

Stabilization of Aluminum Hydroxide Gel by Specifically Adsorbed Carbonate

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Abstract □ Ion-free aluminum hydroxide gel, prepared by the hydrolysis of aluminum tri-*sec*-butoxide, was observed by IR, X-ray analysis, and pH-stat titration to undergo rapid structural changes leading to the formation of pseudoboehmite and bayerite. The rate of development of order was directly related to the water-aluminum molar ratio. The Al—O bands at 625 and 470 cm⁻¹ were the most sensitive indicators of the development of order in the gel structure. Direct evidence for the stabilizing effect of specifically adsorbed carbonate was obtained when carbon dioxide was introduced during the hydrolysis of aluminum tri-*sec*-butoxide. The resulting aluminum hydroxycarbonate gel possessed excellent antacid properties, retained its amorphous nature upon aging, and contained no cations other than aluminum. Hydrolysis of aluminum tri-*sec*-butoxide in the presence of stoichiometric amounts of sodium bicarbonate resulted in the immediate formation of crystalline sodium aluminum hydroxycarbonate (dawsonite).

Keyphrases □ Hydrolysis of aluminum tri-*sec*-butoxide—use of carbon dioxide-saturated water, formation of amorphous aluminum hydroxycarbonate gel, excellent properties, free of sodium and potassium □ Aluminum hydroxide gel—stabilization by specifically adsorbed carbonate □ Ion-free aluminum hydroxide gel—ordered structure, as an antacid

Aluminum hydroxide gel is an effective antacid largely due to its high rate of acid neutralization and its ability to react with acid at a pH of 3.5–4.0 (1). The chemical name implies a compound consisting of three hydroxyl groups per aluminum atom. This formula describes the crystalline forms of aluminum hydroxide known as gibbsite, bayerite, or norstrandite. These polymorphs have a very low rate of acid neutralization and are, therefore, not useful as antacids. However, a number of reports have suggested that the aluminum hydroxide gel used as an antacid contains specifically adsorbed anions and that these anions act to stabilize the gel structure (2–7) and facilitate the acid neutralization reaction (8).

The anions that are incorporated in the gel structure are usually supplied by the reactants used in the precipitation, such as carbonate from sodium carbonate or sodium bicarbonate or sulfate from aluminum sulfate (3). Aluminum hydroxide gel may also be prepared by the controlled hydrolysis of aluminum tri-*sec*-butoxide, I (9–14). This

method permits precipitation under ion-free conditions as well as in the presence of selected ions. This system was used to study the structure and acid reactivity of ion-free aluminum hydroxide gel as well as the stabilizing effect of specifically adsorbed carbonate on the gel structure.

EXPERIMENTAL

Ion-free aluminum hydroxide gel was prepared by dissolving 6.15 g of I in 40 ml of anhydrous isopropyl alcohol and adding the required quantity of water with agitation. For example, 1.35 ml of water was used to hydrolyze I at a water-aluminum molar ratio of 3.

Aluminum hydroxycarbonate gel was prepared by hydrolyzing I with 3 moles of water/mole of I. The water was saturated with carbon dioxide prior to its addition to I. In addition, carbon dioxide was vigorously bubbled into the I solution during the hydrolysis reaction.

Compound I was hydrolyzed in the presence of 1 mole of sodium bicarbonate/mole of I. Because of the limited solubility of sodium bicarbonate, a water-aluminum molar ratio of 41 was needed to dissolve the sodium bicarbonate.

The hydrolysis products were analyzed for equivalent aluminum oxide content (15). Acid reactivity was determined by pH-stat titration of a sample containing 38 meq aluminum oxide at pH 3, 25° (16).

For X-ray analysis, the samples were dried at room temperature and ground to a fine powder. The diffraction patterns were recorded from 4 to 60° 2 θ using CuK α radiation. The same powder samples were diluted in potassium bromide (2 mg/300 mg) and examined by IR spectroscopy.

RESULTS AND DISCUSSION

Ion-Free Aluminum Hydroxide Gel—Ion-free aluminum hydroxide gel, precipitated with 3 moles of water/mole of I, undergoes very rapid structural changes which were observed by IR and X-ray analysis. The development, within a week, of absorption bands at 3670, 3310, and 3100 cm⁻¹ (Fig. 1), indicates that the initial random structure changed rapidly and that the hydroxyl groups became part of a more uniform environment as the gel aged (17).

The most striking changes are observed in the IR region between 1200 and 400 cm⁻¹. The two strong absorption bands at 625 and 470 cm⁻¹ are in a similar position as the Al—O vibrations observed in boehmite (18). The environment around the Al—O bonds became ordered more rapidly during aging than the environment of the hydroxyl groups. Thus, this IR region is more useful for detecting the earliest stages of crystallization. The vibrations in the hydroxyl region have been useful for monitoring long-term aging (17–19).

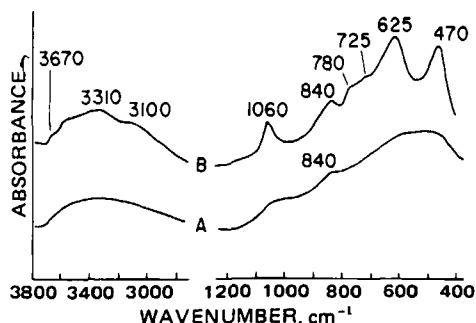


Figure 1—IR spectra of ion-free aluminum hydroxide gel precipitated with water-aluminum ratio of 3. Key: (A) initial; (B) after 1 week at 25°.

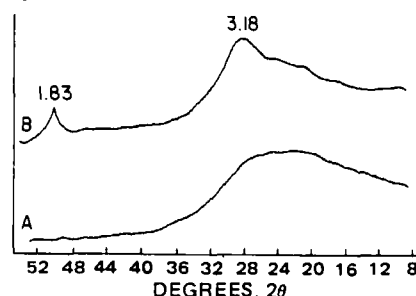


Figure 2—X-ray diffractograms of ion-free aluminum hydroxide gel precipitated with water-aluminum ratio of 3. Key: (A) initial; (B) after 1 week at 25°.

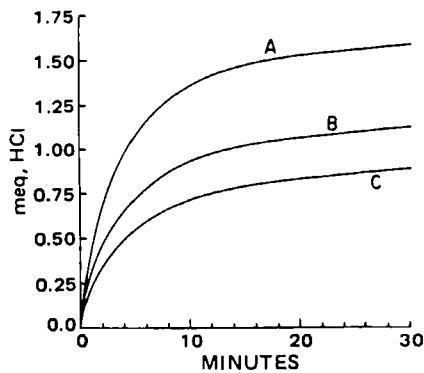


Figure 3—pH Stat titrographs at pH 3, 25° of ion-free aluminum hydroxide gel aged at 25°. Key: (A) initial; (B) after 2 days; (C) after 4 days.

The similarity in the IR spectrum of the hydroxyl vibrations at 3310, 3100 (stretching), and 1060 cm^{-1} (bending) to the spectrum of boehmite suggests that the developing crystalline phase was a disordered boehmite (pseudoboehmite) (13). This conclusion is supported by the X-ray diffractogram (Fig. 2). Initially an amorphous material was formed. At 1 week, the presence of pseudoboehmite was indicated by reflection peaks at 3.18, 1.83, and 1.44 Å (20).

The rate of reaction with acid decreased rapidly as the gel aged. As seen in Fig. 3, the development of an ordered structure in the gel was accompanied by an increase in the fraction of slowly reacting material present in the gel. Theoretically, the 38-meq aluminum oxide sample will neutralize 2.235 meq-HCl. Thus, the ion-free aluminum hydroxide would not be effective as an antacid, since only a small fraction of the ion-free aluminum hydroxide will react during the estimated gastric residence time for antacids of 15 min (21).

The rate of development of order was directly related to the amount of water used to hydrolyze I (13). The IR spectra of the aluminum hydroxide gels prepared using 3, 6, 12, and 24 moles of water/mole of I and aged for 24 hr at 25° are shown in Fig. 4. At lower water-aluminum ratios, amorphous aluminum hydroxide was observed, as indicated by the broad absorption bands.

As noted previously, the Al—O vibration gives the earliest indication of the development of order. At a water-aluminum ratio of 6, a featureless absorption band for the hydroxyl groups was observed between 3700 and 2600 cm^{-1} , while the presence of more ordered Al—O bonds was observed at 620 and 480 cm^{-1} . This absorption, together with the band at 1055 cm^{-1} , indicates that pseudoboehmite, $\text{AlOOH}\cdot\text{H}_2\text{O}$, is forming.

IR spectroscopy (Fig. 4) is a more sensitive technique to follow the development of order than X-ray diffraction, because the X-ray diffractograms of the aluminum hydroxide gels prepared with water-aluminum ratios of 3 and 6 were amorphous. However, in the presence of a large excess of water, a mixture of pseudoboehmite and bayerite was produced. Characteristic bands of pseudoboehmite were observed at 3300,

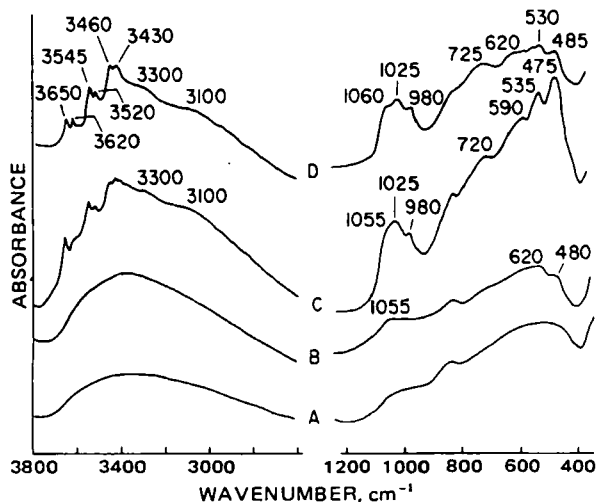


Figure 4—IR spectra after 1 day at 25° of ion-free aluminum hydroxide gel hydrolyzed with various water-aluminum ratios. Key: (A) 3; (B) 6; (C) 12; (D) 24.

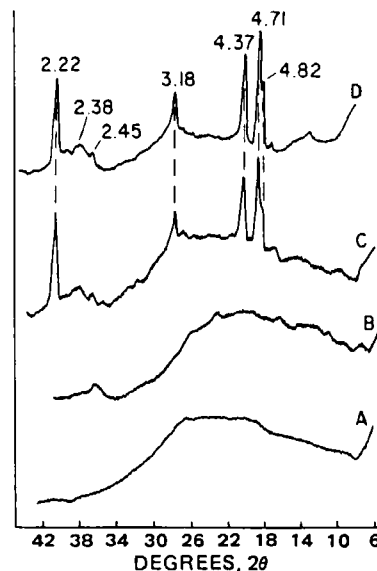


Figure 5—X-ray diffractograms after 1 day at 25° of ion-free aluminum hydroxide gel hydrolyzed with various water-aluminum ratios. Key: (A) 3; (B) 6; (C) 12; (D) 24.

3100, and 1055 cm^{-1} for the hydroxyl stretching and bending vibrations. Bayerite, $\text{Al}(\text{OH})_3$, was observed at a water-aluminum ratio of 12 and predominated at higher water content. The more defined environment of the hydroxyl groups in the bayerite structure was indicated by the sharpness of the absorption bands at 3650, 3545, and 3430 cm^{-1} . The low IR region was not useful in detecting the mixture of pseudoboehmite and bayerite, since the Al—O vibrations are similar in both compounds.

The X-ray diffractograms (Fig. 5) support the conclusions drawn from IR analysis. At a water-aluminum ratio of 12, bayerite was indicated by the peaks at 4.71, 4.37, 3.18, and 2.22 Å. The transformation of pseudoboehmite to bayerite at higher water content was indicated by the loss of the broad background reflection between 30 and 22° 2θ that corresponds to the broad reflection peak at 3.18 Å for pseudoboehmite.

Small amounts of gibbsite were present in the aluminum hydroxide gel precipitated at a water-aluminum ratio of 24 as indicated by the IR bands at 3620 and 3520 cm^{-1} and by the diffraction peak at 4.82 Å (Figs. 4 and 5).

Stabilization of Aluminum Hydroxide Gel—The stabilizing effect of anions present at the time of precipitation has been hypothesized based on indirect evidence such as the relationship between anion content and the rate of loss of acid reactivity (2, 6), the effect of washing (5), and the dependence of the rate of crystallization on the nature of the anion (2, 3). The hydrolysis of I provides an excellent system to demonstrate directly the stabilizing action of anions. The interaction of carbonate anion with aluminum hydroxide was achieved by saturating the water used for hydrolysis with carbon dioxide and by bubbling carbon dioxide into the reaction medium during hydrolysis. X-ray diffraction patterns of the product were amorphous both initially and after aging for 1 month at 25°. This result agrees with Torkar's earlier observation that the reaction product of aluminum ethoxide and water saturated with carbon dioxide remained amorphous for 20 days at 22° (22).

The IR spectrum of the precipitate formed in the presence of carbon dioxide-saturated water (Fig. 6) indicates an amorphous aluminum hydroxycarbonate gel. The broad hydroxyl stretching band at 3460 cm^{-1}

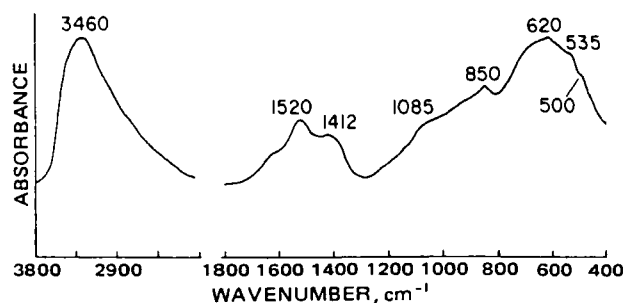


Figure 6—IR spectrum of aluminum hydroxide gel precipitated in the presence of carbon dioxide.

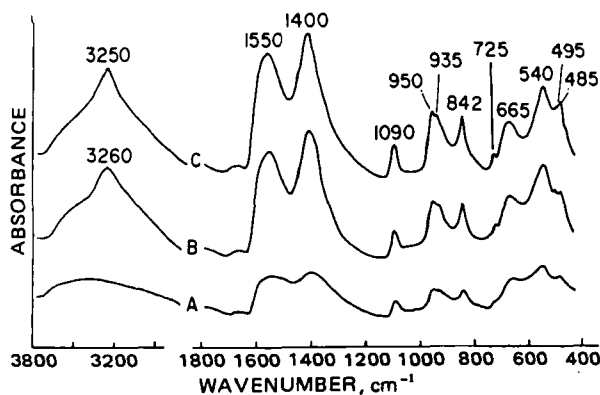


Figure 7—IR spectra of the precipitate obtained by the hydrolysis of I in the presence of sodium bicarbonate aged at 25°. Key: (A) initial; (B) 30 min; (C) 1 day.

indicates that the hydroxyl groups are disordered, while the ν_3 carbonate bands at 1520 and 1412 cm^{-1} indicate that carbonate is directly coordinated to aluminum in the gel structure (4, 6, 23–25). The absorption band at 1085 cm^{-1} (ν_1) also supports the direct coordination of carbonate to aluminum since this absorption is only active in the Raman when the carbonate anion has full symmetry.

The amorphous aluminum hydroxycarbonate gel reacted completely with acid and exhibited a T_{50} of 3 min by pH-stat titration. The rate of acid neutralization was virtually unchanged during the 1-month evaluation period.

Compound I was also hydrolyzed in the presence of carbonate ion using 1 mole of sodium bicarbonate per mole of I. The sodium bicarbonate was dissolved in the water for hydrolysis. This reaction resulted in the immediate formation of sodium aluminum hydroxycarbonate which is known mineralogically as dawsonite (13) and is contained in the USP as dihydroxyaluminum sodium carbonate (26). As can be seen in Fig. 7, the initial IR spectrum showed the split carbonate band, ν_3 , at 1550 and 1400 cm^{-1} , which is characteristic of the distortion of carbonate in dawsonite (13). Rapid structural development occurred during the first 30 min as evidenced by the appearance of a hydroxyl stretching band at 3260 cm^{-1} and the general sharpening of the bands observed in the initial spectrum. Little indication of further structural development is observed in the 24-hr spectrum.

The IR spectrum of the 1-day sample was identical to the spectrum of dawsonite (27), except that the bands are broader suggesting a more poorly ordered structure of a smaller particle size than the mineralogical sample.

The rapid structural development of dawsonite was also observed in the X-ray diffractograms (Fig. 8), which exhibit the major peaks of

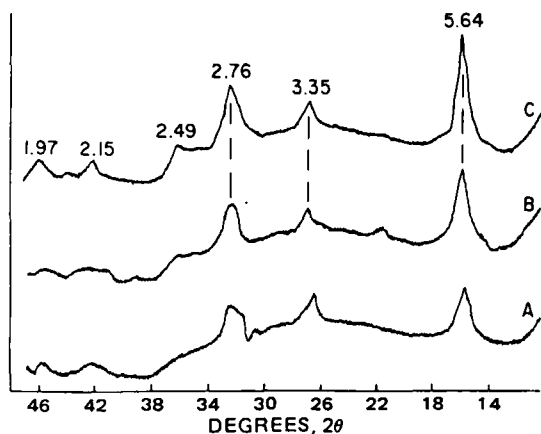


Figure 8—X-ray diffractograms of the precipitate obtained by the hydrolysis of I in the presence of sodium bicarbonate aged at 25°. Key: (A) initial; (B) 30 min; (C) 1 day.

dawsonite immediately after precipitation and show some refinement in the structure upon aging.

The synthetic dawsonite exhibited a rapid rate of acid neutralization as evidenced by its T_{50} of 3 min. The rate of neutralization was virtually unchanged during the 1-month observation period. The presence of a stoichiometric amount of sodium bicarbonate at the time of precipitation produced a highly reactive, crystalline hydroxycarbonate which contains 158 mg of sodium per gram of sodium aluminum hydroxycarbonate.

Summary—Aluminum hydroxide gel produced under ion-free conditions rapidly developed an ordered structure which reacts too slowly with acid to be effective as an antacid. The use of carbon dioxide-saturated hydrolysis water as the source of carbonate ion produced an amorphous aluminum hydroxycarbonate gel which exhibited excellent antacid properties and was totally free of foreign cations such as sodium or potassium. The use of a stoichiometric amount of sodium bicarbonate as the source of carbonate resulted in the formation of crystalline sodium aluminum hydroxycarbonate which possesses excellent antacid properties but which has a high sodium content.

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