Inhibition of Aluminum Oxyhydroxide Precipitation with Citric Acid

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Received March 29, 2005. In Final Form: July 29, 2005

Citric acid has been shown to act as an agent for increasing the solubility of aluminum oxyhydroxides in aqueous solutions of high (>2.47 mol/mol) hydroxide-to-aluminum ratios. Conversely, citric acid also colloidally stabilizes particles in aqueous suspensions of aluminum-containing particles. Solutions of aluminum chloride, with and without citric acid added, were titrated with NaOH(aq). The presence and size of particles were determined using quasi-elastic light scattering. In solutions that contained no citric acid, particles formed instantaneously when NaOH(aq) was added but these were observed to rapidly diminish in size, disappearing at OH/Al ratios below 2.5 mol/mol. When the OH/Al ratio was raised beyond 2.5 by adding more NaOH(aq), suspensions of colloidally stable particles formed. Large polycations containing 13 aluminum atoms were detected by ^{27}Al solution NMR in citric-acid-free solutions with OH/Al ratios slightly lower than 2.5. In comparison, adding citric acid to solutions of aluminum chloride inhibited the formation of large aluminum-containing polycations. The absence of the polycations prevents or retards the subsequent formation of particles, indicating that the polycations, when present, act as seeds to the formation of new particles. Particles did not form in solutions with a citric acid/aluminum ratio of 0.8 until sufficient NaOH(aq) was added to raise the OH/Al ratio to 3.29. By comparison, lower amounts of citric acid did not prevent particles from forming but did retard the rate of growth.

Introduction

Aluminum contamination of soil and groundwater has led to increased research into the speciation of aluminum-containing compounds within natural waters,[1] soil,[2] and blood serum.[3] As a result, interest in the solubility and nature of aluminum-containing compounds has been centered within the physiological pH range of 6−9.[4,5] Of special interest has been the role of citric acid in increasing the concentration of aluminum in principally aqueous media such as blood.[3,5] Our interest is in the nature and solubility of aluminum-containing compounds at high pH (pH ≥ 10) and the effect low molecular weight organics, such as citric acid, has on these compounds under such conditions. Existing data on aluminum solubility at high pH appears to be limited to the primary aluminum-containing species observed in thermodynamically stable solutions.[6] However, the speciation of aluminum under high pH conditions is complex, and the limited data hinders the remediation of hazardous waste, especially that found in the storage tanks for radioactive liquid wastes.[7]

Aluminum-containing phases constitute the bulk of solids precipitating during the processing of radioactive tank wastes.[7,8] Processes designed to minimize the volume of high-level waste through conversion to glassy phases require the transportation of waste solutions near-saturated with aluminum-containing species from a holding tank to a processing center. The uncontrolled precipitation and/or gelation of aluminum-containing substances within transfer lines results in clogged pipes and fouled ion exchangers, with the potential to shut down processing operations.[8] Proposed methods for preventing precipitation include (i) increasing the solubility of aluminum in high pH solutions or (ii) stabilizing particles in high pH suspension.[7]

Past work by our group dealt with the stabilization of aluminum oxide powders using polyelectrolytes (e.g., poly(acrylic acid)) and citric acid as dispersants.[9−12] The strong citrate−alumina surface complex is known to effectively disperse colloidal alumina particles and reduce suspension viscosity.[13] An effective dispersant provides a steric, electrostatic, or electrosteric barrier to particle aggregation.[9−12] Such agents can also act to reduce aggregate size if the agglomerates are first broken up, usually by attrition, and the surfaces are then coated to prevent aggregation.[14]

If the dispersant has functional groups that readily form chemical complexes with surface atoms, then the com-

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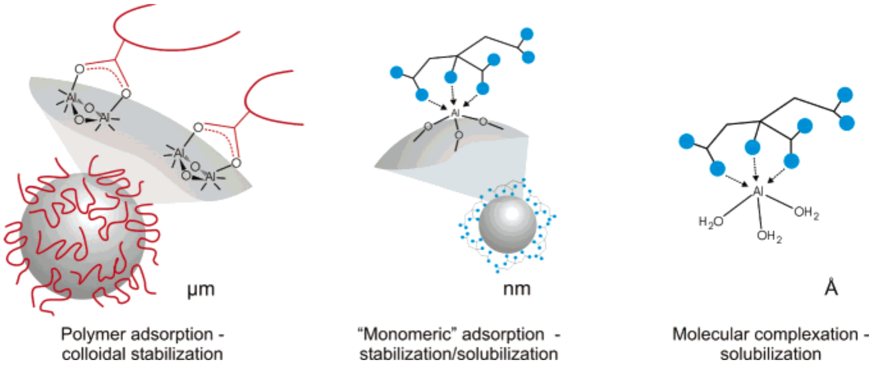

Figure 1. Mechanisms of molecular complexation and colloidal stabilization. Interactions between the complexing agent and the target atom scales from the microscale (surfaces) to the atomic. "Stability", the continued existence of particle or molecule, can be imparted either thermodynamically or kinetically.

plexation of surface atoms is regarded as chemically similar to the complexation of free ions in solution.[15,16] In this view, metal–ligand complexes range across length scales, from the microscopic to the molecular (Figure 1). In the latter case, the small number of constituent atoms (coupled with a large solvation layer) renders the complex soluble.[15] In a like manner, particle surface atoms can be removed from the surface—dissolve—if complete coordination can be achieved by active complexing agents.[17,18] For example, a surface coordination model has been developed to describe the weathering of oxide minerals by aqueous systems.[19,20] In this model, dissolution is promoted through specific interactions between the ligand and the oxide surface. Ligands containing two or more donor atoms (such as citric acid) were shown to be particularly effective in severing the bonds between the surface atom and the body of the oxide surface.[19,20] However, if only partial complexation of the surface atoms occurs, dissolution of the surface atoms can be inhibited as the surface ligands now act to inhibit further interaction between the particle surface and free ligands remaining in solution.[15−18,21]

These similar chemistries, one that promotes dissolution and another that provides surface inhibition, imply that both mechanisms will be observed in a system containing a single complexing agent. Previous work gives examples of systems in which the complexing agent appears to raise the concentration of aluminum in the suspension media, interpreted as partial dissolution of the particles[15−18,21] and/or the fragmentation of aggregates into suspensions of primary particles.[14,21] Similar observations have been made for suspensions of aluminum oxyhydroxide particles and citric acid.[3,5]

To determine chemistries that may be appropriate for use in high pH systems, it is essential to understand the modes of stabilization important in the system of interest, whether solution, suspension, or a combination. In this study, we demonstrate that citric acid is effective under conditions of high hydrolysis, increasing aluminum solubility while also stabilizing particles and maintaining stable suspensions. We explain this dual function as a combination of stabilization mechanisms, kinetic and thermodynamic, which separately are inadequate to explain our observations.

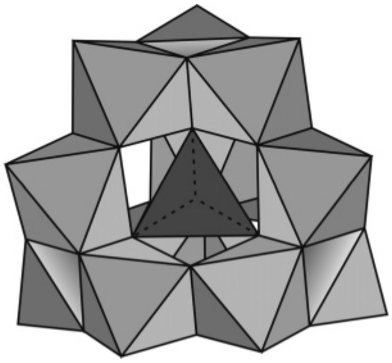

Figure 2. $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ polycation as a Keggin structure composed of a central, tetrahedrally coordinated aluminum atom connected with 12 peripheral, octahedrally coordinated aluminum atoms through bridging oxygens.[22,27]

We began with control solutions of aluminum-containing species under near-saturated conditions, determined by varying the OH/Al ratio (molar), with no citric acid added. On the basis of literature values, near saturation was achieved in aqueous solutions composed of NaOH(aq) and $AlCl_3$(aq) mixed to attain OH/Al ratios ~2.47 (mol/mol) (pH = 4.57 for the experimental solutions used), a condition under which the polycation $Al_{13}O_4(OH)_{24}(H_2O)^{7+}$ (Figure 2) is stable.[22] Increasing the OH/Al ratio beyond 2.47 generated aluminum-containing particles whose persistence in suspension was determined by the solution conditions. It was thought that the large 13-aluminum polycation could act as a seed for the nucleation and growth of larger particles in suspension and its presence at near saturation presaged the nucleation and growth of particles. We have determined that the polycation is absent in solutions containing citric acid and particle precipitation is delayed to higher hydrolysis levels (i.e., higher OH/Al ratios).

Experimental Section

Synthesis. Standard solutions of $AlCl_3$ (0.5 M) were prepared by adding aluminum chloride powder to deionized water, then refluxing the mixture at 60 °C for 2 h while stirring vigorously. The resulting clear solutions were cooled to room temperature and remained free of detectable particles for several months, as determined by photon correlation spectroscopy (PCS). Citric acid was

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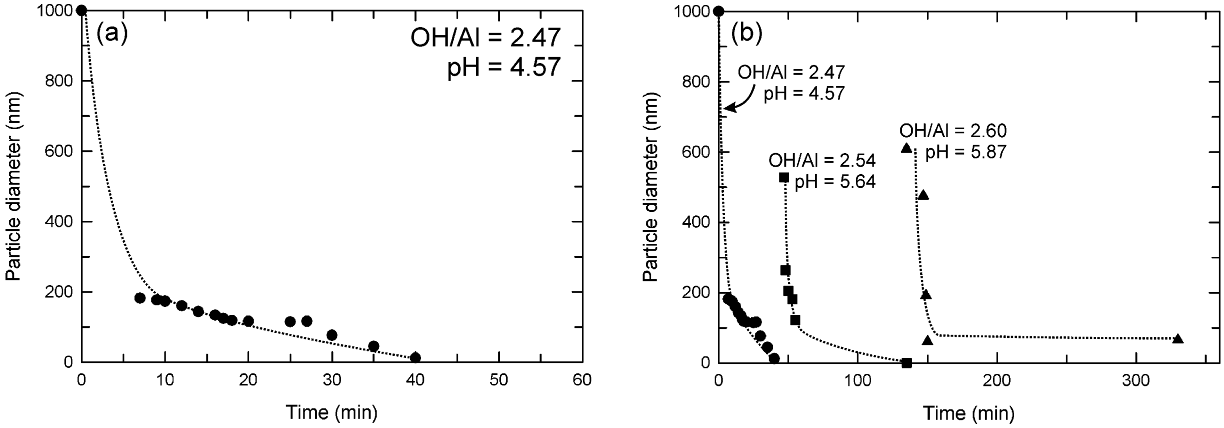

Figure 3. Addition of NaOH(aq) to solutions of AlCl$_3$: (a) OH/Al = 2.47. Particles quickly form and reach large size, then shrink (or deaggregate) and disappear. (b) Successive additions of NaOH(aq) result in a standard profile: large particles form quickly then shrink. At sufficiently high OH/Al ratios (2.60 in the above chart), particles do not completely disappear and stable suspensions are formed. Stable particles are maintained as the OH/Al ratio is raised to 3.29 (corresponding to pH = 10.42).

added as a dry powder to stirred solutions at room temperature. The addition of citric acid had no visible effect on the standard aluminum-containing solutions, which remained clear. To set the desired hydrolysis ratio (OH/Al), the aluminum-containing solutions were again heated to 60 °C and titrated dropwise with 0.2 M NaOH(aq) under fast stirring.[22,23] Solutions with a hydrolysis ratio less than or equal to 2.47 remained free of detectable particles for at least several weeks, again as determined using PCS (AlCl$_3$(s) reagent grade, J. T. Baker, Phillipsburg, NJ 08865; citric acid(s) reagent grade, Sigma-Aldrich, Inc., St. Louis, MO 63103; NaOH(aq) technical grade, Fisher Scientific, Pittsburgh, PA 15275).

Light Scattering. The formation and disappearance of particles from titrated solutions of Al(Cl)$_3$ were followed by in vitro PCS, effective for measuring average particle diameters ranging from a few nanometers up to a few micrometers.[24] Total particle volume was restricted to less than 0.2 vol % of the suspension to reduce interferences due to interactions between particles, such as aggregation.

The PCS instrumentation consisted of a goniometer fitted with an index-matched fluid bath contained in a temperature-controlled cell unit[3] (BI-200SM, Brookhaven Instrument Corporation, Ronkonkoma, NY 11779), a 35 mW HeNe laser source[4] (Stablite 124B, Spectra-Physics, Mountain View, CA 94039), and an external constant temperature water bath[5] (Lauda RM6, Brinkmann, Westbury, NY 11590-0207). The index-match liquid was Decalin ($n_D = 1.481$), which was filtered to reduce dust contamination using a closed loop filtration apparatus just prior to scattering measurements. The photomultiplier tube (PMT) detector[6] (Detector Unit Type TFL, Brookhaven Instrument Corporation, Ronkonkoma, NY 11779) was fixed at 90° to the laser with the aperture pinhole set to 100 μm and the wavelength filter set to 633 nm. During data acquisition, the scattering angle was set to 90° and the temperature maintained at 60 °C. Solution viscosity was approximated as 466.5 mPa·s, and the fluid index of refraction was assumed to be 1.332. Sample time intervals and total acquisition time were set to optimize the decay time of the autocorrelation function of the scattered intensity.

Light scattering measurements were performed on 10 mL solutions contained in 22 cm^3 borosilicate glass test tubes (OD = 20 mm) maintained at 60 °C. The samples could not be stirred while in the cell unit. The titrant was added dropwise to the surface of the solution using a micropipet. PCS measurements were made immediately following each addition of titrant. If scatter was observed, indicating the presence of particles in the liquid, PCS measurements were repeated until the liquid no longer exhibited detectable scattering of the laser or until the apparent particle radius remained unchanged with time.

^{27}Al NMR solutions selected for ^{27}Al solution NMR exhibited no detectable light scattering in PCS measurements (e.g., supernatants were not used for NMR studies) at room temperature. Samples were sealed against evaporation, packaged, and shipped for ^{27}Al solution NMR analysis, requiring several days storage at ambient temperature. No obvious precipitation or cloudiness was observed in the samples before NMR sampling.

Results and Discussion

Aluminum in Solution. The effect of adding NaOH(aq) to solutions of AlCl$_3$(aq) is shown in Figure 3. PCS measurements were started on solutions in which the amount of added NaOH resulted in a solution of OH/Al ratio of 2.47 (pH = 4.57), a condition of near saturation for aluminum oxyhydroxides.[22,23] The principal limitation in the use of PCS in solutions of this type was the low particle content ($<$0.2 vol %) necessary to avoid extensive diffuse reflection within the suspension. As a result, the OH/Al ratio in solution was the variable determining the formation and stability of particles. It should be noted that the pH of the solutions in the quasi-elastic light scattering sample holder could not be measured directly. The indicated values were measured on solutions having the same composition and preparation as the samples used in light scattering.

The relative solubilities of aluminum oxyhydroxides have been calculated using the activities of the aluminum-containing molecules.[25,26] The assumption of thermodynamically stable solutions does not account for the partitioning of aluminum in basic, near-saturated solutions between soluble and insoluble species, the latter including oxyhydroxides such as boehmite (AlOOH) and hydroxides such as gibbsite and amorphous Al(OH)$_3$.[8] Studies on simulated tank wastes near saturation for aluminum-containing species and under basic conditions

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found that the solubility of aluminum first increased and then decreased with increasing hydroxide concentrations, rather than continuously increasing with increasing pH.[8] The kinetics of both precipitation and dissolution of Al-containing phases were shown to depend on the nature and solubility of the aluminum-containing species present in the system. In the determination of overall aluminum solubility under conditions of near saturation, several soluble monomeric and polymeric species were found to be present in solution. The prevalent form of the cation in solution of increasing pH follows the series $Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{2+}$, $Al(OH)_2(H_2O)^{4+}$, $Al_{13}O_4(OH)_{24}(H_2O)^{7+}$, and $Al(OH)_4^-$, as determined by liquid ^{27}Al NMR.[8]

In our light scattering sample solutions (Figure 3), NaOH(aq) was added to the $AlCl_3$(aq) solutions without stirring. Particles formed immediately upon the addition of NaOH(aq), which we assumed was due to the introduction of a very high OH^- concentration at the surface of the solutions, well above that needed for stable particle formation (e.g., >2.47).[22] After sufficient time to permit the OH^- ions to diffuse throughout the solution, and depending on the overall OH/Al ratio (OH/Al < 2.6), the particle size was observed to decrease, eventually falling below the detection limits (~3 nm diameter) of the PCS instrument. The time necessary for the particles to disappear depended on the overall OH/Al ratio. Sequential additions of NaOH(aq) to solutions of $AlCl_3$(aq) (Figure 3) mimicked the initial reaction. As seen in Figure 3, the first aliquot raised the OH/Al ratio in solution to 2.47 (pH = 4.57), forming particles that disappeared from suspension in less than an hour. The next addition of NaOH(aq) raised the OH/Al ratio to 2.54 (pH = 5.64) and again resulted in the formation of transient particles. These secondary particles took more than 90 min to shrink below the detection limit. For comparison, stirred solutions of similar composition (OH/Al set to 2.47 and 2.54, respectively) remained free of detectable particles for long periods when stored at room temperature and sealed against solvent loss.

Three mechanisms are suggested by the above observations. First, the initial large particles were soluble under the solution conditions and so eventually dissolved. Second, large aggregates of small clusters or primary particles formed quickly and then fragmented into smaller particles under the action of the OH^- ions in solution. These primary particles were smaller than the detection limit of the PCS instrumentation. A third mechanism combines fragmentation with dissolution: the fragmentation into smaller particles or clusters increased the surface area and thereby improved dissolution, which may or may not have been complete. Which of these mechanisms might be correct could not be determined on the basis of PCS measurements.

The third and final addition of NaOH(aq) brought the overall solution composition to OH/Al = 2.60 (pH = 5.87) (Figure 3). After the initial reduction in diameter, detectable particles (~30 nm diameter) remained in suspension for several weeks, showing no appreciable change in the measured diameter over that time. However, subsequent additions of NaOH (pushing OH/Al over 2.60) resulted in rapid particle aggregation and precipitation from suspension. Specifically, as we were interested in high pH systems (which we defined as pH > 10), raising the OH/Al ratio to 3.29 resulted in a solution of pH = 10.42. Particles were observed to form, initially shrink, and then precipitate throughout the range of 2.60 to 3.29 OH/Al (5.67 < pH < 10.42).

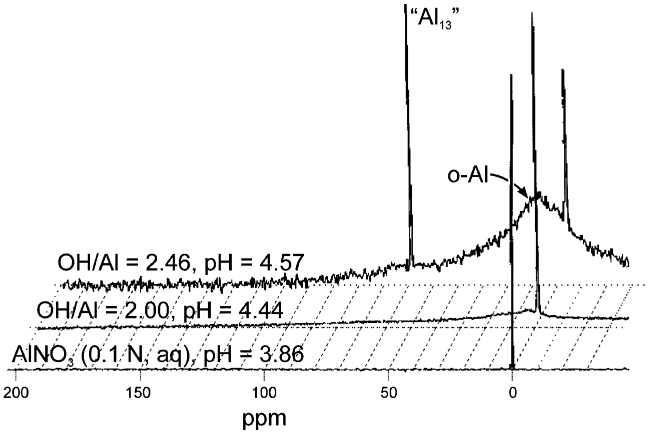

Figure 4. ^{27}Al NMR scans on aluminum standard ($AlNO_3$(aq)) and aqueous solutions containing NaOH and $AlCl_3$ (no citric acid added). The primary soluble species at a lower OH/Al ratio are the monomeric aluminum species, $Al(H_2O)_6^{3+}$ and $Al(OH)(H_2O)_5^{2+}$. Under near-saturation conditions, the polycation $Al_{13}O_4(OH)_{24}(H_2O)^{7+}$ appears.[22] At OH/Al = 2.60, insoluble particles remain in suspension (Figure 3).

^{27}Al NMR measurements on similar solutions clearly show the formation of the polycation $Al_{13}O_4(OH)_{24}(H_2O)^{7+}$ at OH/Al = 2.47 (Figure 4), indicated by the signature tetrahedrally coordinated Al center prominent at $\delta = 63$ ppm and the octahedrally coordinated, oligomeric Al centers indicated by the broad band centered at $\delta = 10$ ppm.[22,27] The concentration of the monomeric, octahedrally coordinated Al ($Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{2+}$) at $\delta = 0$ ppm is seen to decrease in solutions containing the polycation. The NMR spectra of solutions at OH/Al = 2.00 resemble that of the standard solution with an intense peak at $\delta = 0$ ppm and small quantities of oligomeric species indicated by the small, broad peak at $\delta = 4$ ppm.

Role of Citric Acid. At OH/Al ratios below the critical value of 2.47 (pH = 5.67), citric acid in the titrated solutions retarded the dissolution of particles (Figure 5a) formed by the addition of the alkaline to the solution. The addition of citric acid reduced the equilibrium pH of solutions in the series 5.07 (citric acid/Al = 0.33 mol/mol), 4.90 (cit/Al = 0.41), 3.94 (cit/Al = 0.58), and 3.82 (cit/Al = 0.74). The measured pH values were well below that expected for complete and rapid dissolution (pH < 5.87, Figure 3b). However, the significance of the information displayed in Figure 5a concerns the rate at which particles formed and disappeared and the maximum size detected before diminution or precipitation. Simply, particles did not form as quickly and diminished in radius more slowly than those observed in solutions that did not contain citric acid, as would otherwise be expected in solutions of low pH. The particles did eventually disappear, albeit after 10 h from the addition of NaOH(aq). The presence of citric acid was also observed to slow the growth of these transient particles to their maximum diameter, which were also smaller than the maximum achieved in solutions without citric acid present (Figure 3).

At higher OH/Al ratios (Figure 5b), particles nucleated and grew in the presence of citric acid at ratios well below 1:1 citric acid/aluminum (molar) until precipitation. The solution pH values were all above the pH seen for stable particles (5.87, from Figure 3) except at the highest citric acid-to-aluminum ratio. Measured pH values were in the series: 7.14 (citric/Al = 0.49 mol/mol), 6.55 (citric/Al = 6.55), 6.30 (citric/Al = 6.30), and 5.32 (citric/Al = 0.82). Increasing the citric/aluminum ratio to near unity prevented particle nucleation altogether; even the transient particle formation observed in all other systems was not

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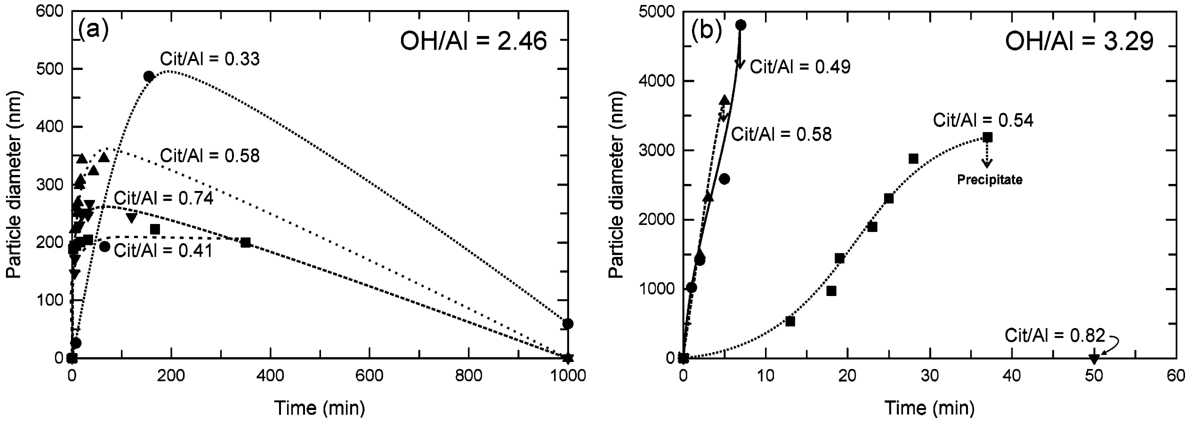

Figure 5. Formation and shrinking or growth and precipitation of particles in the presence of citric acid. (a) Citric-acid-containing solutions of $AlCl_3(aq)$ are titrated with NaOH(aq) to OH/Al = 2.47. The presence of citric acid does not prevent particles from forming but reduces the maximum particle size and retards both particle growth and subsequent shrinking in comparison to control solutions (Figure 3). (b) Citric-acid-containing solutions of $AlCl_3(aq)$ are titrated with NaOH(aq) to OH/Al = 3.29. Particle growth is slowed but not prevented until the citric-acid-to-aluminum ratio approaches unity despite a solution pH above 5.87 for all but solutions with the highest citric acid content. At citrate/Al = 0.82 (pH = 5.32), particles do not form at all and the solution remains clear of particles indefinitely. Particle growth is again slowed in the presence of citric acid, but precipitation eventually occurs if particles are allowed to form (that is, insufficient citric acid is present to prevent particle formation).

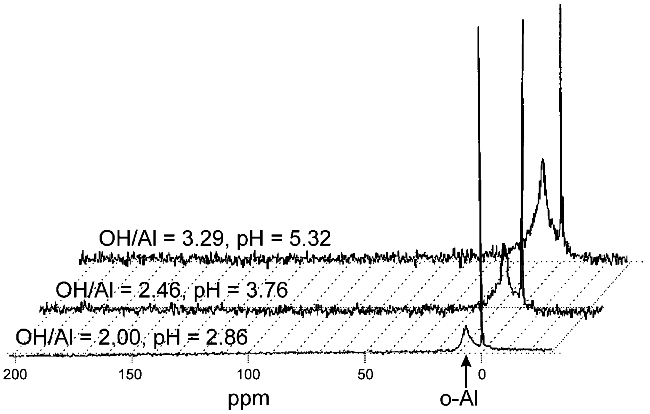

Figure 6. ^{27}Al NMR scans on aluminum-containing aqueous solutions composed of NaOH, $AlCl_3$, and citric acid (citric/Al = 0.82) in water. The 13-Al polycation does not exist in the presence of citric acid. Polymeric octahedral Al are indicated by the growth of the broad band around $\delta = 10$ ppm. The primary soluble species remain the monomeric aluminum species, $Al(H_2O)_6^{3+}$ and $Al(OH)(H_2O)_5^{2+}$, but the increasing polymeric content indicates the presence of seed molecules or clusters undetected by light scattering.

observed. The solutions containing citric acid in the ratio of 0.82 citric acid/aluminum (mol/mol) remained clear of detectable particles for several weeks when sealed against solvent evaporation and held at room temperature.

The most striking difference in particle formation behavior seen at the higher OH/Al ratio (Figure 5b) was the apparent transition from rapid particle formation at pH 7.14 (citric/Al = 0.49), slower particle growth at pH 6.55 (citric/Al = 0.54), and a return to a more rapid particle growth at pH 6.30 (citric/Al = 0.58). This effect was reproducible and could not be explained by any changes in mixing or handling.

The observed changes in particle formation and stability in the presence of citric acid were accompanied by changes in the observed soluble aluminum complexes (Figure 6). The most obvious difference was the absence of the 13-Al polycation peak at $\delta = 63$ ppm under OH/Al = 2.47, indicating that the polycation either did not form or dissociated in the presence of citric acid. The exact mechanism cannot be determined from NMR measurements due to the long time between titration and NMR characterization. It is possible that the polycation may first be protected by interaction with citric acid, as observed with particles, but strong complexation between the aluminums of the polycation and citric acid could eventually lead to the dissociation of the polycation. Or the polycation content could be reduced in a manner similar to the loss of aluminum from alumina particles exposed to excess surfactant in solution:[21] the citric acid preferentially complexes with free aluminum cations in solution, reducing the concentration of the monomeric aluminum in solution and thereby increasing the probability of polycation dissociation.

The absence of the 13-aluminum polycation does not necessarily imply a lack of seeds for particle nucleation. The broad peak at $\delta = 10$ ppm appeared in all solutions for all values of OH/Al (Figure 6), assigned to "polymeric" aluminum-containing species composed of octahedrally coordinated aluminum centers.[22,27] When Figure 6 is compared with Figure 4, in the solutions containing citric acid, all aluminum atoms appear as octahedrally coordinated, both in monomeric ($\delta = 0$ ppm) and in polymeric forms ($\delta = 10$ ppm). The increased content of larger aluminum-containing molecules suggests the increased concentration of possible seed molecules or clusters, of sizes too small to be visible in light scattering. The presence of larger polymeric species would reduce the amount of citric acid needed to coordinate all aluminum centers. Since monomeric aluminum species exhibit one-to-one association with citric acid,[6] the slightly lower citric acid/aluminum ratio required in our solutions to completely arrest particle formation is simply explained by the existence of these soluble polymeric aluminum oxyhydroxides.

We briefly note that when tricarballylic acid (TCA) was used in place of citric acid, little to no effect on solutions of $AlCl_3(aq)$ was seen. Raising the pH of the TCA-containing solutions through the addition of NaOH(aq) did not appear to affect particle formation; once the OH/Al ratio went above 2.47, particles formed just as observed in solutions of $AlCl_3$ without added TCA. Tricarballylic acid is structurally and chemically similar to citric acid but lacks the backbone hydroxyl group; the pK_a values for its carboxylate groups are very close to those for citric acid.[13] The importance of the citric acid hydroxyl group is clearly demonstrated by the very pronounced effect of citric acid on aluminum-containing species.[3,5,13]

Highly reactive atoms and compounds can be stabilized through two different methods: thermodynamic and kinetic stabilization. A thermodynamically stable configuration involves the formation of a resonant structure between neighboring heteroatoms, attachment of electron-donating or -withdrawing substituents, or through complexation with transition metals. A kinetically stabilized structure is a transitional or metastable state protected by the use of sterically obtrusive substituents preventing or hindering the reaction.

In aqueous solutions of $AlCl_3$ without citric acid, the addition of NaOH(aq) caused rapid nucleation and growth of particles or aggregates that then dissolved to form a thermodynamically stable solution or to a stable suspension of particles via kinetic stabilization of the particle surfaces. The rate of particle formation was too rapid to follow with our instrumentation, and the subsequent shrinkage was complete within about 1−1.5 h of mixing. Seeds of large polycations were formed in solution near a critical value of OH/Al ($\sim$2.47), and at slightly higher values ($\sim$2.60), stable particles were formed.

In the presence of citric acid, the seed polycation either did not form or dissociated into smaller units but other polymeric forms of aluminum oxyhydroxides were observed to increase in concentration as the OH/Al ratio increased, perhaps to act as seeds to precipitation above the critical OH/Al ratio. However, precipitation was delayed to hydrolysis conditions well above the control solutions (greater than OH/Al = 3). In solutions having the OH/Al ratio fixed at 2.47 and in the presence of citric acid, the rate of particle growth (1−3 h) and shrinkage (longer than 10 h) was longer than comparable measurements in control solutions of the same OH/Al ratio, while the maximum size of the observed particles (less than 500 nm) was lower than observed in the control solutions. Under conditions of extremely high hydrolysis, OH/Al = 3.29 (Figure 5b), increasing citric acid content generally increased the time to precipitation and could prevent particle formation and growth completely at citric acid/aluminum ratios of 0.82 (pH = 5.32). No transient increase followed by diminution in particle size was observed, in marked contrast to the behavior shown in Figure 3a, wherein a markedly lower pH resulted in transient particle formation in the absence of citric acid.

The behavior of the aluminum oxyhydroxide particles in the presence of citric acid, as measured by PCS, is similar to that observed on the effect of citric acid on the nucleation, growth, and subsequent diminution of colloidal gold particles in suspension.[28] In these systems, nanosized gold particles form from solutions of $AuCl_3$ through the addition of citric acid[29] and evolve from suspensions of large gold aggregates that spontaneously "deweld"[28] into distinct gold nanoparticles, the ultimate diameter of which is set by the citric-acid-to-gold ratio. The mechanism of the gold deaggregation is not known. The stability of gold nanoparticles formed in the presence of citric acid suggests that the citrate adsorbent may have a like effect on the oxyhydroxides and in the aluminum-containing species favoring octahedral coordination of the aluminum in clusters or particles too small to be detected by light scattering. Removing the citrate absorbent from gold nanoparticles allows the particles to sinter under ambient conditions—thus the citrate acts as a kinetic barrier to aggregating and sintering. In a like manner, citrate appears to prevent aluminum-containing molecules, clusters, or particles from spontaneously aggregating.

Our observations and the role of organic ligands in the weathering and protecting of oxide surfaces[15,21] suggest that citric acid is a complexing agent whose interaction with aluminum-containing species is strong enough to enhance solvation of the same but weak enough that the molecule also acts as an effective inhibitor, protecting oxyhydroxide surfaces from dissolution. Both activities are observed in similar solutions in the presence of citric acid: Where particles exist, dissolution, even under conditions of high hydrolysis, is slowed. If citric acid is present, large polycations do not exist in solutions that would otherwise be expected to contain such molecules. The acid effectively complexes with smaller cations and either causes the dissociation of larger cations or prevents the formation of the same. Likewise, with sufficient citric acid present, particles do not form, and below a critical ratio of citrate/Al, particle growth is slowed under conditions in which spontaneous nucleation and rapid growth is expected.

The possibility that the citric acid complexes small clusters, as opposed to molecules, cannot be discounted merely on the basis of light scattering measurements. And NMR measurements indicate the presence of "polymeric" forms of aluminum oxyhydroxides in solution, likely simple structures composed only of octahedrally coordinated aluminum centers, not more complex structures such as that shown in Figure 2. In terms of nucleation and growth, the citric acid acts to reduce the activity of the monomeric and polymeric forms of the soluble aluminum oxyhydroxides, slowing hydrolysis by the hydroxide anions and retarding the growth of particles. The reduced rate at which particles grow and, more noticeably, at which they subsequently disappear, is determined by the presence and amount of the citrate molecule.

Conclusions

Citric acid is observed to stabilize both particles and soluble aluminum oxyhydroxides in the respective suspension or solution. By the use of dynamic light scattering, particle formation and stability can be followed under highly hydrolyzing conditions. In suspensions, the addition of citric acid serves to stabilize the existing particles, limiting or preventing particle growth. In solutions of aluminum cations, citric acid does not prevent the formation of particles upon the addition of a strong base but growth is retarded. At OH/Al ratios equal to or less than 3.00, particles are unstable in the presence of citric acid and disappear. Once pH increases past the critical value, particles do not redissolve and a stable suspension forms. This dual role as effective complexing agent and dispersant suggests that citric acid acts simultaneously as a strong ligand, promoting the solvation of cations, and as a kinetic inhibitor, retarding the dissolution of particle surfaces. In waste remediation, the prevention of precipitation is the principal goal. Whether this is achieved by promoting solvation or suspension fluidity is less important, but the determination that both functions can be achieved with a single agent provides a significant guide to future research.

Acknowledgment. This work was supported by a grant from the U.S. Department of Energy within the Environmental Management Science Program (EMSP), Grant No. DE-FG07-98ER14929.

LA050822F

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