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Alan J. Rubin[a]; Thomas W. Kovac[a]
[a] Water Resources Center, The Ohio State University, Columbus, Ohio

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Aggregation and Restabilization of Colloidal Titania by Aluminum Sulfate

ALAN J. RUBIN* AND THOMAS W. KOVAC

WATER RESOURCES CENTER
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

Abstract

The interaction of aluminum sulfate with three concentrations of a negatively-charged titania sol was investigated. Changes in turbidity during settling were used to determine the critical values of coagulation and stabilization. These data were used to establish the entire log aluminum sulfate–pH stability limit diagram for the sol, and its boundaries were related to the ionic species in equilibrium with aluminum hydroxide. The stability limits, except at the very lowest aluminum concentration, are very similar to those described for other sols. Aggregation was not dependent upon sol concentration whereas the critical aluminum concentration for restabilization increased with sol concentration. Data were obtained to demonstrate that titania obeys the Schulze-Hardy rule.

INTRODUCTION

The study of sol interactions with hydrolyzing metal salts is important both fundamentally and for practical reasons. Aluminum sulfate, for example, is the most widely used chemical for the removal of suspended clays and other sols that contribute to the turbidity of drinking water supplies. In order to fully understand the mechanisms controlling such processes as chemical clarification, it is imperative that the hydrolytic chemistry of aluminum(III) also be understood.

The aqueous chemistry of iron(III), another hydrolyzable metal used in water and waste treatment applications, has been investigated

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*To whom correspondence should be addressed.

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thoroughly and is firmly established (*1–3*). The addition of a ferric salt to water results in its dissolution and hydration followed by lowering of the solution pH. This occurs because a sequence of stepwise hydrolysis reactions takes place in which iron acts as a Bronsted-Lowry acid. In these reactions, hydrogen ions are released from waters of hydration to form a series of hydroxo species. As a consequence of hydrolysis, amorphous ferric hydroxide is precipitated, even in very acid solutions. For example, 0.2 m*M* iron(III) will just begin to precipitate at pH 2.67, so that 99.85% of the metal is insoluble at pH 4. Aging of these suspensions, which occurs fairly rapidly with iron, leads to the formation of even more insoluble crystalline phases. Raising the pH to alkaline levels results in the dissolution of the precipitate; the soluble species being a negatively charged tetrahydroxo ion. An important aspect of iron hydrolysis is the formation of a 4+ charged dimeric ion. This polynuclear species has an olated structure in that the metal atoms are bound through hydroxo bridges rather than directly to one another. Its relative concentration in solution is dependent on the applied concentration of iron as well as pH.

Upon hydrolysis, aluminum(III) undergoes a similar sequence of reactions which also involves the formation of highly charged polynuclear ions (*3–9*). Partly because aluminum is less acid than iron(III), there are some differences, and the exact nature of the hydrolyzed species is still being debated. There is evidence that the method of preparation, temperature, age, and other details of the history of the solution determine the structure and stoichiometry of the species and precipitates that are formed (*8, 9*). As with iron, aluminum is insoluble over most of the pH range. The interaction of aluminum hydroxide with sols is thus also of significance. The major purpose of the research described in this paper was to relate the stability of a rather ideal sol system to the aqueous chemistry of aluminum(III) using a systematic approach over wide pH and metal concentration ranges.

Our approach has been to use turbidity changes during settling, as opposed to particle growth, to indicate aggregation. Data extrapolated from the settling curves were used to establish the entire log aluminum sulfate concentration-pH stability limit diagram for titanium dioxide. Using the technique of precipitate boundary analysis (*10*), we have demonstrated that the straight line portions of the stability limit diagram can be related to the hydrolytic behavior of the metal (*11–13*). It has been possible to distinguish between different modes of aggregation using differences in settling rates. Generally, at low pH a sol settles slowly whereas at higher pH in the presence of aluminum hydroxide very rapid clarification results. The pH ranges over which the insoluble hydroxide is formed is designated at the "sweep zone," and enmeshing of the sol in the flocculating gelatinous precipitate has been proposed to explain the results (*11, 14*). An attempt is made in this paper to account quantitatively for the equilibria responsible for the low pH limits of the sweep zone. This was possible for two reasons: because the principal soluble hydrolyzed species in freshly prepared aluminum solutions have recently been identified and their equilibrium constants determined (*6*), and because titania is coagulated at extremely low aluminum concentrations, down to 1 μM, the results can be interpreted in terms of mononuclear hydrolysis alone.

EXPERIMENTAL

Titanium dioxide suspensions were prepared with Zopaque RG (ASTM D 476-48, Class 1) obtained from the Glidden-Durkee Division of SCM Corporation, Baltimore, Maryland. This material is a water dispersible powder of the anatase crystal type used in paper making. Zopaque RG has an extremely small particle size of 0.1 to 0.4 μm and forms a negatively charged sol in aqueous media. Because of its colloidal properties and high refractive index, about 2.55, titania forms very stable suspensions in dilute concentrations having an intense white to blue color.

All solutions and suspensions and their dilutions were prepared from carbonate-free distilled-deionized water. A Waring blender was used to disperse various weights of the dry powder to prepare the stock suspensions of titania. Suspension age did not appear to have any effect on the stability of the sol except for a short period of time during which larger particles were removed by settling. The diluted experimental suspensions at concentrations of 50.2, 41.9, and 3.2 mg/L are referred to in the text as the high, intermediate and low sol concentrations, respectively. Fresh dilutions from a stock solution of 0.295 M aluminum (reagent grade aluminum sulfate, Merck) were prepared just prior to experimentation. Solutions of reagent grade sodium hydroxide and nitric acid were used for pH adjustment.

Two separate series of solutions were prepared for each experimental run. One series, in small glass vials, consisted of base (if required) and the exact amount of stock titania suspension needed to give the desired initial sample turbidity. The second series, in round 19-mL cuvettes, consisted of aluminum solution, acid (if required), and distilled water. An experimental sample of 15-mL total volume was prepared by adding the contents of a vial to a cuvette. Both acid and base were never added to the same sample. The cuvette was shaken vigorously for about 10 s and then set aside without further mixing for the duration of the experiment. Turbidity and pH readings were made at specified time intervals depending upon the applied aluminum dose and sol concentration.

Absorbance measurements were taken at 550 nm using a broad bandpass spectrophotometer (Coleman model 14). Turbidity measurements for the low sol series were by 90° light scattering (Coleman model 9 Nepho-Colorimeter). Solution pH was measured with Sargent-Welch pH meters fitted with combination electrodes. Streaming current measurements to determine the sign of the charge on the sol were taken with a Water's Associates Streaming Current Detector (*15*).

EXPERIMENTAL RESULTS

Hydrogen Ion Coagulation

The effect of pH on the stability of titanium dioxide in the absence of aluminum (i.e., pH adjustment wtih nitric acid or sodium hydroxide alone) was determined at the three sol concentrations. These studies demonstrated that titania is slowly coagulated by very low concentrations of hydrogen ion. The rate of settling was highly dependent on sol concentration. Approximately 10 h was required to observe an 80% reduction from the initial absorbance with the high sol concentration whereas after 100 h the reduction was only 40% at the low sol concentration. In general, the critical pH, the pH just below which settling occurred, increased slightly with time to a limit where no further change was observed. This critical pH ranged from pH 5.8 to 6.0 at all three sol concentrations. For example, representative turbidity-pH data after 24 h settling at the intermediate sol concentration are shown in Fig. 1. Critical pH values (pH_s) were determined by extrapolating the steepest portions of the curve up to the average initial absorbance. As indicated by the figure, the data in the region of the critical value were rather erratic; however, the several different extrapolations possible all resulted in approximately the same pH_s of around 6.0 (streaming current measurements indicated an isoelectric point at pH 3.2). The hydrogen ion concentration of about 1 μM at the pH_s is well below that predicted by the Schulze–Hardy rule for simple coagulation by indifferent single-plus counterions (*16*).

The pH of freshly prepared titania stock suspensions in distilled water is around 6.1. Within 1 month these dispersions experience a lowering in

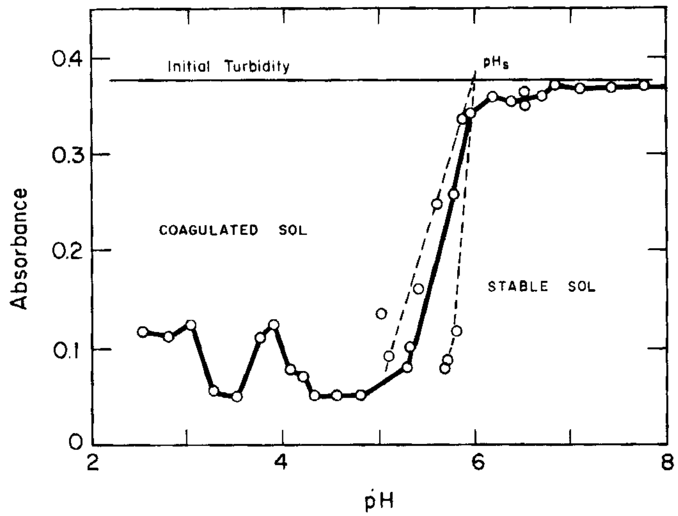

FIG. 1. Effect of pH on the stability of titanium dioxide sol. Twenty-four hour settling data for the intermediate sol concentration.

pH to 5.7 with significant decreases in turbidity. Protecting the suspensions from carbon dioxide absorption and maintaining the pH at 6 or above resulted in relatively stable suspensions which changed only slightly in absorbance. Suspensions initially adjusted to pH 7 and exposed to the atmosphere have remained stable for over 2 years.

Studies with Aluminum Sulfate

Aggregation of titanium dioxide with aluminum was examined over the concentration range 1×10^{-1} to 1×10^{-8} *M* $Al(SO_4)_{3/2}$. Most of the experiments were run in a series holding the metal concentration constant while systematically varying the solution pH. Typical results at the intermediate sol concentration are shown in Figs. 2-4. Critical pH values for coagulation (pH_c) and stabilization (pH_s) were determined by extrapolating the steep portions of the settling curves up to the line of initial absorbance. The pH_c may be defined as a limit such that a slightly higher pH results in aggregation and settling. The pH_s is the solution pH above which stabilization (restabilization or no coagulation) is just completed. Aggregation occurs in the pH range between a pH_c and a pH_s, while stabilization occurs in the pH range between a pH_s and a pH_c and is characterized by a stable unsettleable sol. Each of these extrapolated values at its initial or applied aluminum concentration gives one point along a boundary of the aluminum sulfate concentration–pH stability limit diagram (domain) for colloidal titanium dioxide.

Figure 2 shows the results with 1×10^{-3} *M* aluminum. Three distinct zones or regions can be distinguished. Between pH 4 and 9 is a region of rapid aggregation characterized by heavy floc formation and excellent clarification. This is the sweep zone in which the solution is oversaturated with respect to aluminum hydroxide. To its left is a region of slower clarification, presumably due to coagulation by hydrogen ion. On the right is a region of stability, that is, of no coagulation or aggregation.

It was observed that small volumes of highly concentrated sodium hydroxide would act as a coagulant. In these cases the right stability region would slowly settle, behaving very much like the slow coagulation region on the left. Upon using larger quantities of more dilute base to

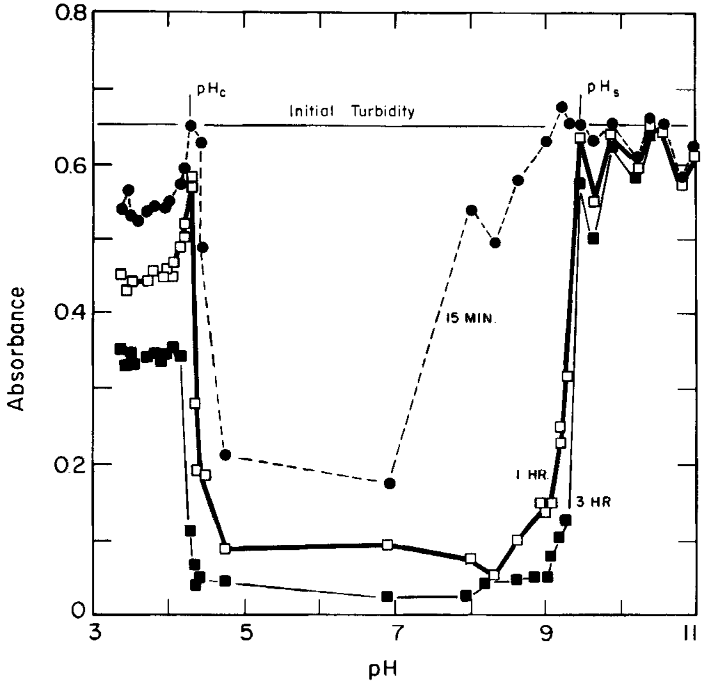

FIG. 2. Aggregation of titanium dioxide with 1.0×10^{-3} *M* $Al(SO_4)_{3/2}$. Intermediate sol concentration. Settling times: (●) 15 min, (□) 1 h, (■) 3 h, (◇) 6 h, (▲) 12 h, (♦) 18 h, (○) 24 h, (△) 40 h.

achieve the same pH adjustment, stability in the right-hand zone was maintained. Consequently, dilute base solutions were used for increasing the pH in all subsequent studies. In general, the left boundary at the pH_c was relatively time independent compared to the boundary between the sweep zone and the stabilization region. An attempt was made to extrapolate the critical pH values after the time-dependence period of the boundaries had passed.

An unusual feature of the turbidity-pH curve in Fig. 2 is the very narrow region of stability near pH 4.3 at the boundary between the rapid and slow coagulation zones. This stability "spike" disappeared within 3 h, resulting in an apparent shift of the boundary with time. A similar sharp stability region with aluminum sulfate has been observed for the bacterium *Escherichia coli* (*12*) and the clay montmorillonite (*17*) and by Black and Hannah (*18*) in their studies with kaolinite, montmorillonite, and fuller's earth. They found that the spike corresponded to the point of greatest mobility of the sols in the positive direction.

With a decrease in aluminum dosage to 1 × 10^{-4} *M*, as shown in Fig. 3, the stability spike has now expanded into a fully developed region of stability between the slow and rapid settling zones. The turbidity of

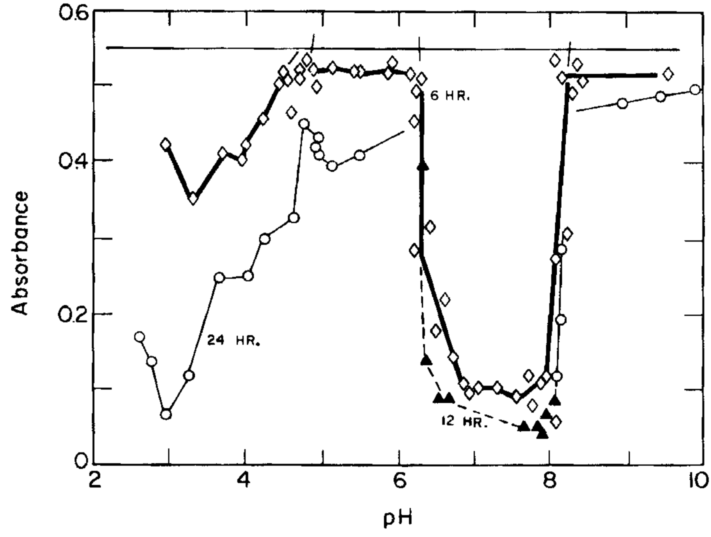

FIG. 3. Aggregation of titanium dioxide with 1.0 × 10^{-4} *M* $Al(SO_4)_{3/2}$. Intermediate sol concentration. Settling times: (◇) 6 h, (▲) 12 h, (○) 24 h.

samples in this pH range decrease in time but at a considerably lower rate than in the slow coagulation region. The sweep zone has further narrowed, occupying the range between pH 6.2 and 8.2. After 12 h of settling, the right boundary is comparatively time independent.

Figure 4, representing the addition of 3.16 × 10^{-5} *M* $Al(SO_4)_{3/2}$, shows a further broadening and shifting of the central stability region to the basic side. The sweep zone continued its narrowing trend with decreasing alum dose, and 40-h readings were necessary to clearly differentiate between the various zones. It is also to be noticed that sample turbidities in the slow coagulation zone between pH 2.5 and 5.0 are not greatly different from those in the central stability region. Figure 3 also indicates the formation of this new zone which is approximately equal in width with the central stability region. Assuming that stability occurs because of restabilization and charge reversal, since hydrogen ion coagulation would be expected, the abrupt drop in turbidity at the left extremity (pH 2.5 in Fig. 4) of this "extended" zone could not be caused by coagulation with nitrate ions introduced as nitric acid for pH adjustment. Most likely the extended zone was not observed at higher aluminum sulfate concentrations because of coagulation by sulfate ions. The extended zone

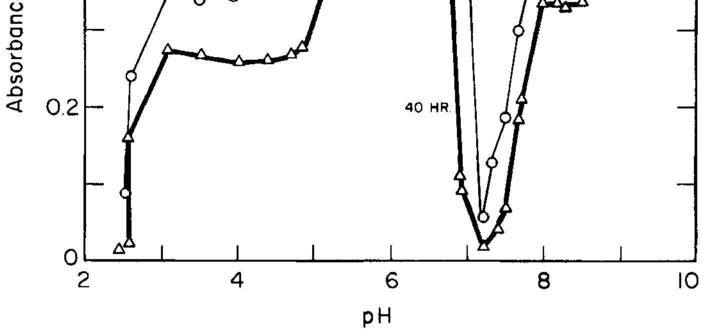

FIG. 4. Aggregation of titanium dioxide with 3.16 × 10^{-5} *M* $Al(SO_4)_{3/2}$. Intermediate sol concentration. Settling times: (○) 24 h, (△) 40 h.

is outside the range of aluminum hydroxide formation whereas the samples in the central stability region are saturated with the precipitate (*6*).

Several experimental series were also run by varying the aluminum concentration at constant pH, as shown in Fig. 5 for pH 5.71. Similar data were also obtained at other pHs, indicating three consecutive boundaries (i.e., the "irregular series"). Critical coagulation concentration (c.c.c.) and critical stabilization concentration (c.s.c.) values were extrapolated from these curves in the same fashion as described for obtaining the critical pH values. Again, the c.c.c. and c.s.c. at their corresponding pH are points along the boundaries of the stability limit diagram for titania.

At pH 5.71, readings at 24 h were required to obtain the time-independent values of −3.82 for the log c.c.c. and −5.20 for the log c.s.c. at the intermediate sol concentration. The lowest log c.c.c. of −6.1 was found with both the high and intermediate sol concentrations.

Similar studies at very low aluminum concentrations, less than 1×10^{-6} *M*, gave results that were essentially a reproduction of the data shown in Fig. 1. Results at the other sol concentrations were almost identical with those just described except for the extent of the central stability region. These results are discussed in the following sections.

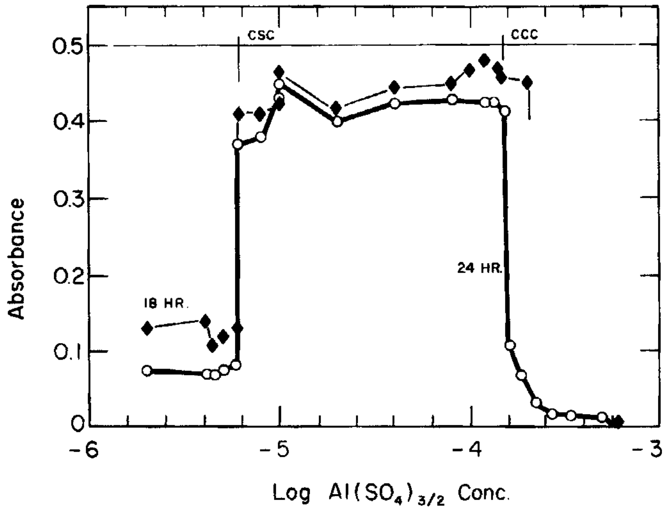

FIG. 5. Aggregation of titanium dioxide with aluminum sulfate at pH 5.71. Intermediate sol concentration. Settling times: (♦) 18 h, (○) 24 h.

DISCUSSION AND CONCLUSIONS

Stability Limit Diagram

The critical pH and concentration values obtained from Figs. 2–5 and similar data were plotted as log molar aluminum concentration against pH to establish the stability limit diagram as shown in Fig. 6. The open symbols are critical data obtained for intermediate titania concentration while the filled symbols represent data for low sol concentration. Circles are critical pH values and diamonds are critical concentration values. The data at the high sol concentration are represented by the dotted line and, except for the restabilization zone, are in perfect agreement with the results at the other concentrations. These data are not shown since they would only serve to clutter the figure. The slopes of the straight line

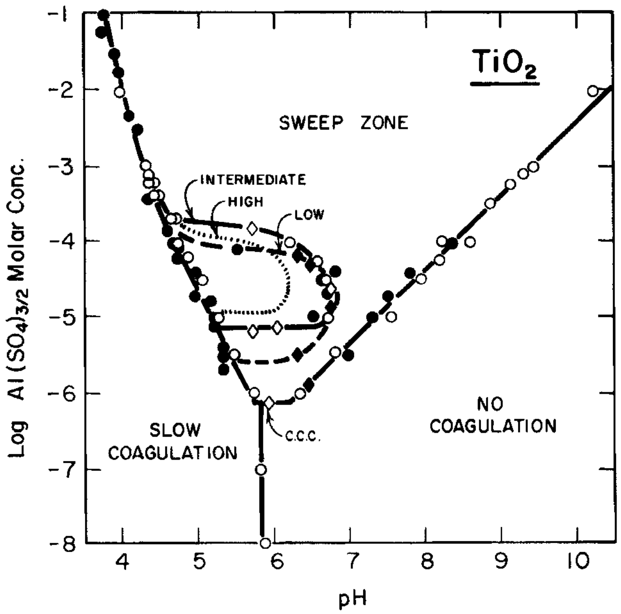

FIG. 6. Aluminum sulfate concentration-pH stability limit diagram for titanium dioxide showing the restabilization zone at three sol concentrations. Low TiO_2 concentration (●- -♦), intermediate TiO_2 concentration (○——◇), high TiO_2 concentration (· · ·), critical pH data (●, ○), critical concentration data (♦, ◇).

boundaries of the figure and their intercepts were determined by least squares analysis of the data for all three titania concentrations.

The stability limit diagram is characterized by four distinct zones. The central area is dominated by the sweep zone where heavy floc formation results in rapid clarification. This zone surrounds the central stability zone and narrows with decreasing concentration, reaching a minimum at a c.c.c. of 8×10^{-7} M aluminum. This minimum is independent of sol concentration and considerably lower than what has previously been observed with other sols. Although the area of the sweep zone to the right and beneath the central stability region is not characterized by extensive floc formation, the times required for clarification are much less than for the slow coagulation zone.

The vertical line below the c.c.c. and the left boundaries of the sweep zone form the upper limits of the slow coagulation zone. The lower vertical boundary was obtained by drawing the line through the critical point at 10^{-7} M aluminum. This gives a pH of about 5.8 which is in good agreement with the pH established in Fig. 1. As discussed earlier, in this zone the principal coagulating species is the hydrogen ion. There was no evidence, such as increased settling rates, to indicate coagulation by soluble aluminum species in this zone. The extended stabilization zone indicated in Fig. 4 is not shown because of insufficient data.

It seems fairly well established that the boundary between the sweep zone and the region of stability on the right is determined by the equilibrium between aluminum hydroxide and aluminate ion:

$$\mathrm{Al(OH)_3(s)} + \mathrm{H_2O} \rightleftharpoons \mathrm{Al(OH)_4^-} + \mathrm{H^+} \qquad (1)$$

where

$$K_4 = [\mathrm{H^+}][\mathrm{Al(OH)_4^-}] \qquad (2)$$

Thus the right stability region is a zone of no coagulation due to the formation of the soluble aluminate ion. Taking the negative logarithm of Eq. (2) and assuming that equilibrium conditions prevail, that the boundary is the limit such that aluminum hydroxide is present but only in infinitely small amounts, and that the single predominant soluble species is the aluminate ion such that its concentration is equal to the total applied (analytical) concentration of aluminum, C, then:

$$\log C = \mathrm{pH} - \mathrm{p}K_4 \qquad (3)$$

This equation predicts that the slope of the boundary should be exactly

+1 and its intercept is the negative of pK_4. Literature values of the latter range upward from 12.2 (*3, 19*). The experimentally determined values for the slope and intercept are +0.96 and −12.0, respectively. Corresponding values found in previous work are +1.02 and −12.3 with aluminum nitrate (*11*) and +0.88 and −11.0 with aluminum sulfate (*12*). There is evidence for slight sulfate complexing with aluminum hydroxide along this boundary (*6*), that may account for the slightly decreased values of the slope and intercept.

Several polynuclear hydrox species of aluminum have been proposed including the $Al_8(OH)_{20}^{4+}$ ion described by Matijević et al. (*20, 21*). Hayden and Rubin (*6*) demonstrated with aluminum nitrate solutions that this octameric ion and $AlOH^{2+}$ are the only two soluble hydrolyzed species in equilibrium with the hydroxide precipitate that are present in significant concentrations at low pH. If the octameric ion were the predominant species, its solution concentration would be one-eighth of the applied aluminum(III) concentration and at equilibrium:

$$Al_8(OH)_{20}^{4+} + 4H_2O \rightleftharpoons 8Al(OH)_3(s) + 4H^+ \tag{4}$$

and therefore, as before:

$$\log C = -4\mathrm{pH} + (\mathrm{p}K + \log 8) \tag{5}$$

This equation predicts a slope of −4 for the boundary on the left between the sweep zone and the slow coagulation zone. On the other hand, for the monohydroxy species, the equilibrium at the boundary is

$$AlOH^{2+} + 2H_2O \rightleftharpoons Al(OH)_3(s) + 2H^+ \tag{6}$$

or

$$\log C = -2\mathrm{pH} + \mathrm{p}K' \tag{7}$$

Thus, if the monohydroxy species were predominant, a slope of −2 for the boundary would be predicted.

Experimentally determined values for the slopes of the boundary between the sweep and slow coagulation zones were, respectively, −3.53 and −1.98 above and below the applied aluminum concentration of about 10^{-4} *M*. With *Escherichia coli* the values for the upper slope were −3.50 and −3.46 with aluminum nitrate and aluminum sulfate, respectively. The data in those studies were not adequate to obtain the lower slope, although qualitatively it was less negative.

In the presence of polynuclear species the distribution of hydrolyzed ions is dependent upon both the solution pH and the analytical concentration; the concentration of polymeric ions decreasing with a lowering of the total metal concentration. Thus the slope of −3.5 indicates that a highly charged, presumably 4+ species is present but is not predominant. In essence, the upper boundary is a very flat curve. This slope can be calculated by taking into account the relative concentrations of the hydrolyzed species. It would be expected, then, that $AlOH^{2+}$ plays an increasingly important role in the formation of precipitate in dilute aluminum solutions. This is evidenced by the gradual transition in slope from −3.58 to −1.98, the latter being very nearly identical with the predicted value.

Further support for the preceding arguments can be gained by comparing the experimentally determined intercept of the lower boundary (pK' in Eq. 7) with a value calculated from hydrolysis constants listed in the literature. Consider the following:

$$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^- \tag{8}$$

where

$$K_{s_0} = [Al^{3+}][OH^-]^3 \tag{9}$$

or

$$K_{s_0}/K_w^3 = [Al^{3+}]/[H^+]^3 \tag{10}$$

and

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \tag{11}$$

where

$$K_1 = [H^+][AlOH^{2+}]/[Al^{3+}] \tag{12}$$

Combining the negative logs of Eqs. (10) and (12) gives

$$3pK_w - pK_{s_0} - pK_1 = pK' \tag{13}$$

Values for pK_1 and pK_{s_0} cluster around 5 and 32, respectively. Taking pK_w to be 14, Eq. (13) predicts a value of around 5. Experimentally, the intercept of the lower boundary was determined to be +5.3, which agrees very well with the expected value. Thus, it appears that the equilibrium between $AlOH^{2+}$ and $Al(OH)_3(s)$ adequately accounts for the lower limits of the sweep zone.

A similar approach may be used to obtain an approximate value of the formation constant for the octameric ion:

$$8Al^{3+} + 20H_2O \rightleftharpoons Al_8(OH)_{20}^{4+} + 20H^+ \qquad (14)$$

where

$$\beta_{8,20} = [H^+]^{20}\,[Al_8(OH)_{20}^{4+}]/[Al^{3+}]^8 \qquad (15)$$

Taking the negative logarithm of Eq. (15) and substituting Eqs. (5) (assuming a slope of −4) and (10), as before:

$$p\beta_{8,20} = 24pK_w - 8pK_{s0} - pK \qquad (16)$$

The intercept of the upper boundary between the sweep and slow coagulation zones had a value of +12.1, therefore, by Eq. (5), p*K* is about 11 and $p\beta_{8,20}$ would have a value of about 69. This is excellent agreement with the value of 68.7 determined from potentiometric data at an ionic strength of 0.15 (*6*).

Schulze-Hardy Rule

The usual assumption is that the lower boundary of the sweep zone is determined by coagulation with the 4+ octameric ion. Further, it is assumed that the octamer is the predominant aluminum species at the concentration and pH of the c.c.c. Based on calculations with hydrolysis constants and the arguments in the previous section, these assumptions would seem to be considerably in error. However, if the octamer were the predominant species at the c.c.c. and pH 6, its concentration would be one-eighth of the total applied concentration of aluminum or approximately 1×10^{-7} *M*.

In addition to determining the c.c.c. for aluminum, corresponding values with titania were determined for the nitrate salts of sodium and calcium. The c.c.c. values were 1.05×10^{-2} and 6.8×10^{-4} *M*, respectively, for the univalent and divalent cations. The value for calcium was essentially independent of pH in the range 6 to 10. The c.c.c. for sodium was determined at pH 6.59.

As demonstrated by Težak and co-workers (*16*) and applied to other sols in previous work, a plot of the logarithm of the c.c.c. against the counterion charge yields a straight line. Figure 7 shows such a plot of the c.c.c. data for titania along with similar results for latex sol (*22*), *Escherichia coli* (*10, 23*), colloidal coal (*12*), and silver bromide sol (*24*), demonstrating the applicability of the Schulze-Hardy rule. The linearity of the plot suggests that these three ions destabilize the sol by *simple* coagulation. There are no specific interactions between the sol and the coagulating ion. That is, at the c.c.c. they coagulate without adsorption or other than electrostatic interaction with the sol. As stated above, comparison with the pH for hydrogen ion (c.c.c. about 10^{-6} *M*) suggests that H^+ strongly interacts with the sol surface leading to *adsorptive* coagulation.

The apparent contradiction in results, $Al_8(OH)_{20}^{4+}$ completely negligible in one case and predominant in the other, is indicative of the state of affairs in explaining coagulation data. Further studies in the millimolar to micromolar aluminum concentration region are needed. Unfortunately, analytical and experimental techniques remain to be developed.

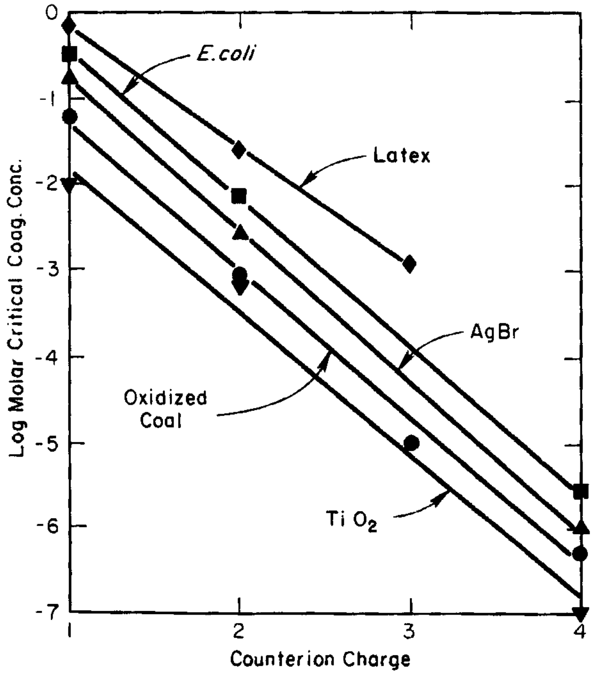

FIG. 7. Težak plot of the Schulze-Hardy rule for titania and other sols.

Restabilization

It has been postulated that hydrolyzed species, in particular the octameric 4+ ion in aluminum systems, is responsible for the presence of the central restabilization and extended stabilization zones (*4*). Supposedly, the octamer exists in high enough concentrations to adsorb onto the sol surface to such an extent that charge reversal occurs, resulting in a positively charged sol. Isotherms for the adsorption of hydrolyzed iron(III) on silica sols have been obtained by O'Melia and Stumm (*25*), and other workers have shown that sols are reversed in charge in the presence of hydrolyzed metal species (*26*). Thus, the lower sol concentration-independent c.c.c. and the subsequent c.s.c. and c.c.c. that define the lower and upper boundaries of the central stability region at higher aluminum concentrations give rise to the phenomenon known as the "irregular series." That is, the sol is destabilized by the metal at a given concentration; increasing the concentration leads to charge reversal and restabilization if the metal is adsorbed. A further increase causes destabilization again, being coagulation of the sol by the anion added with the metal salt.

Based on the adsorption mechanism, dependence of the lower limit of the restabilization zone on sol concentration would be expected. An increase in sol concentration increases the total surface area available for adsorption, consequently increasing the amount of metal required to effect charge reversal. Figure 6 shows that this boundary, as indicated by c.s.c. data, is in fact dependent on the concentration of the sol. This zone is saturated with aluminum hydroxide, and streaming current measurements suggest that the precipitate is positively charged.

Since the concentration of octamer is greatest at the left boundary of the sweep zone, decreasing at higher and lower pH, the right boundary of the restabilization zone would be expected to move toward lower pH with increasing sol concentration. This is evident upon comparing the right limits for the high and low sol concentration. However, aging of the solutions also appears to have an effect since the solubility of aluminum hydroxide and, consequently, the concentration of soluble hydrolyzed species decreases with time. Therefore, as extended periods of time were needed to observe settling with the low sol concentration series, some movement of its boundary might also be anticipated. Apparently, it is entirely coincidental that the restabilization zone for the sol at low concentration extended to the same pH as with the intermediate sol series.

Coagulation of the recharged (positive) sol, at the top boundary of the zone, is by sulfate counterions. Although the higher c.c.c. is expected to be sol concentration independent, some movement of the boundary was observed. In part this could be due to aging of the solution during settling, resulting in less stable limits (see Fig. 5), or possibly because of sulfate complexing. The spike in the restabilization region is indicated by the upper limit of the zone near the slow coagulation zone boundary. Since extensive $AlSO_4^+$ ion-pairing is to be expected (*27*), species such as $AlOHSO_4$(s) could account for this region. The extent of the left boundary has been shown to be greatest at stoichiometric concentrations of aluminum and sulfate (*6, 12*).

Conclusion

As with other sols, the stability of colloidal titanium dioxide is strongly dependent on solution pH and aluminum sulfate concentration. The sol is slowly coagulated by very small concentrations of hydrogen ion. Above pH 6, titania is stable in aluminum solutions less concentrated than 8×10^{-7} *M*. This c.c.c. is lower than has been reported for other sols and is therefore characteristic of titanium dioxide. The concentration of aluminum required for restabilization was found to increase with increasing sol concentration and, apparently, is also related to some surface property of the sol.

The left and right stability limits defining the zone of rapid clarification are sol concentration independent and are essentially the same as found with other colloid systems. Indeed, these stability limits are identical with the solubility limits of aluminum hydroxide. This is shown in the present work by comparing the intercepts of the limits with the equilibrium constants of soluble hydrolyzed aluminum species. These ions were $Al(OH)_4^-$ at high pH and $AlOH^{2+}$ and $Al_8(OH)_{20}^{4+}$ in acid solutions. The limits of the central restabilization zone fall within the concentration-pH ranges of aluminum hydroxide formation and are adequately accounted for by the adsorption of the octameric ion. There can be no doubt that aggregation in the sweep zone is controlled by the parameters affecting the solubility of the hydroxide precipitate.

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