

Precipitation from Supersaturated Aluminate Solutions

IV. Influence of Citrate Ions

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The influence of citrate on the precipitation in unseeded and seeded supersaturated aluminate solutions is reported. At high Cit/Al ratios (>0.1) extensive complex formation takes place but already at low ratios (10^{-4} – 10^{-2}), where this effect hardly changes the supersaturation, the precipitation rate is strongly retarded. The formation of bayerite appears to be more sensitive to citrate concentration than that of pseudoboehmite and can even be prevented at rather low Cit/Al ratios (~ 0.01). Transformation of pseudoboehmite into bayerite is also inhibited at these low Cit/Al ratios. Citrate may therefore be used to selectively precipitate pseudoboehmite. A simple adsorption model is introduced to explain the role of citrate in retarding growth. Evidence is presented to show the dual role played by citrate in the nucleation of bayerite as revealed by long time lags in relaxation experiments. More nuclei are generated with increasing citrate concentration but the growth of these particles is slowed down.

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INTRODUCTION

In the precipitation of $\text{Al}(\text{OH})_3$ from supersaturated aluminate solutions, solid modifications differing considerably in their state of structural order may be formed. In a systematic study of this precipitation behavior conducted with the constant pH relaxation technique, it was observed that the most soluble and least ordered phase was the first one to develop (1, 2). The precipitation sequence: amorphous phase \rightarrow pseudoboehmite \rightarrow bayerite \rightarrow gibbsite was noted to be dictated largely by the supersaturation degree. We also reported (3) that the presence of Li^+ promoted a drastic and selective increase in the precipitation rate of bayerite.

This study of the effect of Li^+ on the precipitation behavior in supersaturated alkaline solutions prompted us to initiate an investigation of the role of other foreign additives. In a series of preliminary experiments a number of additives, for example, citrate, sulfate, fluoride, and others were in-

troduced. We selected for further research the citrate ion, because it was noted to influence the rate of formation of the solid phase when present in extremely small amounts. Under these conditions the supersaturation, the driving force for the precipitation reaction, will not be altered through possible complexing reactions.

Organic acids are frequently present in natural waters and in soils and a number of such acids, for example, oxalic and citric acids show strong complexing or chelating tendencies with aluminum. Kee Kwong and Huang (4) aged $\text{Al}(\text{III})$ solutions titrated to an OH/Al ratio = 3 in the presence of citrate and observed a delay (in) or even an inhibition of the formation of crystalline $\text{Al}(\text{OH})_3$. Kodama and Schnitzer (5) found in similar aging experiments that fulvic acid favored the formation of pseudoboehmite to the crystalline polymorphs, bayerite, gibbsite, and nordstrandite. It has been suggested (4, 5) that the occurrence of noncrystalline aluminum hydroxide in (slightly) acid soils and of

pseudoboehmite in European bauxites (6) are associated with the presence of these organic acids.

In this study we report on the influence of citrate on the precipitation rate and aging behavior of bayerite and pseudoboehmite.

EXPERIMENTAL

Details of the experimental setup and procedure have been given in previous publications (1-3). In most experiments the initial aluminate concentration was $4 \times 10^{-3} M$ (final volume 3 liters) and the ionic strength was kept at 0.15 M (KNO_3). The seeded growth experiments were performed by adding gibbsite particles (Merck) to the solutions just before the desired supersaturation was reached. The solid products were characterized by means of X-ray diffraction, infrared spectroscopy, electron microscopy, and the specific surface was evaluated in a Quantasorb BET adsorption apparatus.

RESULTS

a. A Survey of Various Ionic Additives

In a series of preliminary experiments the influence of various ionic additives on the precipitation kinetics of bayerite was investigated. The formation of this solid phase is in general characterized by a time lag after which precipitation starts first slowly, reaches a maximum rate, and then slows down again. A relaxation time (t_r) is defined operationally as the time at which the maximum precipitation rate is reached (1-3). The influence of the additives, the anions, citrate (Cit^{3-}), CO_3^{2-} , SO_4^{2-} , F^- , and the cations, Li^+ , Mg^{2+} , tetraethylammonium (TEA^+) on the relaxation time t_r is displayed graphically in Fig. 1. This figure gives a dimensionless plot of the ratio $t_r(X)/t_r(0)$ as a function of the logarithm of the reduced concentration X/Al , where $t_r(X)$ is the relaxation time in the presence of the particular additive at a concentration X and $t_r(0)$ is the relaxation in the absence of the additive at the same total initial con-

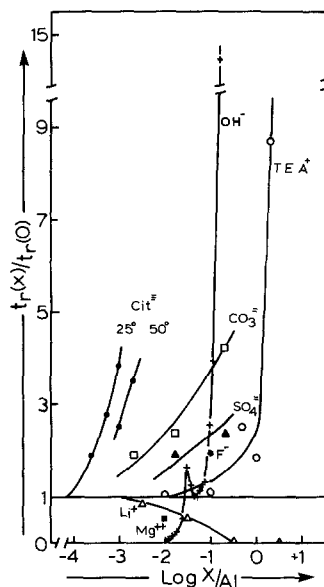


FIG. 1. Reduced relaxation time versus $\log(X/Al)$ for various additives. See text for further details.

centration Al of the aluminate anion. An initial aluminate concentration of $4 \times 10^{-3} M$ was chosen in all the experiments and the relaxation times were evaluated at $pOH = 3.85$ except for the studies with TEA^+ that were done at $pOH = 3.75$. The measurements were done at a constant temperature of $25^\circ C$ except for the experiments with TEA^+ and the one experiment with F^- at $50^\circ C$. We also include in this figure a dimensionless plot of the relaxation time versus $\log OH/Al$ at $50^\circ C$ in the absence of additives. The dimensionless time is now evaluated by introducing as reference point the relaxation time at $pOH = 3.85$ ($t_r(0)$ in the case of the other curves).

This method of organizing the experimental data provides a convenient and rapid survey of the influence of foreign additives at a fixed initial supersaturation. The relaxation time and therefore also the overall precipitation kinetics are seen to be very sensitive to the presence of different additives. With the exception of the cations Li^+ and Mg^{2+} all the tested foreign species clearly retard the formation of bayerite. It would

appear that acceleration of the precipitation process is reserved for a few cationic species which are capable of providing a precursor phase (3).

From Fig. 1 we may locate a so-called point-of-zero-(kinetic) influence (pzi) for each additive. This pzi determines for a given initial supersaturation the reduced (or absolute) concentration of the additive at which the ratio $t_r(X)/t_r(0)$ approaches unity. For example, the carbonate ion which would accumulate to high values in alkaline aqueous solutions has a pzi between 10^{-6} M ($p\text{CO}_3 = 6$) and 10^{-5} M ($p\text{CO}_3 = 5$) under the experimental conditions depicted in Fig. 1. For the citrate ion an even lower pzi is indicated. Furthermore, for those additives which retard the precipitation process a concentration at which complete inhibition ($t_r(X)/t_r(0) \rightarrow \infty$) occurs may also be evaluated (see, for example, the TEA^+ curve). The retardation and eventual inhibition effects of citrate and TEA^+ are seen to run parallel. The effect of the citrate ion is felt, however, at concentrations lower by approximately 3 decades compared to TEA^+ . This comparison should be done at the same temperature. At 50°C the citrate curve is displaced to the right of the plotted curve at 25°C but relative to the TEA^+ curve (50°C) this displacement is quite small. It is also interesting to note that although the fluoride ion is known to be a strong complexing agent for the cation Al^{3+} it would appear (albeit based on very limited experimentation) to be in alkaline solution a less effective retarding agent than the di- and trivalent anions.

The special role of the hydroxyl ion in the precipitation process is accentuated in Fig. 1. This anionic species, of course, determines directly the supersaturation and therefore the driving force for the precipitation process. The reduced relaxation times vary from zero to infinity within 1 decade change in the OH^- concentration. Within this narrow concentration range, the nature of the precipitate changes from being practically pure pseudo-boehmite (along the left-hand side and rising

branch of the total curve) to being pure bayerite (along the right-hand side and rising branch). This relaxation curve has been discussed in some detail (1, 2) and we are now interested in the possible changes introduced by additives. The influence of an accelerating additive, Li^+ , has already been reported on (3).

In the presence of citrate considerable retardation of the precipitation process is noted at low ($\sim 10^{-6}$ M) absolute concentrations (relative concentration, $\sim 10^{-3}$). Under these conditions changes in the supersaturation of the system by complexation reactions between the additive and aluminate should be hardly detectable. Also changes in the physical properties of the solution (for example, viscosity) are not expected. The observed retardation due to citrate when present in such dilute amounts must therefore be related almost entirely to its activity at the solid/solution interface. In the next section we present evidence that strong interactions between citrate and aluminate exist, to underscore this suggested surface activity.

b. Titration of Aluminate Solutions in the Presence of Citrate

Figure 2 presents acid titration curves (pH versus OH/Al) of supersaturated solutions at

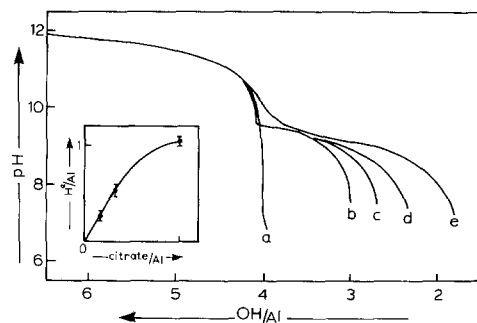


FIG. 2. Titration curves, pH versus OH/Al , at different citrate concentrations: (a) 4×10^{-3} M citrate (no aluminate present); (b) 4×10^{-3} M aluminate (no citrate present); (c) 4×10^{-3} M aluminate, citrate/Al = 1/6; (d) 4×10^{-3} M aluminate, citrate/Al = 1/3; (e) 4×10^{-3} M aluminate, citrate/Al = 1. Inset: relative excess of acid (H^+/Al) versus citrate/Al (see text).

25°C, constant ionic strength (0.15 M) but containing varying amounts of citrate. Curve b is obtained on titrating a 4×10^{-3} M aluminate solution without citrate present. This curve divides into two regions, the left-hand part describes the neutralization of the excess base (KOH) and the right-hand part corresponds to the precipitation of an amorphous $\text{Al}(\text{OH})_3$ phase (1). Curve a depicts the titration of an alkaline solution of 4×10^{-3} M citrate in the absence of aluminate. In the presence of increasing amounts of citrate, as expressed by the ratio of the concentration of citrate to that of total aluminate (Cit/Al), the amount of acid needed to neutralize the solution increases regularly. It is also noted that the additional amount of acid is consumed largely in the "precipitation" part of the titration curve. The precipitation of a solid phase was clearly observed during the titration experiment resulting in the titration curve c (Cit/Al = 1/6), in the titration experiment represented by curve d (Cit/Al = 1/3) the solution in the later stages was observed to become slightly turbid and in the titration experiment which resulted in curve e (Cit/Al = 1) the solution remained clear throughout the titration.

These experiments lead us to conclude that the excess acid needed in the titration of solutions with increasing citrate (at the absolute concentrations involved) must be due to interactions between citrate and aluminate ions. The relative excess of acid (H^+ /Al) is plotted against the reduced citrate concentration (Cit/Al) in the inset shown in Fig. 2. The demonstrated nonlinear dependence of the excess amount of acid on the citrate concentration suggests that more than one type of interaction must occur. In the titration experiment at Cit/Al = 1 (curve e) where no solid phase was observed to form, the extra amount of acid consumed accounts roughly for the formation of a complex of composition $\text{Al}(\text{OH})_2(\text{Cit})^{2-}$.

Experience teaches that specific adsorption of a particular ionic species onto special sites at a given solid/solution interface correlates

well with a strong complexation reaction between the involved chemical species in the bulk solution. The demonstrated strong complexing reactions between citrate and aluminate (Fig. 2) in the solution may therefore be cited as evidence in favor of the specific adsorption of citrate at the solid $\text{Al}(\text{OH})_3$ /liquid interface. Now at the much lower Cit/Al ratios employed in the relaxation studies depicted in Fig. 1, the amount of complexation in the solution will be negligibly small. The retardation effect of citrate at these low citrate concentrations (Fig. 1) therefore must be largely due to the specific interaction of citrate with the solid surface. At the pH of experimentation (pH \sim 10) the citrate species will exist as a trivalent anion and in the saturated alkaline solution of this pH, the solid would be negatively charged if no specifically adsorbed species (other than lattice ions) are present in the solution phase. Specific adsorption of citrate will alter the composition and charge of the inner region of the electrical double layer and be responsible for the retardation effect in supersaturated solutions.

c. The Influence of Citrate on the Precipitation of Pseudoboehmite and Bayerite

After having established in a series of preliminary experiments the retardation effect of citrate and its complexing ability in solution, we decided to follow in more detail the influence of this agent on the kinetics of precipitation of pure pseudoboehmite and pure bayerite. At 50°C the experimental conditions (pOH) can be chosen so as to separate the stage of formation of relatively pure pseudoboehmite and bayerite (1). See also the t_r versus OH/Al curve plotted in Fig. 1. The effect of varying citrate concentrations on the constant pH relaxation of supersaturated aluminate solutions (total aluminate concentration 4×10^{-3} M) under conditions where either pseudoboehmite or bayerite precipitates, is illustrated in Fig. 3.

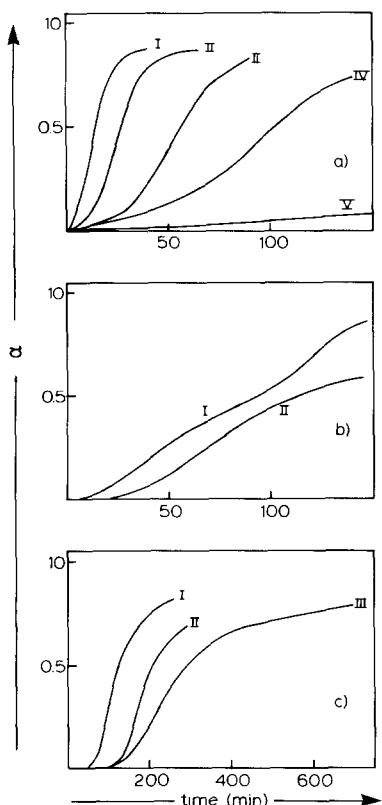


FIG. 3. Relaxation curves, α versus time (min), as a function of pOH and citrate/Al at 50°C and initial aluminate concentration $4 \times 10^{-3} M$, ionic strength 0.15 M . (a) pOH = 4.35, Cit/Al ratios: I, zero; II, 0.01; III, 0.02; IV, 0.04; V, 0.1. (b) pOH = 4.15, Cit/Al ratios: I, zero; II, 0.01. (c) pOH = 3.65, Cit/Al ratios: I, zero; II, 10^{-3} ; II, 2×10^{-3} .

In Fig. 3a typical examples of the relaxation curves, α versus time, where α is the cumulative uptake of acid at time t divided by the total amount of aluminate ($4 \times 10^{-3} M$), are given. Curve I depicts the precipitation of pure pseudoboehmite at pOH = 4.35 in the absence of citrate. The other four curves illustrate a regularly decreasing precipitation rate of this solid modification at the same pOH with increasing citrate concentration (Curve II, Cit/Al = 0.01; Curve III, Cit/Al = 0.02; Curve IV, Cit/Al = 0.04; and Curve V, Cit/Al = 0.1). At pOH = 4.15 and without citrate two stages are visible in the relaxation curve I of Fig. 3b (as indicated by two

inflection points). The first stage corresponds with the formation of pseudoboehmite, and the second stage with bayerite (2). Curve II with Cit/Al = 0.01 shows a retardation of the first stage and the inhibition of the second stage, the formation of bayerite. In Fig. 3c we note that at pOH = 3.65 where in the absence of citrate (Curve I) bayerite forms, the presence of very small amounts of citrate (Curve II, Cit/Al = 1/1000; Curve III, Cit/Al = 1/500) retard the precipitation rate of this crystalline phase. The time lag preceding the observation of detectable amounts ($\alpha \geq 0$) of solid phase is found to increase to very high values when the Cit/Al ratio is further increased. In an experiment performed at Cit/Al = 0.01, pOH = 3.85 at 25°C no formation of a solid phase could be registered over a period of 72 h. Experiments with long time lags are not attractive because drifts in the electrode potential will confuse the measurements.

Solid-state analyses revealed that in the pOH region where without citrate bayerite formed, the small amounts of citrate added (Curves II and III, Fig. 3c) did not change the nature of the precipitating phase. The characteristic conical-shaped bayerite particles (2) were still observed with a BET specific surface of about 5 m^2/g . The highest Cit/Al ratio (0.1) used in the pseudoboehmite precipitation region (see Fig. 3a) led to a product which according to IR and X-ray measurements showed only faint characteristics of pseudoboehmite. At the lower Cit/Al ratios the presence of pseudoboehmite was established without doubt. The specific surface of these precipitates vary between 300 and 350 m^2/g which is somewhat higher than that (250–300 m^2/g) in the absence of citrate. We reported in earlier publications (1–3) that pseudoboehmite when kept in suspension, transforms into bayerite. Depending on the circumstances (for example, the amount of bayerite already present) a large percentage was transformed in a period of about 3 weeks. The pseudoboehmite precipitates formed in the presence of citrate, however,

were not observed to transform into bayerite for aging times as long as 6 months at 50°C. IR and X-ray studies of these products showed instead that aging resulted in an improved pseudoboehmite material.

We note that the Cit/Al ratios introduced in the relaxation studies at pOH values where pseudoboehmite forms would lead to extremely high time lags (or nucleation periods) when applied in the region (higher pOH) where pure bayerite should form. It is therefore quite likely that at these Cit/Al ratios, the nondetectable transformation of pseudoboehmite to bayerite is largely due to the strong retarding effect exerted by citrate on the nucleation of bayerite.

On adding citrate, not at the start of a relaxation experiment but at a later time, when the nucleation period is completed, also a reduction in the rate of development of the solid phase is noted. This observation indicates that even the late stages of the growth process are influenced by the presence of citrate. To study the effect of citrate on the growth stage we performed relaxation studies in the presence of 10 g gibbsite seeds in the bayerite region. The results are presented in Fig. 4 from which we note that the rate of uptake of acid decreases consistently with increasing citrate concentration. On comparing this figure with the results shown in Fig. 3c we note the absence of a time lag in the seed experiments. Of interest is the

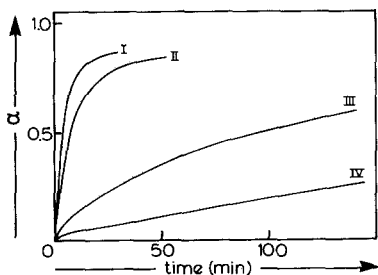


FIG. 4. Relaxation curves, α versus time (min), in seeded experiments at 50°C, pOH = 3.75, initial aluminate concentration $4 \times 10^{-3} M$, ionic strength 0.15 M . I, no citrate; II, Cit/Al = 1/333; III, Cit/Al = 1/83; IV, Cit/Al = 1/33.

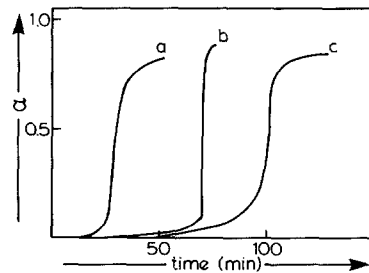


FIG. 5. Relaxation curves, α versus time (min), at 50°C, pOH = 3.75, Li/Al = 1, initial aluminate concentration $4 \times 10^{-3} M$, ionic strength 0.15 M at varying Cit/Al ratios. (a) 10^{-4} , (b) 10^{-3} , (c) 10^{-2} .

finding that at Cit/Al ratios where the relaxation times in unseeded experiments are already markedly increased only small changes in the seeded growth studies are observed.

The observation that small amounts of citrate effectively block the (detectable) nucleation of bayerite whereas addition of lithium essentially promotes fast nucleation of this phase led us to an investigation of the influence of citrate on the constant pH relaxation of supersaturated aluminate solutions in the presence of a fixed amount of lithium. Experiments were done at 50°C, an initial aluminate concentration of $4 \times 10^{-3} M$, a constant ratio Li/Al = 1 and at pOH = 3.75 where generally pure bayerite precipitates. Figure 5 illustrates the effect of three different Cit/Al ratios (10^{-4} , 10^{-3} , 10^{-2}) on the α vs time curves. The relaxation time is seen to increase with increasing Cit/Al ratios as is also observed in the absence of Li^+ but the maximum growth rate (or acid uptake rate), $(d\alpha/dt)_{\text{max}}$, is largest at the intermediate Cit/Al ratio (10^{-3}). We shall refer to this finding in more detail in the discussion.

DISCUSSION

The retarding effect of citrate on both the precipitation rate of pseudoboehmite and of bayerite is best visualized by plotting the measured relaxation time as a function of pOH at different Cit/Al ratios. This is done in Fig. 6 for an initial aluminate concentra-

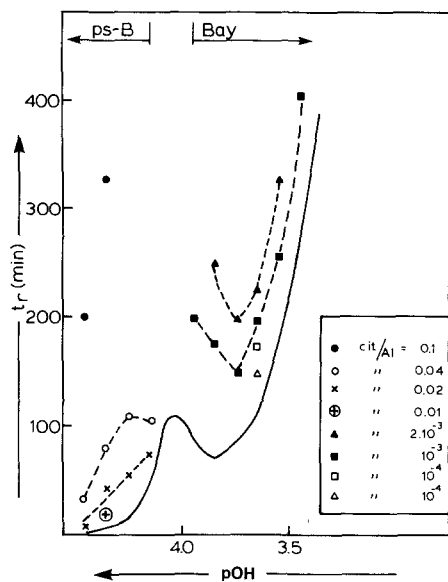


FIG. 6. Relaxation time (min) versus pOH at different Cit/Al ratios. Solid curve measured in absence of citrate. Initial aluminate concentration $4 \times 10^{-3} M$, $50^\circ C$, ionic strength $0.15 M$, Cit/Al ratios as indicated.

tion of $4 \times 10^{-3} M$ at $50^\circ C$. The curve describing the dependence of t_r on pOH in the absence of citrate has already been described in the general discussion of Fig. 1. Of importance is to note that relaxation times in the bayerite region (to the right of the minimum in the curves) are increased markedly at much lower citrate concentrations than in the pseudoboehmite region (to the left of the maximum in the curve at Cit/Al = 0). Another difference in the effect of citrate on the precipitation kinetics of these two solid modifications is that the time lag preceding detectable formation of the solid phase can be extended considerably in the bayerite region, whereas in the pseudoboehmite region no time lag (uptake of acid starts immediately) is noted even at Cit/Al = 0.1 (see Fig. 3a).

Since by a suitable choice of pOH and Cit/Al ratios both the nucleation of bayerite and the transformation of pseudoboehmite to bayerite can be avoided, citrate may be used to precipitate selectively pseudoboehmite

which then improves, in texture and structure, on aging. This is in accord with the finding of other investigators (4, 5) referred to in the introduction. We have already mentioned that Li^+ can be used to selectively precipitate bayerite. The opposite effects of citrate and lithium ions on the precipitation of bayerite allow the following generalization to be made; the most structured phase will be most sensitive to compositional changes in the precipitating medium.

A clear distinction between the nucleation and the growth stages in the precipitation process is seldom possible in the relaxation experiments. The demonstrated influence of citrate, both on the lag time in unseeded experiments and on the growth rate in seed experiments (Fig. 4) in the bayerite precipitation region provides some insight into these two stages. The discussion to follow will consider separately the growth and nucleation stages. Information about the nucleation stage will be extracted mainly from the experiments performed with a combination of Li^+ and citrate.

Growth Rate and the Influence of Citrate

We have already argued that the influence of citrate must be related to its adsorption at the solid/solution interface. Adsorption of citrate can lead to changes in, for example, surface charge and interfacial tension and can influence the kinetics of a number of elementary steps involving the incorporation of the growth unit from the solution into the growing solid phase. The observed retardation due to citrate under all the experimental conditions suggests, however, that the chief effect of this ion is to occupy certain surface sites whereby the incorporation of growth units is blocked.

This blocking effect may be described quantitatively by introducing a simple and admittedly crude model. Let a fraction θ of the surface sites available for growth be occupied by citrate. We now assume that the rate of incorporation of growth units is determined by adding two independent rates

$$R(c) = \theta \cdot R(\infty) + (1 - \theta)R(0), \quad [1]$$

where $R(c)$ is the growth rate actually measured at a concentration c of citrate in solution, $R(\infty)$ is the growth rate at sites covered by citrate, and $R(0)$ the rate at unoccupied sites. We may now define a relative growth rate r such that

$$r = \frac{R(c)}{R(0)} = 1 - \theta \left(1 - \frac{R(\infty)}{R(0)} \right) \\ = 1 - \theta Q \quad [2]$$

with Q a constant equal to unity if $R(\infty) = 0$ and equal to zero if $R(\infty) = R(0)$. If the adsorption of citrate or its occupation of surface sites may be described by a Langmuir isotherm:

$$\theta = \frac{c}{c^* + c}, \quad [3]$$

where c^* is the solution (equilibrium) concentration at which $\theta = 1/2$, then Eq. [2] may be expressed in the form

$$r = 1 - Q \left(\frac{c}{c^* + c} \right). \quad [4]$$

On inverting and rearranging the terms in Eq. [4] we find the expression

$$\frac{c}{1-r} = \frac{c^*}{Q} + \frac{c}{Q}. \quad [5]$$

A plot of $c/(1-r)$ versus c should yield a straight line and allow the parameters c^* and Q to be evaluated. We should note that an identical model has been used by Bliznakov *et al.* (7, 8) to explain growth retardation in a number of crystal growth systems.

In order to apply Eq. [5] we must find an expression for the growth rates $R(c)$ and $R(0)$. In previous publications (1, 2) we postulated empirical relations of the type:

$$\frac{d\alpha}{dt} = k_0 \cdot \alpha^{2/3} (1 - \alpha)^m, \quad [6]$$

where $d\alpha/dt$ is the rate of solid phase formation, $\alpha^{2/3}$ is a measure for the surface area, $(1 - \alpha)$ is proportional to the aluminate

concentration, and k_0 is a proportionality constant. On applying this expression to an analysis of the relaxation curves with bayerite as growing phase the exponent m was found to equal 2, whereas for pseudoboehmite m was approximately equal to unity. In the presence of citrate both the constant and the value of m were observed to change. For bayerite growth, at the different pOH values investigated, a somewhat higher value of m is found (at Cit/Al = 10^{-3} , $m = 2.3 \pm 0.1$; at Cit/Al = 2×10^{-3} , $m \approx 2.5$) also a smaller value for the constant in Eq. [6] is indicated, as is expected due to the blocking mechanism. For pseudoboehmite growth in the presence of citrate mainly the proportionality constant is lowered.

We restricted the application of Eq. [5] to the seeded growth experiments (Fig. 4) where the surface area remained essentially constant during growth and to the pseudoboehmite experiments (Fig. 3a) in which no time lag was observed. The test was not applied to the unseeded bayerite experiments because, through adsorption of citrate, the already very low Cit/Al ratios would be decreased markedly during the relaxation period which is accompanied by an increase in surface area. Our analysis of the experimental results with the aid of Eq. [6] also led us to a simpler method for testing Eq. [5] which avoids a detailed calculation of the relative growth rate and yields the same results. This method utilizes the following (rough) estimate of the relative growth rate

$$r = \frac{R(c)}{R(0)} \approx \frac{t(0)}{t(c)}, \quad [7]$$

where t is a characteristic time (inversely proportional to the growth rate in the presence of citrate (concentration c) and in the absence of citrate) for which we arbitrarily chose the time needed to reach an $\alpha = \frac{1}{3}$. The test of the crude model based on Eqs. [5] and [7] is illustrated in Fig. 7, for growth of pseudoboehmite (pOH = 4.35) and of gibbsite seeds in the bayerite region (pOH

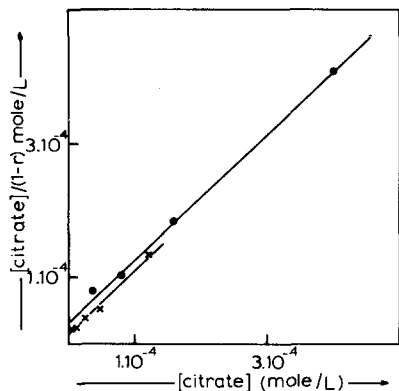


FIG. 7. Test of Eq. [5], see text. (●) Pseudoboehmite solid phase (see Fig. 3a). (×) Gibbsite seed experiments (see Fig. 4).

= 3.75). For both systems a reasonably good straight line plot as predicted by Eq. [5] is obtained. From these plots a value of $Q \approx 1$ is obtained for both growth conditions and c^* values of 4.3×10^{-5} and 1.9×10^{-5} mole/liter, respectively, for pseudoboehmite and seeded growth of bayerite. Considering the crudeness of the model, the accuracy of the measurements and the limited experimental data we may nevertheless conclude that the effect of citrate on the growth rate can be understood by assuming citrate to be very effective ($Q \approx 1$) in blocking growth sites at relatively low absolute concentrations ($\sim 10^{-5}$ mole/liter). This analysis also provides a general method for determining the effectiveness of certain additives in retarding growth as a function of pOH (in the case of oxides), temperature, and solid modification (see Fig. 1).

Nucleation of Bayerite in Citrate Solutions

Information on the nucleation step in the precipitation process is largely contained in the observed time lags and their dependence on the initial composition in relaxation experiments (see, for example, Fig. 3c). One should not forget, however, that the length of the observed time lag will also depend on the sensitivity of the measuring technique

used to detect the first appearance of the solid phase. The experimental finding that small amounts of citrate are capable of delaying or even completely preventing the formation of bayerite, therefore must imply that, in addition to retarding growth, this additive also influences the nucleation stage. This type of "stabilization" of supersaturated solutions has also been noted in other systems. For example, in the presence of tripolyphosphate (9) the nucleation of BaSO_4 is found to be strongly retarded.

In our analysis of the experimental study of the precipitation of bayerite in the absence of citrate, we have uncovered evidence that points to the heterogeneous nucleation of this crystalline phase. For example, only small changes in specific surface area (1 to 5 m^2/g), which mean relatively small changes in particle size, were measured on varying the supersaturation and the temperature of the system (1, 2). Electron microscopic studies of the growing solid (2) and an analysis of the observed growth rate (11) suggest that a two-dimensional (surface) nucleation step rather than the homogeneous nucleation of a primary particle is the rate-determining step in the precipitation process. Also the measured relaxation times and the growth rates show roughly a similar dependence on the supersaturation (2).

With this background information, the retarding role of citrate, as expressed experimentally by increased time lags, may be simply accounted for. Sites on foreign surfaces (be they dust particles, container walls, etc.) which would normally be available as nucleation centers for bayerite are occupied by citrate and thereby heterogeneous nucleation of bayerite is delayed or even prevented. This simple explanation, however, is not satisfactory when we consider evidence provided by a series of relaxation experiments in presence of both lithium and citrate, together with the established role of citrate in retarding the growth of formed bayerite particles.

The results of these experiments, of which a few relaxation curves have been given in

Fig. 5, are presented graphically in Fig. 8. Here we plot as a function of $\log(\text{Cit}/\text{Al})$ the relaxation time (t_r), the maximum growth rate ($[d\alpha/dt]_{\text{max}}$) and the BET specific surface of the end product, measured in the different experiments. We note a regular increase in t_r with increasing Cit/Al ratio. This increase was also observed in the absence of lithium except that much longer relaxation times are measured in its absence. Without Li^+ it is for practical reasons not possible to make measurements over as wide a citrate concentration range as that indicated in Fig. 8. The specific surface of the final product is also seen to increase continuously with increasing citrate concentration. Comparative electron microscopic investigations showed this increase in specific surface to be accompanied by a decrease in the average particle size and therefore with an increase in particle number. For example, at $\text{Cit}/\text{Al} = 10^{-5}$ the average particle size is about 10^4 \AA ; at $\text{Cit}/\text{Al} = 10^{-3}$ the particle size is about 10^3 \AA . It should be noted that in all the experiments bayerite was the only detectable solid phase, although at low Cit/Al ratios ($\leq 10^{-4}$) also small amounts of lithium aluminate could be detected (3). In contrast to this monotonic

increase in t_r and specific surface with increasing Cit/Al ratios, the maximum growth rate is seen to go through a clearly established maximum around $\text{Cit}/\text{Al} = 10^{-3}$. This curve gives information about the overall growth rate of the particles once they have been nucleated.

From Fig. 8 we may conclude that although more particles are generated in the presence of increasing amounts of citrate, the time (t_r) at which significant growth takes place is also increased. The most remarkable feature of these experiments is the maximum in the maximum growth-rate curve. This maximum in the curve must reflect a dual role of citrate which relates to two opposing effects illustrated by Fig. 8. At identical initial supersaturations more particles nucleate (and grow) with increasing citrate concentration (as revealed by EM and BET adsorption investigations) but the individual particles grow slower with increasing additive concentration (also revealed by seeded growth experiments).

We may show that these two effects give rise to the maximum in curve a (Fig. 8) by referring to Eq. [6]. The coefficient k_0 determines the absolute value of $d\alpha/dt$ and of $(d\alpha/dt)_{\text{max}}$. Its (k_0) value is in turn determined by a number of variables of which the most important are temperature, pH, citrate concentration, and number of particles (N). Assuming isotropic growth of monodisperse particles, the surface area of the developing solid phase may be shown (2) to be proportional to the product, $N^{1/3} \cdot \alpha^{2/3}$. The incorporation rate of growth units per unit surface area in the presence of citrate will be reduced, for example, according to Eq. [1]. In the presence of citrate we may now write for the overall growth rate

$$\frac{d\alpha}{dt} = k'_0(T, \text{pH})N(c)^{1/3} \cdot R(c) \times \alpha^{2/3}(1 - \alpha)^m. \quad [8]$$

The fact that $N(c)$ increases with citrate concentration and $R(c)$ decreases with increasing concentration then accounts for the observed maximum.

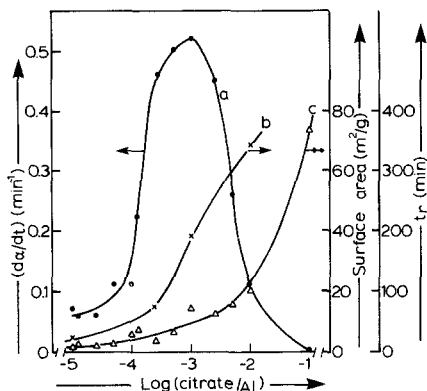


FIG. 8. Summary of experimental results obtained in relaxation experiments. Conditions: $\text{pOH} = 3.75$, $T = 50^\circ\text{C}$, $I = 0.15 \text{ M}$, $\text{Li}/\text{Al} = 1$, initial aluminate $4 \times 10^{-3} \text{ M}$. Curve a: maximum precipitation rate (min^{-1}) versus \log citrate/Al. Curve b: specific surface (m^2/g) of end products versus \log citrate/Al. Curve c: relaxation time (min) versus \log citrate/Al.

The exact shape and the height of the growth-rate curve in Fig. 8 are influenced by a complicating factor. During the precipitation process the surface area increases and especially in those experiments at low Cit/Al ratios ($<10^{-3}$) the citrate concentration in solutions is so low ($<10^{-6} M$) that it will be reduced considerably by adsorption of citrate onto the growing particles. This effect will give rise to a sudden acceleration of the precipitation rate once enough surface has been generated (see Fig. 5). At the higher Cit/Al ratios this effect will be less pronounced as the relative decrease in citrate concentration will be smaller and as a result sufficient citrate remains in solution to retard the growth.

Rizkalla (9) and Naono (10) tried to explain the absence of precipitation of, respectively, $BaSO_4$ and $SrSO_4$ in the presence of tripolyphosphate by an increase in the free energy for the formation of a critical nucleus. Our results indicate that the formation of nuclei is actually facilitated by an adsorbing (or complex forming) species but that this adsorption makes further outgrowth of the nuclei more difficult. At the concentrations of citrate employed in these experiments the change in supersaturation due to complexing effects is negligible. In this sense the citrate does not directly influence the nucleation process, but by screening through adsorption,

the nucleated particle from the bulk solution it apparently forces the supersaturated system to create more nuclei in order to compensate for the growth retardation.

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