INFLUENCE OF pH, CONCENTRATION, AND CHELATING POWER OF ORGANIC ANIONS ON THE SYNTHESIS OF ALUMINUM HYDROXIDES AND OXYHYDROXIDES[1]

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Abstract—Chelating organic acids hampered the hydrolytic reactions of Al and affected the nature of the crystalline aluminum hydroxides. Chemical composition, structure, size, nature of functional groups, and concentration of each organic anion, as well as the pH of the system, controlled the rate of $Al(OH)_3$ crystallization. The order of effectiveness of the various acids was: glutaric < succinic = phthalic < glycine < malonic < glutamic < aspartic < oxalic < salicylic = malic < citric < tartaric. An increase in the stability of complexes formed between the organic ligands and Al decreased the rate of crystallization and changed the final aluminous products from bayerite to nordstrandite and/or gibbsite and then to pseudoboehmite and/or amorphous material. In the presence of anions with a great affinity for Al, particularly at pH equal to or less than 9.0, the reaction products were commonly poorly crystalline or structurally distorted. In the range of pH 8.0 to 10.0 moderately or strongly chelating anions acted to retard or prevent olation and facilitated the formation of stable pseudoboehmite or X-ray-amorphous products. The stronger the chelating power or the higher the concentration of organic anions, the easier was the formation of pseudoboehmite or amorphous material.

Key Words—Aluminum hydroxide, Aluminum oxyhydroxide, Carboxylic acid, Chelation, Crystallization, Pseudoboehmite.

INTRODUCTION

Aluminum hydroxides and oxyhydroxides have incited great interest in pedology and chemistry because of their occurrence as weathering products in soils and their specific adsorptive properties for anions and cations (Huang and Keller, 1972; Kinniburg *et al.*, 1976; Hsu, 1977; Parfitt, 1978). Various laboratory studies have been carried out on the effect of chelating organic acids, usually present in soil solutions, on the hydrolytic reactions of aluminum, as well as on the formation of crystalline and noncrystalline Al-hydroxides (Kwong and Huang, 1975, 1977, 1979a; Violante and Violante, 1978; Violante and Jackson, 1979, 1980).

Aluminum hydroxide crystallizes in three polymorphs: gibbsite, bayerite, and nordstrandite, but the factors governing their formation are not completely understood. Foreign anions, clay surfaces, precipitation rate, and pH appear to influence their synthesis (Schoen and Roberson, 1970; Luciuk and Huang, 1974; Kwong and Huang, 1975; Violante and Jackson, 1979, 1980). According to Aldcroft *et al.* (1969), the formation of a trihydroxide is governed by the solubility and solution rate of the pseudoboehmite that is formed as an intermediate phase between the initially formed amorphous Al-hydroxide and the final $Al(OH)_3$ product. Hsu (1977) reported that rapid precipitation and crystallization in neutral or alkaline media yields bayerite; in contrast, slow crystallization favors gibbsite, as occurs in acidic environments. However, it is not

clear why nordstrandite and gibbsite, rather than bayerite, are more common in alkaline soils or in bauxite deposits (Lodding, 1961; Keller, 1964; Violante and Jackson, 1979 and references therein). Recently, Violante and Jackson (1979, 1980) demonstrated that in neutral and alkaline solutions, citrate anions favor the crystallization of nordstrandite and/or gibbsite, particularly in the presence of montmorillonite which acts as a catalyst.

The aim of the present work is to demonstrate that pH of the system and organic agents of different chelating power control the crystallization rate of $Al(OH)_3$ and influence the nature of the final aluminous products.

EXPERIMENTAL METHODS

Aluminum hydroxides were precipitated between pH 7.0 and 10.0 by the slow addition with stirring of 0.05 N NaOH to a mixture of $AlCl_3$ and carboxylic acid (glutaric, succinic, phthalic, aminoethanoic (glycine), glutamic, aspartic, malonic, oxalic, salicylic, malic, citric, or tartaric acid). The rate of addition of NaOH was about 1 ml/min. The concentration of total Al in the suspension after precipitation was 3×10^{-3} M; the concentrations of carboxylic acid were chosen to give molar Al:carboxylic acid ratios of 100, 70, 35, 20, 10, and 6. All samples were aged in polyethylene bottles, and pH values were kept constant for 60 days by adding 0.1 N NaOH or HCl. All samples were prepared in duplicate.

Oriented aggregate specimens for X-ray powder diffraction (XRD) were obtained by drying washed aliquots of variously aged samples on glass slides. XRD patterns were obtained with an Ital Structure diffrac-

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Table 1. Aluminum hydroxides and oxyhydroxides formed in the presence of complexing organic acids after 60 days at 20°C.

Al:carb- oxylic acid molar ratio	Acids								
	Succinic	Glycine	Glutamic	Aspartic	Oxalic	Malic	Salicylic	Citric	Tar- taric
			Samples aged at pH 8.0						
70	B, (G)	B, (G)	—	G	G, (P)	G, P	—	P	P
35	B, (G)	B, (G)	G, N (B)	P, G, (N)	G, P or P	P	P	A	A
20	B, (G)	B, G	G, N	P, (G)	P	P	P	A	A
6	G, N, B	G	P	A	A	A	A	A	A
			Samples aged at pH 9.0						
35	B	B, (N)	B, N	N	N, B	N, P	N, P	P	P
20	B	B, N	N	G, N, P	N, (P, B)	P, (N, G)	P, N, (G)	P	A
6	B, N	N, (P)	G, N, P	G, P	G, P or P	P	P, (N, G)	A	A
			Samples aged at pH 10.0						
20	B	B	B	B	B, (P)	B, N	N, (B)	N	P
6	B	B	B, (P)	B, P	N, B, (P)	N, P	N, P, (G)	P	A

A = Amorphous Al-hydroxides; P = pseudoboehmite; B = bayerite; G = gibbsite; N = nordstrandite; ( ) indicates small amounts; — = no aluminum hydroxides or oxyhydroxides detected.

tometer with CuKα radiation generated at 35 kV and 20 mA. A scanning rate of $0.5°2\theta$/min was generally used to provide high precision in determining the 2θ values as necessary to distinguish the Al(OH)$_3$ polymorphs (bayerite = 4.72 Å; nordstrandite = 4.79 Å; gibbsite = 4.85 Å).

For transmission electron microscopic (TEM) examination, a drop of suspension was deposited on a grid covered with a carbon film and allowed to evaporate at 40°C. Samples for Pt/C-shadowed replicas and scanning electron microscopy (SEM) investigation were "quench frozen" by immersion in liquid nitrogen and then dried in vacuo at a temperature below the freezing point. TEM and SEM electron micrographs were taken with a Philips model EM 300 and a Cambridge S4 Stereoscan microscope.

RESULTS AND DISCUSSION

Organic anions delayed or inhibited the crystallization rate of Al(OH)$_3$ polymorphs to varying degrees. Depending on their nature and molecular structure, the organic acids studied affected the kinetics of crystal formation in the following order: glutaric < succinic = phthalic < glycine < malonic < glutamic < aspartic < oxalic < salicylic = malic < citric < tartaric. The effectiveness of each organic anion increased when its concentration was increased and when the pH was decreased.

Table 1 shows the aluminous species (gibbsite, bayerite, nordstrandite, pseudoboehmite, amorphous alumina) obtained after 60 days of aging at pH 8.0, 9.0, and 10.0 in the presence of the organic compounds studied. Data for glutaric, phthalic, and malonic acid are not reported in the table, but are discussed in the text. Figure 1 shows XRD patterns of Al-hydroxides and oxyhy-

droxides formed at pH 9.0 and an Al:carboxylic acid molar ratio of 10.0 after the mixture had been aged for 6 months.

The above reported results clearly indicate that pH, concentration, and retarding power of the organic anions control the nature of the precipitation products. Horizontal reading of the table shows that at a given pH and Al:organic acid ratio there is a change in the final aluminous products formed from bayerite to nordstrandite and/or gibbsite and finally to pseudoboehmite and amorphous material, approximately according to the increasing chelating power of the organic anions (see below). The same order of formation of the various aluminous precipitation products was found at a given pH by increasing the concentration of some of the organic compounds.

Influence of pH and nature of carboxylic acids

Because succinic and phthalic acids weakly complex aluminum ions (Murmann, 1969) by forming unstable 7-membered rings (Figure 2a), their presence had a negligible influence on the crystallization rate, particularly at pH >8.0. At pH 9.0 and 10.0 bayerite had already crystallized a few hours after the sample preparation (Figures 1a and 3a), as in the samples prepared in the absence of organic anions (control systems), where the hydroxide formed was usually pure bayerite (Violante and Violante, 1978). Weak influence of these acids on the crystallization of gibbsite and/or nordstrandite over bayerite was ascertained at pH 8.0 and at an Al:carboxylic acid ratio of 6 (Table 1), but also in these samples large amounts of bayerite formed.

In contrast, glycine (aminoethanoic acid), a bidentate agent, like phthalic and succinic acids, complexes aluminum ions by forming a more stable 5-membered ring
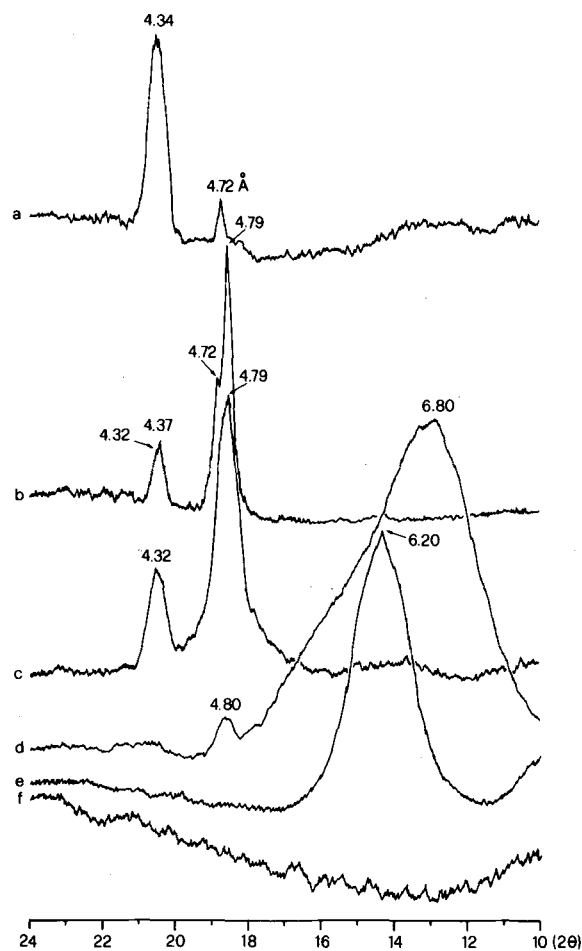
Figure 1. X-ray powder diffractograms (CuKα radiation) of aluminous precipitates aged 180 days at pH 9.0 with an Al:carboxylic acid molar ratio of 10: (a) bayerite (4.72, 4.34 Å) formed in the presence of succinate after 2 days (unchanged after 180 days); (b) mainly nordstrandite (4.79, 4.32 Å) with bayerite (4.72, 4.37 Å) formed in the presence of glycinate; (c) almost pure nordstrandite formed in the presence of glutamate; (d) pseudoboehmite (6.80 Å) with very low amounts of Al(OH)₃ polymorphs, probably gibbsite and nordstrandite, formed in the presence of salicylate; (e) pure pseudoboehmite synthesized in the presence of malate; (f) amorphous alumina obtained in the presence of tartrate.

Figure 2. Possible ways of complexing by (a) weakly and (b) moderately chelating organic acids.

(Figure 2a). Consequently in glycinate systems, particularly at the lowest Al:glycine ratios and at pH 8.0 and 9.0, the rate of Al(OH)₃ crystallization was slower than in succinate or phthalate systems, and the formation of gibbsite (at pH 8.0) and nordstrandite (at pH 9.0) was favored.
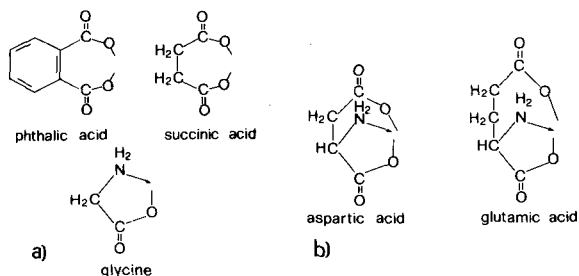
The XRD pattern of the sample prepared with an Al:glycine ratio of 10 and aged at pH 9.0 showed a peak of nordstrandite higher than that of bayerite (Figure 1b). At a higher concentration of glycine (Al:glycine ratio of 6), at the same pH, almost pure nordstrandite (with rare triangular crystals of bayerite) was obtained (Figure 3b). At pH 10.0 glycinate did not decrease the crystallization rate nor did it hinder bayerite formation even a few hours after preparation of the samples (Figure 3c).

With more effective retarding agents, such as glutamic and aspartic acids, gibbsite, nordstrandite, and pseudoboehmite formed easily at pH 8.0 and commonly at pH 9.0. Aspartic and glutamic acids are both tridentate, but in the presence of aspartic acid, the crystallization rate of aluminum hydroxide was lower than in the presence of glutamic acid. In samples where aspartic acid was present, gibbsite, nordstrandite, or pseudoboehmite formed more readily than bayerite (Table 1). Aspartic acid, in fact, acted as a stronger retarding agent, probably because the –COOH group at the end of the aliphatic side-chain in the β-position of the –NH₂ group might stabilize the complex by chelating Al ions with two stable 5- and 6-membered rings (Figure 2b). On the contrary, glutamic acid might complex Al ions more weakly by forming a stable 5-membered ring and an unstable 7-membered ring (Figure 2b). The formula in Figure 2b was reported by Das Sarma (1956) for complexes of glutamate with Ni(II) and Cd(II). According to this author, glutamate, aspartate, and other α-amino acid anions do not always easily form a tridentate ligand to a single ion, and other structures, apparently less stable, were suggested as alternatives where these an-

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Figure 3. Transmission electron micrographs: (a) pure bayerite formed at pH 10.0 and an Al:phthalic acid ratio of 50 after 2 days; (b) mainly nordstrandite (with rare triangular particles of bayerite) synthesized at pH 9.0 and an Al:glycine ratio of 6, after 60 days of aging. Scanning electron micrograph: (c) macrocrystal of bayerite obtained at pH 10.0 and an Al:glycine ratio of 70, 3 days after the preparation. Transmission electron micrographs: (d) nordstrandite formed at pH 9.0 and an Al:glutamic acid ratio of 10; (e) gibbsite and nordstrandite formed at pH 9.0 and an Al:aspartic acid of 10, both after 60 days of aging; (f) amorphous aluminum hydroxide obtained at pH 7.0 and an Al:salicylic acid ratio of 10 after 80 days of aging.
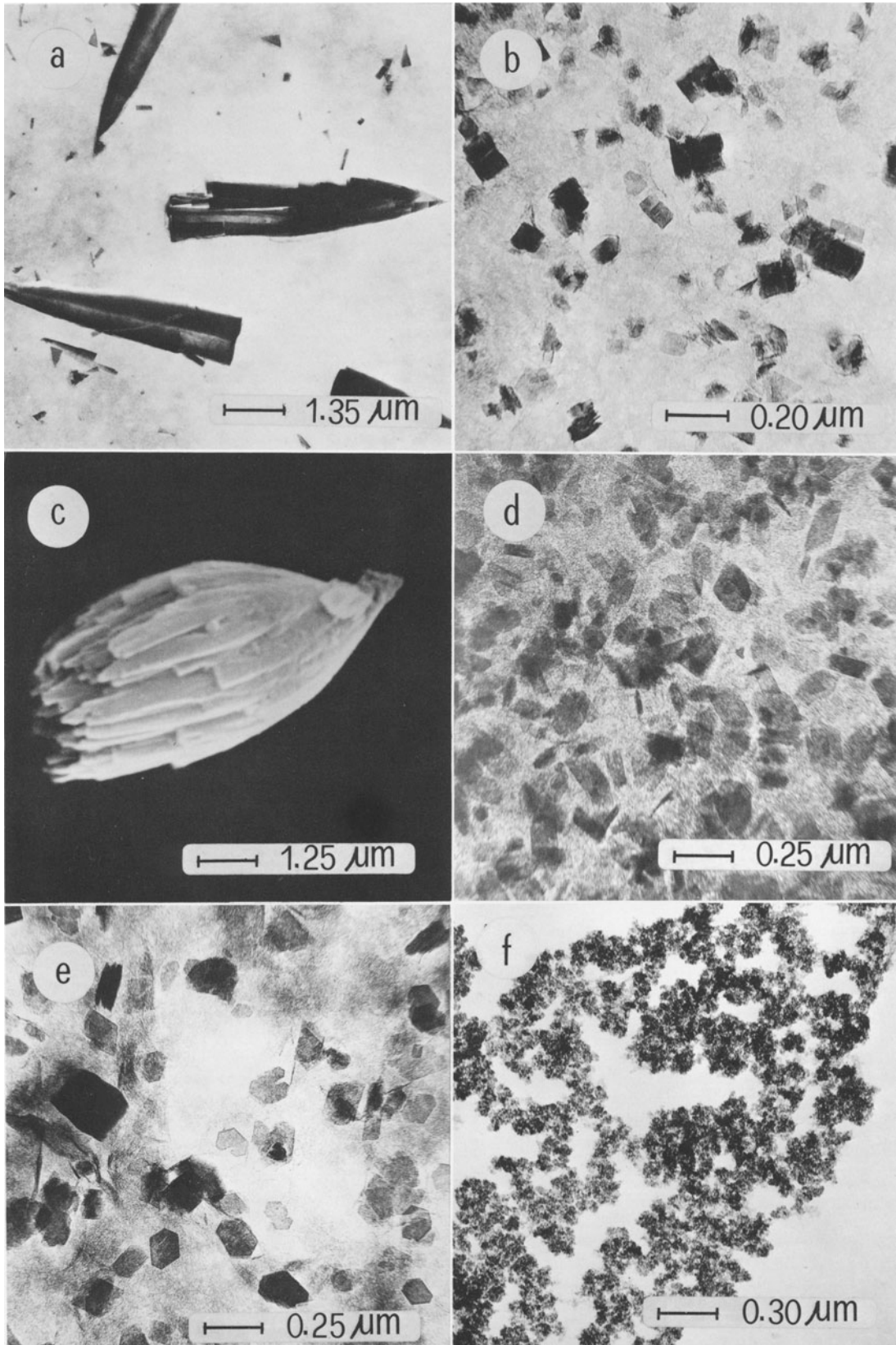
ions behave as either tri- or bidentate ligands. However, the above formulae easily explain the greater influence of aspartic over glutamic acid in retarding the crystallization of Al(OH)$_3$.

It was also noted that even at high pH values, gibbsite was commonly favored over nordstrandite when the crystallization rate was particularly slow. In fact, at pH 9.0 and at an Al:glutamic acid ratio of 10, almost pure nordstrandite was synthesized (Figures 1c and 3d), whereas in the presence of aspartate, gibbsite and nordstrandite were formed (Figure 3e). In addition, a concentration increase of a complexing organic anion produced not only a transition from bayerite to nordstrandite (Violante and Jackson, 1979), but also a progressive increase in the ratio of gibbsite to nordstrandite.

Figure 4 shows that oxalate anions at low concentrations (Al:oxalic acid ratio of 70) did not inhibit bayerite crystallization (diffractogram "a"); however, by increasing the concentration of this anion, more nordstrandite was always found (diffractograms "b" and "c"). Finally, with an Al:oxalic acid ratio of 6, gibbsite with pseudoboehmite was synthesized (diffractogram "d"). In a duplicate of the latter sample, pseudoboehmite was found stable for one year. Oxalic acid had a greater influence than malonic, succinic, and glutaric acids (in the order listed) in hindering the crystallization of Al(OH)$_3$ and, consequently, in favoring the formation of gibbsite, nordstrandite, and/or pseudoboehmite. This may be explained by considering that chelate 5- or 6-membered rings are more stable than larger ones, so that the closer the carboxyl groups, the more active is the bicarboxylate anion. The carboxyl group in glutarate, and probably in higher homologues (e.g., adipate, pimelate) are too far apart; hence, these anions behaved like monocarboxylates (i.e., acetate; Violante and Violante, 1978). In fact, at the concentrations and pH values used, glutarate anions had negligible influence in retarding Al(OH)$_3$ crystallization, so that in their presence bayerite easily formed.

Malic and salicylic acids showed a high inhibiting power for Al(OH)$_3$ crystallization. With an Al:carboxylic acid ratio <35 and at pH 7.0 and 8.0, X-ray-amorphous material was found even after 80 days of aging (Figure 3f). Malate was found to be a stronger retarding agent in the crystallization process than aspartate and oxalate. The results of Kwong and Huang (1979b) showed that the stability of Al-malate is stronger than that of
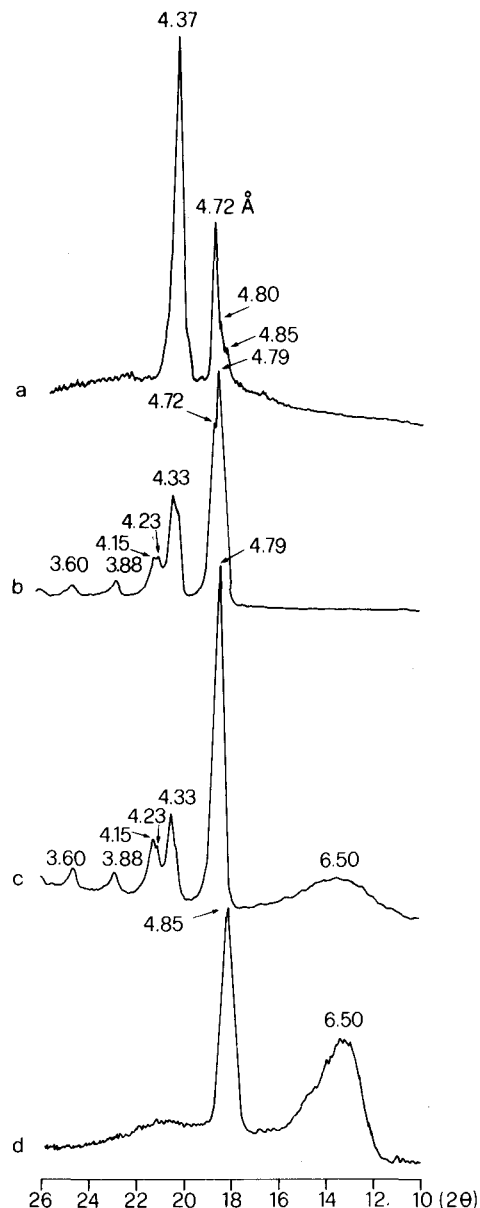

Figure 4.   X-ray powder diffractograms of Al(OH)$_3$ formed at pH 9.0 in the presence of different concentrations of oxalic acid after 60 days of aging: (a) mainly bayerite (4.72, 4.37 Å) obtained at an Al:oxalic acid ratio of 70; (b) bayerite and nordstrandite (4.79, 4.33, 4.23, 4.15, 3.88, 3.60 Å) obtained at an Al:oxalic acid ratio of 30; (c) pure nordstrandite formed at an Al:oxalic acid ratio of 10; (d) gibbsite (4.85 Å) and pseudoboehmite (6.50 Å) formed at an Al:oxalic acid ratio of 6.

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Figure 5.   Transmission electron micrographs of pseudoboehmite and distorted crystals of nordstrandite and gibbsite synthesized at pH 9.0 (a) at an Al:malic acid ratio of 10; (b) at an Al:salicylic acid ratio of 10; both after 60 days of aging; (c) a high magnification micrograph of (b) showing microcrystals of gibbsite blended into pseudoboehmite. (d) Pt/C-shadowed replica micrograph of nordstrandite synthesized at pH 10.0 and an Al:salicylic acid ratio of 10 after 20 days of aging. (e) Scanning electron micrograph of pure nordstrandite synthesized at pH 10.0 and an Al:malic acid ratio of 10 after 25 days of aging. (f) Transmission electron micrograph of pseudoboehmite with some unidentified microcrystals obtained at pH 10.0 and an Al:tartaric acid ratio of 70 after 1 year.
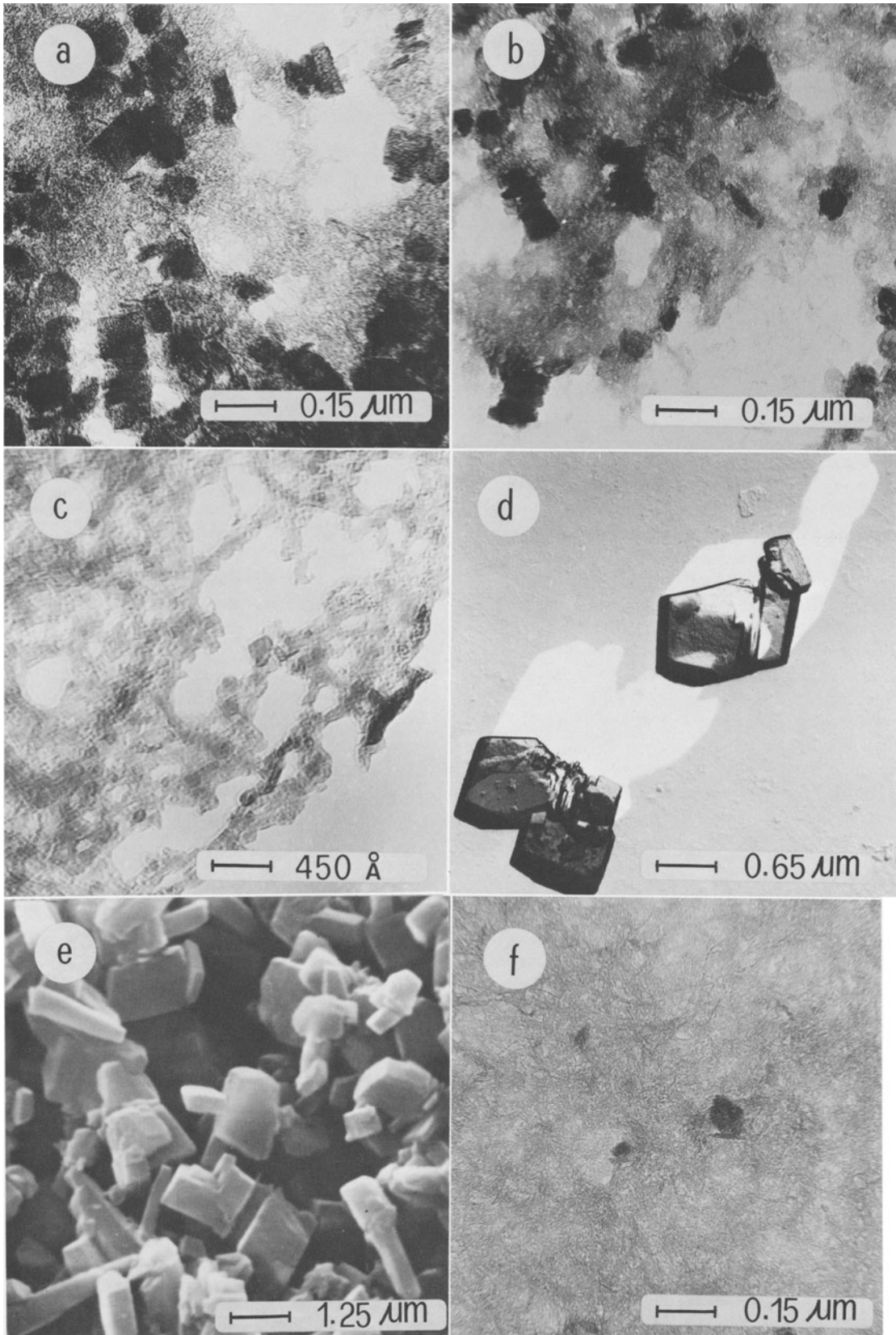
Al-aspartate and support the present observations. Malic acid differs from aspartic acid only in having an –OH group instead of a –NH$_2$ group. Probably Al ions may have greater affinity towards agents that complex by means of oxygen than by means of nitrogen, as has been shown for ions having a small size and high charge (Murmann, 1969).

The lesser influence of oxalate than malate or salicylate anions in hindering the crystallization is somewhat surprising; however, several works (Parfitt, 1978 and the references therein) suggested that organic anions are specifically adsorbed on Al-hydroxides, Fe-oxides, and allophanic soils and that the sorption of these anions could be described by a sorption–pka–pH relationship. Struthers and Sieling (1950) found that oxalic acid is very effective in preventing phosphate "fixation" on Al-hydroxides at acidic pH, but that its influence strongly decreases above pH 7.0. Moreover, Cornell and Schwertmann (1979) reported that dicarboxylic acids (oxalic, succinic, malonic, maleic) are much less efficient than hydroxy-carboxylic acids (citric, tartaric, malic) in retarding the crystallization of Fe-oxides formed from ferrihydrite at high pH.

In the presence of salicylic and malic acids, particularly at a pH equal to or less than 9.0 and at Al:carboxylic acid ratios less than 35, the reaction products formed were commonly poorly crystalline or structurally distorted. Figures 5a and 5b show distorted crystals of nordstrandite and gibbsite formed at pH 9.0 and at an Al:malic or salicylic acid ratio of 10, respectively. In the latter micrograph, a gel-like material, recognized as pseudoboehmite by XRD (Figure 1d), is evident in the background. At very high magnification, however, microcrystals of gibbsite can be seen blended into the gel-like material (Figure 5c).

Figures 5a, 5b, and 5c show that at the same pH and Al:carboxylic acid ratio the crystals formed after 60 days of aging in the presence of malate or salicylate are more distorted in outline than those formed in the presence of glutamate or aspartate (Figures 3d and 3e). These findings suggest that the higher the affinity of chelating anions for Al, the higher their capacity to occupy the coordination sites of Al and distort the arrangement of the unit layers (Kwong and Huang, 1979a). In the presence of malate and salicylate, nordstrandite was formed at pH 10.0 only at Al:carboxylic acid ratios lower than 35 (Figures 5d and 5e).

Finally, citric and tartaric acids strongly inhibited the formation of Al-hydroxide polymorphs. At pH 7.0, 8.0, and 9.0, amorphous material or pseudoboehmite always formed even after 180 days of aging (Table 1 and Figures 1e and 1f). At pH 10.0 nordstrandite crystallized in citrate systems, as has been extensively reported in previous works (Violante and Jackson, 1979, 1980), but pseudoboehmite or amorphous material formed in tartrate systems (Table 1 and Figure 5f).
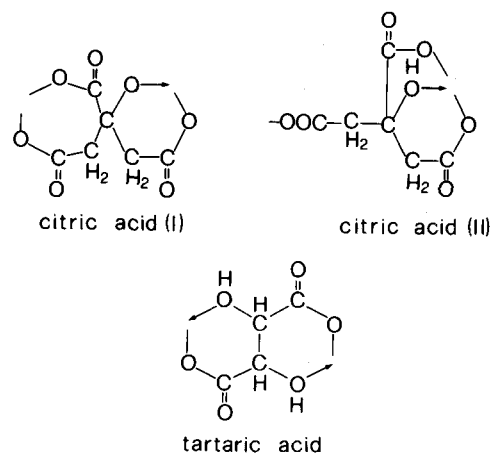

citric acid (I)   citric acid (II)

tartaric acid

Figure 6.   Possible ways of complexing by strongly chelating organic acids.

Al(OH)$_3$ polymorphs were difficult to obtain in tartrate or citrate systems even at pH >9.0, obviously because of the great stability of the complexes with aluminum.

Several formulae, involving rings of various sizes, have been proposed for citrate and tartrate complexes; e.g., one 6-membered ring and one 7-membered ring with two different metal ions (Bailar, 1956, Figure 6(I)); and one 5-membered chelate ring and one 6-membered ring involving two carboxyl groups and one hydroxyl group in citrate complexes (Huang and Kiang, 1972; Kwong and Huang, 1979b; Figure 6(II)). Stable 6- or 5-membered rings (Figure 6) are possible in the tartrate complexes (Bailar, 1956).

The data of Kwong and Huang (1979b) that the stability constants (expressed as log K$_1$) for complexes formed between Al and p-hydroxybenzoic, aspartic, malic, and citric acids are respectively 1.66, 2.60, 5.14, and 7.37, strengthen the present interpretation that the higher the chelating power of the organic compound, the easier is the formation of nordstrandite, gibbsite, and pseudoboehmite (and/or amorphous material) rather than bayerite at pH >7.0.

The greater effect of tartrate than citrate in favoring pseudoboehmite or amorphous material at neutral and alkaline pHs cannot, however, be explained in terms of a stronger chelating power, because citrate-Al complexes have greater stability than tartrate-Al complexes (Earl et al., 1979). Because tartrate anions are sorbed on the Al-rich materials to a greater extent than citrate, although the latter has a stronger influence in removing Al from gels (Earl et al., 1979), it is possible to hypothesize that the transformation by dissolution and recrystallization (Bye and Robinson, 1964) of amorphous Al-gel or pseudoboehmite into Al(OH)$_3$ could be particularly inhibited by tartrate anions strongly sorbed on the Al-gels.
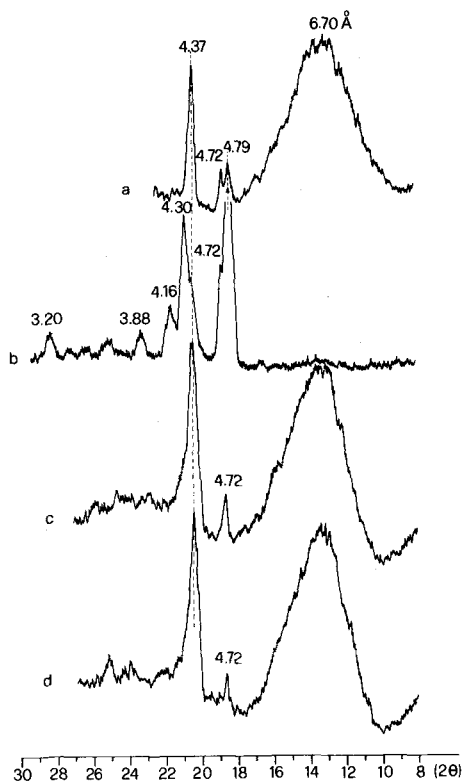
Figure 7. X-ray powder diffractograms of Al(OH)₃ formed in the presence of carboxylic acids: (a) at pH 10.0 and an Al:citric acid ratio of 70 after 2 days of aging showing pseudoboehmite (6.70 Å), bayerite (4.72, 4.37 Å) and nordstrandite (4.79 Å); (b) the same sample after 3 months of aging showing nordstrandite (4.79, 4.30, 4.16, 3.88 Å) and bayerite (4.72, 4.37 and 3.20 Å); (c) and (d) at pH 10.0 and an Al:aspartic acid ratio of 10 after 2 days and 1 year of aging, respectively, showing pseudoboehmite (6.70 Å) and bayerite (4.72, 4.37 Å).

Formation and stability of pseudoboehmite in the presence of chelating anions

At pH 8.0 and 9.0, even at very low concentrations, strongly chelating anions such as malate, salicylate, citrate, and tartrate facilitated the formation of pseudoboehmite rather than Al(OH)₃ polymorphs, whereas moderately chelating anions, such as glutamate and aspartate, were influential only at higher concentrations (Table 1). Where the pH of the samples was particularly high (pH 10.0), stable pseudoboehmite without any Al(OH)₃ crystals formed only in the presence of citrate and tartrate. In contrast, weakly chelating anions, such as phthalate or succinate, did not cause the crystallization of stable pseudoboehmite even at pH 8.0 and at an Al:carboxylic acid ratio of 6 (Table 1 and Figure 1).

Generally, at pH >8.0, the stronger the chelating power or the greater the concentration of a foreign anion, the greater the amount of pseudoboehmite found several months after the sample preparation (Figures 1 and 4); however in some samples in the presence of citrate or tartrate anions, aluminous precipitation products resulted which were still amorphous to X-rays even after 60 days or longer (Table 1 and Figure 1f). Chelating anions probably displaced –OH and H₂O groups and prevented or retarded olation (Bailar, 1956; Hsu, 1967, 1977; Lahodny-Sarc *et al.,* 1978; Kwong and Huang, 1979b). Several authors have found that in neutral or alkaline systems, pseudoboehmite is a transitory phase between the amorphous material initially formed and Al(OH)₃ polymorphs (Souza Santos *et al.,* 1953; Bye and Robinson, 1964; Aldcroft *et al.,* 1969).

In the present study bayerite crystallized quickly in the presence of weakly complexing anions and at a pH higher than 8.0, and pseudoboehmite did not form during the aging process (Figure 1a). Indeed, XRD patterns of many samples showed broad peaks of pseudoboehmite that appeared within a few days, decreased in intensity during the aging process, and in some samples disappeared completely. Figure 7a shows the XRD patterns of pseudoboehmite and bayerite that formed at pH 10.0 in the presence of a low concentration of citrate (Al:citric acid = 70) 2 days after the sample preparation. After 3 months of aging the same sample showed peaks of nordstrandite and bayerite, the latter in a smaller amount, with pseudoboehmite completely absent (Figure 7b).

Finally, at certain pHs and concentrations of moderately or strongly chelating anions, pseudoboehmite with Al(OH)₃ polymorphs formed in a few hours or days and persisted without change in intensity during the aging process (Figures 7c and 7d).

The above reported results indicate that so-called pseudoboehmite is a material with varying degrees of order and hence a wide range of solubilities (Bye and Robinson, 1964). Because pseudoboehmite did not always appear to be a transitional phase between the amorphous material initially formed and the final Al(OH)₃ polymorph, the formation of each Al-hydroxide might involve a more specific mechanism different from that proposed by other authors (Souza Santos *et al.,* 1953; Bye and Robinson, 1964; Aldcroft *et al.,* 1969).

CONCLUSIONS

Organic anions influence both the rate of Al(OH)₃ crystallization and the nature of the precipitated product. The effectiveness of an organic compound in delaying or inhibiting Al(OH)₃ crystallization increases when its concentration rises and the pH decreases. The nature and geometric structure of each molecule influences the crystallization rate, and the following order of effectiveness of various organic chelating acids in delaying the kinetics of Al(OH)₃ crystallization at pH above 7.0 was found: glutaric < succinic = phthalic < glycine < malonic < glutamic < aspartic < oxalic < salicylic = malic < citric < tartaric.

Although the mechanism governing the formation of Al-hydroxide polymorphs, particularly in neutral or alkaline systems, is not yet fully clear, the present work shows that rapid crystallization yields bayerite and that very slow crystallization favors gibbsite, even at high pH. Intermediate conditions favor nordstrandite, particularly at pH >8.0, in keeping with the occurrence of this polymorph in natural alkaline environments.

Furthermore, the importance of moderately and strongly chelating anions in favoring the formation of stable pseudoboehmite or X-ray-amorphous products is clearly established.

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Резюме—Хелатообразующие органические кислоты прептствовали гидролитическим реакциям Al и влияли на природу кристаллических гидроокисей алюминия. Скорость кристаллизации контролировалась химическим составом, структурой, размером, природой функциональных групп и концентрацией каждого органического аниона, а также pH системы. Порядок эффективности различных кислот был следующий: глутаровая < янтарная = фталевая < аминоуксусная < малоновая < глутаминовая < аминоянтарная < щавелевая < салициловая = оксиянтарная < димонная < винная. Увеличение стабильности комплексов, формированных между органическими аддендами и Al, уменьшало скорость кристаллизации и изменяло конечные алюминиевые продукты от байерита до нордстрандита и/или гиббсита потом до псевдобемита и/или аморфного материала. В присутствии анионов, которые имеют большое химическое сродстве с Al, особенно для pH равного или меньшего чем 9,0, продукты реакции были обычно плохо выкристаллизированы или структурно искаженные. В диапазоне pH от 8,0 до 10,0 умеренно или сильно хелатообразующие анионы задерживали или предупреждали олацию и облегчали образование стабильного псевдобемита или рентгеновско-аморфных продуктов. Чем сильнее была хелатообразующая способность или чем большая была концентрация органических анионов, тем легче была образование псевдобемита или аморфных материалов. [E.C.]

Resümee—Chelatkomplex-bildende organische Säuren verhindern die hydrolytischen Reaktionen von aluminium und beeinflussen die Art der kristallinen Aluminiumhydroxide. Die chemische Zusammensetzung, die Struktur, die Größe, die Art der funktionellen Gruppen, und die Konzentration jedes einzelnen organischen Anions sowie der pH-Wert des Systems bestimmen die Kristallisationsgeschwindigkeit von $Al(OH)_3$. Die Reihenfolge der Wirksamkeit der verschiedenen Säuren war: Glutarsäure < Bernsteinsäure = Phthalsäure < Glycinsäure < Malonsäure < Glutaminsäure < Asparaginsäure < Oxalsäure < Salicylsäure = Monohydroxibernsteinsäure < Zitronensäure < Weinsäure. Eine Stabilitätszunahme der Komplexe aus den organischen Liganden mit dem Aluminium verringerte die Kristallisationsgeschwindigkeit und veränderte die Aluminium-Endprodukte von Bayerit nach Nordstrandit und/oder Gibbsit und danach zu Pseudoboehmit und/oder amorphe Substanz. In der Gegenwart von Anionen mit einer großen Affinität für Aluminium waren die Reaktionsprodukte, vor allem bei pH-Werten gleich oder kleiner 9,0, im allgemeinen schlecht kristallisiert oder hatten eine verzerrte Struktur. Im pH-Bereich von 8,0 bis 10,0 wirkten mässig oder stark Chelatkomplex-bildende Anion verzögernd oder verhindernd auf die Olation und begünstigten die Bildung von stabilem Pseudoboehmit oder von röntgenamorphen Substanzen. Je größer die Komplexierungsfähigkeit oder je höher die Konzentration an organischen Anionen war, umso leichter war die Bildung von Pseudoboehmit oder amorphem Material. [U.W.]

Résumé—Des acides organiques chélatants ont rendu plus difficiles les réactions hydrolitiques d'Al et affecté la nature des hydroxides d'aluminium cristallins. La composition chimique, la structure, la taille, la nature des groupes fonctionnels, et la concentration de chaque anion organique, ainsi que le pH du système ont contrôlé l'allure de la cristallisation d'$Al(OH)_3$. L'ordre d'efficacité des acides variés était le suivant: glutarique < succinique = phthalique < glycine < malonique < glutamique < aspartique < oxalique < salicylique = malique < citrique < tartarique. Un accroissement de la stabilité des complexes formés par les liants organiques et Al a diminué l'allure de cristallisation et changé les produits alumineux finaux de bayerite en nordstrandite et/ou gibbsite et ensuite en pseudobohémite et/ou matériel amorphe. En présence d'anions ayant une grande affinité pour Al, particulièrement à un pH égal à ou inférieur à 9, les produits de réaction étaient souvent pauvrement cristallins ou structuralement dérangés. Dans la gamme de pH de 8 à 10, des anions modérément ou très chélatants ont agi de façon à retarder ou empêcher l'olation et ont facilité la formation de pseudobohémite stable ou de produits amorphes aux rayons-X. Plus le pouvoir de chélation des anions organiques était grand, ou plus leur concentration était haute, plus la formation de pseudobohémite ou de matériel amorphe était facile. [D.J.]