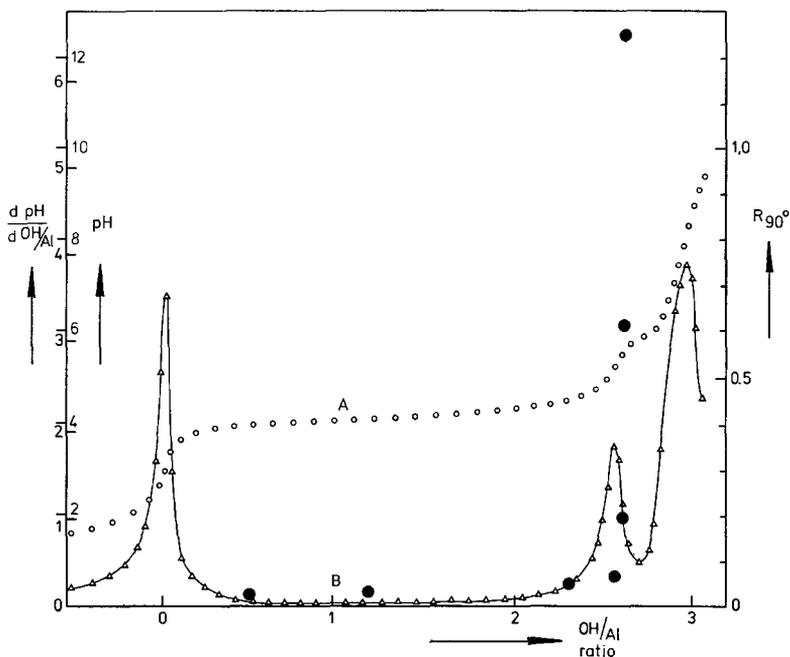


FIG. 4. Precipitation by injection at 24°C. Curve A: Experimental titration curve, pH versus OH/Al ratio. Curve B: Derivative of titration curve, d(pH)/d(OH/Al) versus OH/Al. Large circles give light scattering data (Rayleigh Ratio, R<sub>90°</sub>) for a 0.07 M Al(NO<sub>3</sub>)<sub>3</sub> solution titrated with NaOH.

In Table I the pH of the midpoint of the first platform (the lowest point in the broad shallow minimum of the differentiated curve) and of the deflection point in the second platform (lowest point of the narrow trough of the differentiated curve) are summarized for all the experiments. The changes in the pH values

of the characteristic features with temperature can be ascribed to within ±0.15 pH units to the shift of the equilibrium of the water dissociation (20) with temperature. This suggests that regardless of temperature the same processes are responsible for the observed changes.

TABLE I  
CHARACTERISTICS OF INJECTION AT DIFFERENT TEMPERATURES

Temperature °C	Initial concentration of Al (NO <sub>3</sub> ) <sub>3</sub> (M)	Alkali	pH midpoint first plateau	pH midpoint second plateau	pH visible precipitate
90	0.072	KOH	2.80	4.75	4.9
90	0.72	KOH	2.3	4.3	2.0
60	0.072	KOH	3.4	5.4	5.6
40	0.072	KOH	3.8	5.8	5.9
28	0.072	KOH	4.0	6.1	6.1
24	0.072	NaOH	4.1	5.9	6.1
Comparative data for urea decomposition					
90	0.07		2.9	4.8	4.9
90	0.7		2.35	4.4	4.5

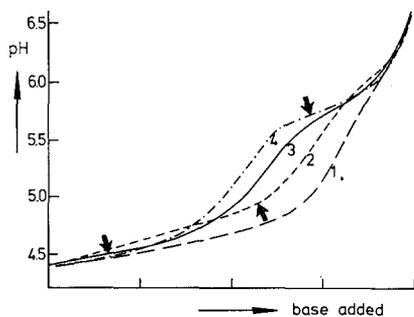


FIG. 5. Illustrating the effect of methods of alkali addition on the shape of the pH curve at 25°C. (1) Fast dropwise addition (5 ml/min). (2) Slow dropwise addition (1.8 ml/min). (3) Fast injection (10 ml/min). (4) Slow injection (1 ml/min). Aluminum nitrate concentration (initial). Arrows indicate the points of visible precipitation.

#### *Effect of Method of Alkali Addition*

The dependence of the location of the second platform on the method and rate of addition of alkali was also investigated. Four experiments were performed including a fast (5 ml/min) and a slow (1.85 ml/min) dropwise addition of base and a fast (10 ml/min) and slow (1 ml/min) injection of base. The relevant parts of the observed titration curves are depicted in Fig. 5. A rapid dropwise addition of alkali is seen to eliminate completely the second platform, but at a much lower rate of dropwise addition its presence may be noted. Even at a relatively high injection rate this plateau, though diminished in extent, is still clearly visible. Except for the fast dropwise addition the points at which a precipitate becomes first visible are indicated by arrows on Fig. 5. In the fast dropwise experiment a precipitate already appeared at a pH value of 2.0. These experiments clearly demonstrate why previous investigators failed to observe such details in the titration curves.

#### *Structure of Precipitates*

Table II summarizes the results obtained by x-ray diffraction methods with samples at various temperatures, pH values, and aging times. At pH values below 10 the solids are found to be either amorphous or micro-

crystalline (as evidenced by line broadening effects). At temperatures below 60°C the material is either amorphous or a poorly crystallized bayerite  $[\text{Al}(\text{OH})_3]$ . These precipitates consist of very small particles that are difficult to separate from the liquid phase by filtration. Well-crystallized bayerite at these temperatures is present in solutions at pH 10. As far as can be deduced from the diffraction patterns, bayerite is the only crystalline form of aluminum hydroxide present. If a precipitate formed at 60°C is aged in the solution at a pH of 10 then in contrast to the observations at lower temperatures, gibbsite is formed. The precipitates at 90°C give patterns that may be ascribed to gelatinous boehmite (19).

Ginsberg, Hüttig, and Stiehl (21) investigated the structure of precipitates obtained by the usual method of dropwise addition of alkali to acid aluminum salt solutions. These authors observed bayerite at room temperature only when the pH of the solution exceeded a value of 11. This observation is in reasonable accord with our determinations. At temperatures above 80°C they found only poorly

TABLE II  
X-RAY STRUCTURE OF PRECIPITATES

pH	Temperature (°C)				
	24	28	40	60	90
6	A				A (U) A
7	Microbay		A	A	A
8	Microbay		A	A	
9	Microbay		A	A	Gelbo
10	Microbay	Bay	A	Microbay	Gelbo (Gibb)
	↓		↓	↓	(Bay)
	Bay		Bay	Bay	
				↓	
				Gibb	

A = amorphous; microbay = amorphous with few diffuse lines of bayerite; gibb = gibbsite; bay = bayerite; Gelbo [gelatinous boehmite, Lippens (19) aged precipitate] →; U (precipitated with urea).

All other precipitations by injection. At 24°C alkali used was NaOH; at all other temperatures KOH was used.

crystallized solids. In contrast to the finding of Ginsberg *et al.* we did not obtain diffraction patterns ascribable to gelatinous boehmite at room temperature. Fast dropwise alkali addition, however, does give such a precipitate. This clearly indicates that the method of alkali addition can effect the crystal structure of the resultant precipitate.

#### DISCUSSION

By means of potentiometric titrations of acidified aluminum nitrate solutions we have clearly demonstrated certain characteristic features of the pH-time curves. These features depend on the experimental procedure, are perfectly reproducible, and are almost independent of the temperature and concentration range studied.

Our continuous titration experiments show the pH curve to be partitioned into two plateaus by three pH jumps. These characteristics, in particular the observed second plateau, were also noticed by Hantelmann and Kohlschütter (18) in 1941 and in the fifties by Denk and his co-workers (22-24). Unfortunately their studies received but scant attention. However, there are important distinctions to be made between the work of these investigators and our own study. The special experimental procedures followed by the German authors (aging at OH/Al ratios between 2 and 2.5) is shown not to be essential for the appearance of the second plateau. It is possible to observe this feature in continuous titration experiments if during base addition the occurrence of locally high OH<sup>-</sup> concentrations is eliminated.

A new insight into the precipitation process of aluminum hydroxide is gained from these reproducible curves. The inflection point located in the first pH jump at low pH (Fig. 4) determines the equivalence point in the neutralization of the excess acid initially present. Acidification of the initial titrant solution is important to avoid chance precipitation of the hydroxide which is reluctant to dissolve and also to assure that the only dissolved aluminum species at this stage are hydrated

trivalent Al<sup>3+</sup> cations. Acidification to a pH below one does not change the shape of the curve at all. The inflection point (maximum in the differentiated curve, Fig. 4) of the second jump in nitrate solutions lies at an OH/Al ratio of about 2.5. Up to this point we never observed a precipitate or colloidal particles in the aqueous phase even after standing for months. One may conclude that the second platform is associated with the formation of the solid phase. This conclusion is supported by evidence from light-scattering experiments (Fig. 4). The scattering data obtained on samples of different ages (1 week to 2 months) all yield identical results. A visible precipitate is always observed at an OH/Al ratio in excess of 2.5. The inflection point of the third pH jump falls at an OH/Al ratio of three which determines the equivalence point for the neutralization of the Lewis acid Al<sup>3+</sup>. Micro-electrophoretic measurements show the particles to be positively charged up to a pH value of about 10 and negative beyond this point.

If, as has been more common in previous investigations, the hydroxyl ion concentration is rapidly and nonuniformly added to the system a different behavior is observed. Dependent on the rate of alkali addition the solid phase is formed at OH/Al ratios less than 2.5. As a result of this, the second plateau becomes obscured and may be completely suppressed.

From x-ray diffraction studies a difference in the structure of the solid product is also noted. The continuous titration method yields small particles resulting in an amorphous product which at higher pH values transforms to pure crystalline bayerite. Poorly crystallized solids (with some bayerite and boehmite lines) are the products of standard dropwise titration methods. This again suggests that the mechanisms by which the two precipitate types are formed are different.

Further work to elucidate the formation of solid hydrated alumina from acid solutions (kinetics of the hydrolysis-precipitation-dissolution reactions) as well as the character-

ization of the structure, texture, and properties of the solid phase are now in progress.

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#### REFERENCES

1. BROSSET, C., *Acta Chem. Scand.* **6**, 910 (1952).
2. AVESTON, J. *J. Chem. Soc.* 4438 (1965).
3. MESMER, R. E., AND BAES, C. F., JR., *Inorg. Chem.* **10**, 2290 (1971).
4. MACDONALD, D. D., BUTLER, P., AND OWEN, D., *J. Phys. Chem.* **77**, 2474 (1973).
5. KUBOTA, H., *Diss. Abstr.* **16**, 864 (1956).
6. NAZARENKO, V. A., AND NEVSKAYA, E. M., *Russian J. Inorg. Chem.* **14**, 1696 (1969).
7. BROSSET, C., BIEDERMANN, G., AND SILLÉN, L. G., *Acta Chem. Scand.* **8**, 1917 (1954).
8. SILLÉN, L. G., *Quart. Rev.* **13**, 146 (1959).
9. MATIJEVIC, E., MATHAI, K. G., OTTEWILL, R. H., AND KERKER, M., *J. Phys. Chem.* **65**, 826 (1961).
10. JANDER, G., AND WINKEL, A., *Z. Anorg. Allgem. Chem.* **200**, 257 (1931).
11. RAUSCH, W. V., AND BALE, H. D., *J. Chem. Phys.* **40**, 3391 (1964).
12. PATTERSON, J. H., AND TYREE, S. Y., JR., *J. Colloid Interface Sci.* **43**, 389 (1973).
13. WEISER, H. B., AND MILLIGAN, W. O., *Chem. Rev.* **25**, 1 (1939).
14. VAN DER GIESSEN, A. A., *Philips Res. Repts. Suppl.* No. 12 (1968).
15. WILLARD, H. H., AND TANG, N. K., *Ind. Eng. Chem. Anal. Ed.* **9**, 357 (1937).
16. SHAW, W. H. R., AND BORDEAUX, J. J., *J.A.C.S.* **77**, 4729 (1955).
17. WEISER, H. B., MILLIGAN, W. O., AND PURCELL, W. R., *Ind. Eng. Chem.* **33**, 669 (1941).
18. KOHLSCHÜTTER, H. W., AND HANTELMAH, P., *Z. Anorg. Allgem. Chemie* **248**, 319 (1941).
19. LIPPENS, B. C., Ph.D. dissertation, Delft University, Delft, The Netherlands.
20. Gmelins Handbuch der Anorganische Chemie, Teil Sauerstoff 8. Auflage Lieferung 5, p. 1619.
21. GINSBERG, H., HÜTTIG, H., AND STIEHL, H., *Z. Anorg. Allgem. Chem.* **309**, 233 (1961).
22. DENK, G., AND BAUER, L., *Z. Anorg. Allgem. Chem.* **267**, 89 (1952).
23. DENK, G., AND ALT, J., *Z. Anorg. Allgem. Chem.* **269**, 244 (1952).
24. KLEINERT, G., AND DENK, G., *Z. Anorg. Allgem. Chem.* **301**, 171 (1959).