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Effect of Polybasic Acids on Structure of Aluminum Hydroxycarbonate Gel

MING K. WANG *, JOE L. WHITE *, and STANLEY L. HEM *[‡]

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Abstract □ The effect of oxalic acid, citric acid, and their sodium salts on the structure of aluminum hydroxycarbonate gel was studied to illustrate the various mechanisms by which polybasic acids interact with aluminum hydroxycarbonate gel. Analysis of changes in the pH-stat titrgram, the carbonate to aluminum ratio, the aluminum content of the supernate following centrifugation, and the adsorption of the organic solute indicates that polybasic acids may: (a) partially neutralize the aluminum hydroxycarbonate gel by a general acid effect, (b) modify the aluminum hydroxycarbonate surface by adsorption of the anionic form of the polybasic acid, (c) extract aluminum by the formation of a soluble complex, and (d) lead to the precipitation of a new crystalline phase.

Keyphrases □ Polybasic acids—oxalic acid, citric acid, and their sodium salts, effect on aluminum hydroxycarbonate gel structure, complexation of polybasic acids with aluminum, adsorption of polybasic anion, acid neutralization □ Complexation—polybasic acids and their sodium salts with aluminum hydroxycarbonate gel, acid neutralization, structural changes in aluminum hydroxycarbonate gel □ Acid neutralization—complex formation with polybasic acids and aluminum hydroxycarbonate gel □ Aluminum hydroxycarbonate—complexation with polybasic acids and their sodium salts, structural changes, acid neutralization

Citric acid, oxalic acid, and other polybasic acids can inhibit the crystallization of aluminum hydroxide and form complexes with aluminum (1-3). Gibaldi and Mufson (4) found that the neutralization of dried aluminum hydroxide gel was inhibited when sodium citrate or sodium tartrate was added to the 0.1 N HCl used as the reaction medium. It was concluded that dried aluminum hydroxide gel reacts with sodium citrate or sodium tartrate to produce a water-soluble complex as well as to reduce surface area by flocculation.

Polybasic acids are important in soil-weathering reactions due to their role in complexing and solubilizing aluminum (5, 6). In addition, it was found that the edge faces of gibbsite (7), as well as synthetic goethite (8), can adsorb oxalate anion.

The nature of the interaction of polybasic acids with the surface of aluminum hydroxycarbonate has not been ex-

amined in detail. This study describes the mechanisms by which polybasic acids interact with aluminum hydroxycarbonate and the effect of these interactions on the acid reactivity of aluminum hydroxycarbonate gel.

EXPERIMENTAL

An aluminum hydroxycarbonate gel that exhibited a moderate rate of acid neutralization was selected so that any increase or decrease in the acid neutralization rate would be observed easily. The gel was amorphous to X-rays and had an IR spectrum characteristic of aluminum hydroxycarbonate gel (9).

Mixtures containing 0.2 M equivalent aluminum oxide and either 0.1 or 0.2 M polybasic acid or salt were prepared by dissolving the polybasic acid or salt in water and adding the solution to an appropriate quantity of aluminum hydroxycarbonate gel with mixing.

The acid neutralization reaction was monitored by an automated pH-stat titration at pH 3.0 and 25° (10).

The carbonate content was determined by gasometric displacement using the Chittick apparatus¹ (11) and is expressed as the molar ratio of carbonate to aluminum.

The aluminum content of the supernate was determined by centrifuging at 15,000 rpm (27,000×g) for 30 min and measuring the aluminum content of the supernate by atomic absorption spectroscopy. The result represents the aluminum-ion content as well as the aluminum content of hydroxyaluminum polymers that remain in the supernate after centrifugation. The aluminum content of the supernate depended on the conditions of centrifugation, and all results reported were obtained under carefully standardized conditions.

The distribution of the organic solute was monitored by analyzing both the supernate and the solid phase for organic carbon content by the Walkley-Black method (12). In every case, the sum of the organic carbon in solution and in the solid phase was 82-101% of the theoretical carbon content.

The solid phase that formed when 0.2 M citric acid was added to the aluminum hydroxycarbonate gel was analyzed by X-ray diffraction² and IR spectroscopy. A sample of the solid phase was vacuum dried over phosphorus pentoxide and ground to a fine powder with an agate mortar

¹ Sargent-Welch Scientific Co., Skokie, Ill.

² Siemens AG Kristalloflex 4 generator, type F diffractometer, Karlsruhe, West Germany.

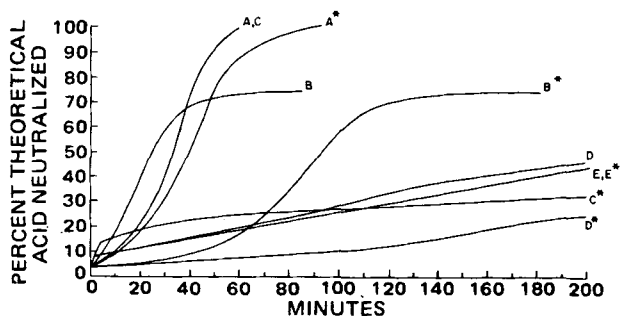


Figure 1—The pH-stat titrgrams at pH 3.0 and 25° for aluminum hydroxycarbonate gel equivalent to 0.2 M Al₂O₃ with 0.1 M polybasic acids. Key: A, control; B, oxalic acid; C, sodium oxalate; D, citric acid; E, sodium citrate; and *, aged at 40° for 2 weeks.

and pestle. Powder mounts for X-ray diffraction were prepared using McCreery mounts. The diffraction pattern was recorded from 6 to 55° 2θ under the following conditions: CuK_α radiation, 40 kv, 20 mamp, 500 cps full scale, and 2°/min scan speed. IR spectra³ were obtained by pressing a disk containing 0.5 mg of the dried powder with 300 mg of potassium bromide.

RESULTS

Figure 1 shows the pH-stat titrgrams of aluminum hydroxycarbonate gel immediately following the addition of 0.1 M oxalic acid, citric acid, sodium oxalate, or sodium citrate and after aging for 2 weeks at 40°. As expected, the acid neutralization rate decreased slightly during aging of the control aluminum hydroxycarbonate gel (Fig. 1A).

Oxalic acid (Fig. 1B) caused an initial decrease in the total amount of neutralized acid that was related directly to the oxalic acid concentration. In addition, a more rapid acid neutralization rate was observed immediately following oxalic acid addition. However, the acid neutralization rate decreased much more rapidly with aging (Fig. 1B*) than did the rate for the control aluminum hydroxycarbonate gel.

Sodium oxalate initially did not affect the pH-stat titrgram (Fig. 1C). However, a totally different acid neutralization profile was observed upon aging; it was characterized by a two-phase titrgram in which ~15% of the acid was neutralized immediately and the major portion followed a slow, zero-order reaction (Fig. 1C*).

The addition of citric acid substantially decreased the acid neutralization rate (Fig. 1D), which decreased further upon aging (Fig. 1D*). However, the pH-stat titrgram still shows evidence of the three-phase titrgram that characterized aluminum hydroxycarbonate gel (9).

The addition of sodium citrate resulted in a slow, two-phase neutralization reaction, which did not change during aging (Fig. 1E).

The polybasic acids caused a decrease in pH accompanied by a decrease in the carbonate to aluminum ratio (Table I). This effect also was observed when 0.1 M HCl was added to the aluminum hydroxycarbonate gel. The carbonate to aluminum ratio was not affected by the addition of sodium oxalate or sodium citrate.

Oxalic acid caused an initial increase in the aluminum content of the supernate, which decreased slowly during aging. Citric acid initially produced a high level of aluminum in the supernate, which dropped significantly during aging. The addition of 0.2 M citric acid converted the liquid gel into a solid within 30 min of mixing. Hydrochloric acid increased the aluminum content in the supernate, which increased further upon aging.

Sodium oxalate caused a small increase in the aluminum content of the supernate, which did not change during aging. A substantial increase in the aluminum content of the supernate occurred following the addition of sodium citrate, with approximately half of the aluminum in the gel solubilized by the addition of 0.2 M sodium citrate.

The adsorption of the polybasic acid or its salt was measured by determining the carbon content of the supernate and the solid phase (Table I). Approximately 40% of the added oxalic acid was in solution immediately following the addition of oxalic acid. The oxalic acid concentration in solution slowly decreased during aging. Sodium oxalate showed the same pattern, except that higher levels of oxalate ion were found in solution.

³ Model 180, Perkin-Elmer Corp., Norwalk, Conn.

Table I—Effect of Polybasic Acids and Their Salts on the Composition of Aluminum Hydroxycarbonate Gel^a

Polybasic Acid or Salt Added	pH			Molar Ratio of Carbonate to Aluminum			Total Aluminum in Supernate, %			Total Carbon in Supernate, %		
	Initial	1 Week	2 Weeks	Initial	1 Week	2 Weeks	Initial	1 Week	2 Weeks	Initial	1 Week	2 Weeks
	Control	6.5	6.4	6.1	0.36	0.34	0.33	0.3	0.3	0.3	41.3	30.8
0.1 M Oxalic acid	4.6	5.1	5.2	0.21	0.08	0.08	3.8	2.2	1.4	37.5	24.1	25.0
0.2 M Oxalic acid	4.1	4.4	4.3	0.15	0.03	0.02	11.5	9.0	7.8	53.6	46.2	36.4
0.1 M Sodium oxalate	9.3	8.8	8.8	0.36	0.32	0.31	2.3	2.3	2.3	61.5	52.6	41.7
0.2 M Sodium oxalate	9.6	8.9	8.9	0.36	0.32	0.33	2.4	2.8	2.3	44.3	8.4	6.2
0.1 M Citric acid	4.0	4.6	4.7	0.26	0.10	0.10	28.0	5.1	2.3	64.2	66.2	56.3
0.2 M Citric acid ^b	—	—	—	—	—	—	—	—	—	—	—	—
0.1 M Sodium citrate	10.0	10.1	10.2	0.36	0.33	0.33	15.7	19.2	22.6	79.0	71.0	87.7
0.2 M Sodium citrate	10.5	10.3	10.3	0.35	0.34	0.34	34.0	57.5	62.1	—	—	—
0.1 M Hydrochloric acid	4.2	4.6	4.4	0.24	0.07	0.07	13.9	15.3	17.2	—	—	—

^a Samples were maintained at 40°. ^b Sample turned solid within 30 min of preparation.

Table II—X-Ray Powder Diffraction Pattern of the New Phase Formed when 0.2 M Citric Acid Was Added to Aluminum Hydroxycarbonate Gel Equivalent to 0.2 M Al₂O₃, Compared to the 10 Most Intense Peaks for Citric Acid, Sodium Citrate, and Aluminum Citrate^a

New Phase		Citric Acid Monohydrate ^b		Sodium Citrate Dihydrate ^c	
Inter-planar Spacing, Å	Relative Intensity, %	Inter-planar Spacing, Å	Relative Intensity, %	Inter-planar Spacing, Å	Relative Intensity, %
14.26	100	5.82	100	7.86	100
7.63	10	4.87	90	3.70	35
7.20	10	3.980	65	5.05	30
6.92	16	3.849	55	5.49	18
6.66	21	2.741	40	3.01	14
6.28	12	4.94	25	2.438	14
6.19	12	3.639	25	9.54	12
5.64	10	3.045	25	3.258	12
5.10	6	2.684	18	2.742	12
5.01	6	4.66	16	4.83	10
3.82	9	3.744	16	3.23	10
3.65	22	3.025	16	2.964	10
3.49	16	2.913	16	2.414	10
3.47	16				
3.35	16				
3.29	20				
3.13	14				
3.10	14				
3.02	7				
2.93	10				
2.15	7				

^aSample obtained from Pfaltz and Bauer, Stamford, Conn., was amorphous to X-rays. ^bData from A.S.T.M. Card 15-985. ^cData from A.S.T.M. Card 16-1170.

A high citric acid level was seen in solution initially but dropped sharply during aging. Most of the added sodium citrate was present in solution both initially and during aging.

The X-ray diffractogram and IR spectrum of the solid that formed upon the addition of 0.2 M citric acid are shown in Table II and Fig. 2, respectively. The appearance of a new phase is indicated by the peaks in the X-ray diffractogram, which differ from that of citric acid, sodium citrate, or aluminum citrate. The reaction of citric acid with aluminum to form citrate anion in the new phase was confirmed by the shift of the carbonyl stretching band of citric acid at 1730 cm⁻¹ to an unresolved doublet with maxima at 1615 and 1640 cm⁻¹.

DISCUSSION

Polybasic acids and their salts cause significant changes in the structure of aluminum hydroxycarbonate gel that affect both acid reactivity and stability, and several mechanisms may be responsible for these changes.

Oxalic acid appears to act by a general acid effect, which causes partial neutralization of the aluminum hydroxycarbonate gel. This effect is suggested by the decrease in the total amount of acid neutralized, the loss of carbonate from the gel structure, and the increased aluminum content of the supernate.

The increased acid neutralization rate following the addition of oxalic acid agrees with the previous observation (13) that the reaction of structural carbonate with acid disrupts the gel structure and increases the porosity. This effect facilitates diffusion of acid into the gel and leads to an accelerated acid neutralization rate. However, the gel is expected to polymerize more rapidly upon aging in the absence of structural carbonate. This behavior was confirmed by the large decrease in the acid neutralization rate upon aging (Fig. 1B*).

Adsorption of the oxalate anion produced in the neutralization reaction of oxalic acid and aluminum hydroxycarbonate gel may occur, as suggested by the decreased concentration of organic carbon in solution. Evidence for the adsorption of oxalate anion also was seen when sodium oxalate was added to the aluminum hydroxycarbonate gel. No immediate effect was observed on the pH-stat titrgram, but the slow, constant rate of acid neutralization observed after aging (Fig. 1C*) suggests that oxalate anion is adsorbed by the aluminum hydroxycarbonate surface and that the acid neutralization rate is controlled by the diffusion of protons

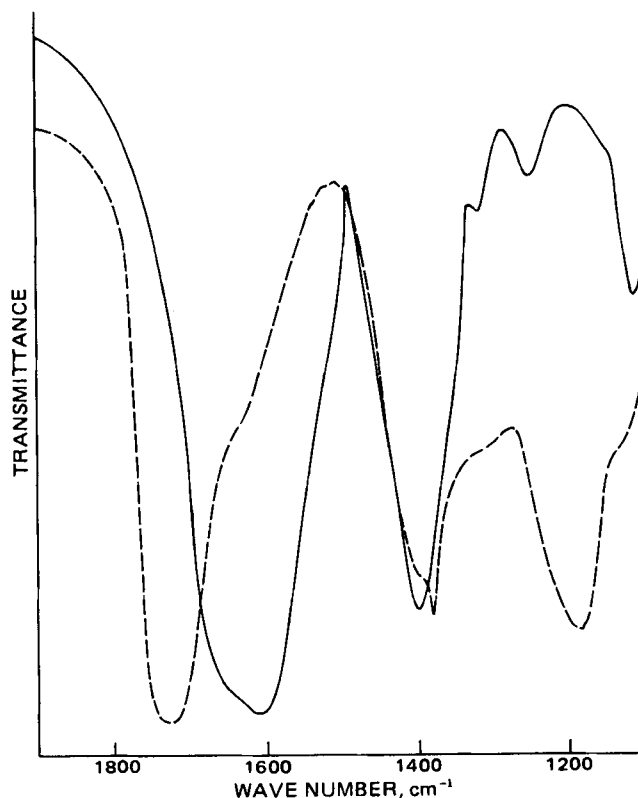


Figure 2—IR spectra of citric acid (---) and the solid phase that formed from a mixture of 0.2 M citric acid and aluminum hydroxycarbonate gel equivalent to 0.2 M Al₂O₃ (—).

through the adsorbed oxalate layer to the aluminum hydroxycarbonate gel surface.

The carbonate to aluminum ratio was not affected by sodium oxalate. However, the amount of oxalate anion in solution decreased during aging, and only a relatively small increase in the aluminum content of the supernate was observed. This behavior supports the proposed surface adsorption mechanism.

The addition of sodium citrate to aluminum hydroxycarbonate gel also produced a pH-stat titrgram consisting primarily of a slow, zero-order acid neutralization reaction, which did not change during aging.

It is hypothesized that citrate anion is adsorbed by the aluminum hydroxycarbonate surface, producing the same type of diffusion-controlled acid neutralization as was seen in the aged sodium oxalate sample.

Adsorption of citrate anion occurs immediately in contrast to oxalate anion. The increase in the aluminum content of the supernate to ~60% following aging of the 0.2 M sodium citrate sample and the high levels of citrate anion in solution suggest that, following citrate anion adsorption, aluminum is extracted from the aluminum hydroxycarbonate through the formation of a soluble complex.

Citric acid caused the greatest decrease in the acid neutralization rate. After aging for 2 weeks at 40°, only 30% of the theoretical amount of acid was neutralized in 200 min (Fig. 1D*).

The decrease in the carbonate to aluminum ratio and the high initial aluminum content of the supernate suggest that citric acid acts by a general acid effect to neutralize partially the aluminum hydroxycarbonate gel. However, the mechanism by which citric acid affects the gel structure appears to be more complex than that observed for oxalic acid.

The sharp decrease in both aluminum in the supernate and organic carbon in solution during aging suggests the precipitation of a new phase containing aluminum and citrate. When 0.2 M citric acid was added, the aluminum hydroxycarbonate gel turned solid within 30 min. The structure of the solid phase that formed is not known; the new phase contained citrate anion, but the X-ray diffractogram differed from that for sodium or aluminum citrate.

Although the crystalline phase was not identified, its formation rate is dependent on the citric acid concentration. The crystalline phase does not exhibit acid neutralization properties when measured by pH-stat titration at pH 3, and its formation destroys the antacid properties of aluminum hydroxycarbonate gel.

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Deiodination Kinetics of Water-Soluble Radiopaques

YU-CHANG JOHN WANG

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Abstract □ Deiodination of diatrizoic acid, an anionic radiopaque, was found to be catalyzed by Cu(II). Through a detailed study of *o*-iodobenzoic acid, a model compound, the copper-catalyzed S_N1 mechanism was established based on observations of common ion, salt, and pH effects. *Meta*- and *para*-iodobenzoic acids were unreactive. Deiodination thus was facilitated by a neighboring carboxylate that attracted copper. Iopamidol, a nonionic radiopaque, also underwent deiodination. At pH 7 or above, the hydroxide-ion substitution predominated. At pH below 7, the reaction is in favor of the copper-catalyzed S_N1 mechanism.

Keyphrases □ Diatrizoic acid—radiopaque, deiodination kinetics □ *o*-Iodobenzoic acid—deiodination, metal-catalyzed S_N1 mechanism □ Iopamidol—radiopaque, deiodination mechanism □ Kinetics—aromatic S_N1 deiodination of radiopaques □ Radiopaques—diatrizoic acid and iopamidol, deiodination kinetics □ Metal catalysis—neighboring carboxylate deiodination

The most important radiopaques are the water-soluble, anionic compounds such as diatrizoic acid (I), iothalamic acid, and iopamide. These compounds are benzoic acid derivatives with two or three iodines attached to the benzene ring. There appears to be no evidence in the literature that appreciable deiodination occurs in products containing any of these compounds (1). However, experiments in these laboratories showed that significant deiodination took place in the absence of chelating agents.

Since the mechanism of this reaction was not established, this paper will discuss the deiodination kinetics of diatrizoic acid as a representative of anionic radiopaques. A model compound, *o*-iodobenzoic acid, was studied to support the proposed mechanism. A new nonionic radiopaque, iopamidol (II) (2), also was examined, and its deiodination kinetics were compared with those of diatrizoic acid.

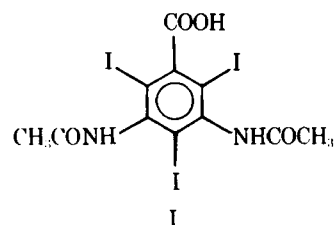
EXPERIMENTAL

Materials—Diatrizoic acid¹, iopamidol², 8-hydroxyquinoline³, and

¹ Renografin, E. R. Squibb & Sons, New Brunswick, N.J.

² C₁₇H₂₂I₃N₃O₈, *N,N'*-bis[2-hydroxy-1-(hydroxymethyl)ethyl]-5-[(2-hydroxy-1-oxopropyl)amino]-2,4,6-triiodo-1,3-benzenedicarboxamide (Bracco 15,000, SQ 13,396), E. R. Squibb & Sons, New Brunswick, N.J.

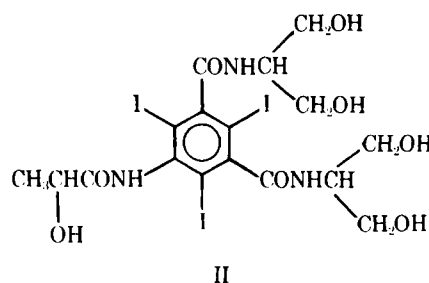
³ Eastman Kodak Co., Rochester, N.Y.



m- and *p*-iodobenzoic acids³ were used without further purification; *o*-iodobenzoic acid³ was recrystallized twice from ethanol-water. All other chemicals were reagent grade. The water used complied with the USP specifications for purified water.

Deiodination of Diatrizoic Acid—Diatrizoic acid was dissolved in water with a stoichiometric amount of sodium hydroxide. Sørensen phosphate buffer (3) was added to bring the final phosphate concentration to 0.0067 M. The chelating agent employed was edetate disodium USP at 0.04% (w/v). The amount of iodide produced after stressed conditions was determined by the USP method (4), which specifies the measurement of the absorbance of iodine in a toluene extract at 495 nm⁴ after the iodide has been oxidized to iodine. The concentration was calculated from a standard curve obtained from potassium iodide solutions. Similar to the USP specification, the amount of iodide found was expressed as the percentage of the weight of iodide with respect to the weight of radiopaque in the same solution.

Kinetic Studies for *o*-Iodobenzoic Acid—*o*-Iodobenzoic acid was dissolved in water with a stoichiometric amount of sodium hydroxide. Sørensen phosphate buffer at 0.0067 M and cupric sulfate at 0.5 ppm of Cu(II) were used unless stated otherwise. Solutions were immersed in a constant-temperature (±0.1°) oil bath⁵, and samples were removed periodically for UV assay. Absorbances of the samples at 295 nm were used



⁴ Model 25 spectrophotometer, Beckman Instruments, Irvine, Calif.

⁵ Constant-temperature circulator model FJ, Haake Inc., Saddle Brook, N.J.