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GEOLOGICAL SURVEY WATER—SUPPLY PAPER 1827-G

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By C. J. LIND *and* J. D. HEM

CHEMISTRY OF ALUMINUM IN NATURAL WATER

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EFFECTS OF ORGANIC SOLUTES ON CHEMICAL REACTIONS OF ALUMINUM

By C. J. LIND and J. D. HEM

ABSTRACT

Concentrations of organic matter in the general range of 1–10 milligrams per litre organic carbon are common in natural water, and many naturally occurring organic compounds form aluminum complexes. The aluminum concentrations in near-neutral pH solutions may be 10–100 times higher than the values predicted from solubility data if formation of such organic complexes is ignored. The processes of polymerization of aluminum hydroxide and precipitation of gibbsite are inhibited by the presence of the organic flavone compound quercetin in concentrations as low as $10^{-5.3}$ mole per litre. Quercetin forms a complex, with a probable molar ratio of 1:2 aluminum to quercetin, that has a formation constant (β_2) of about 10^{12}. A complex with a higher aluminum-quercetin ratio also was observed, but this material tends to evolve into a compound of low solubility that removes aluminum from solution.

In the presence of both dissolved aluminum and aqueous silica, low concentrations of quercetin improved the yield of crystallized kaolinite and halloysite. Small amounts of well-shaped kaolinite and halloysite crystals were identified by electron microscopy in solutions with pH's in the range 6.5–8.5 after 155 days aging in one experiment and 481 days aging in a repeated experiment. The bulk of the precipitated material was amorphous to X-rays, and crystalline material was too small a proportion of the total to give identifiable X-ray diffraction peaks. The precipitates had aluminum-silicon ratios near 1, and their solubility corresponded to that found by Hem, Roberson, Lind, and Polzer (1973) for similar aluminosilicate precipitated in the absence of organic solutes.

The improved yield of crystalline material obtained in the presence of quercetin probably is the result of the influence of the organic compound on the aluminum hydroxide polymerization process.

Natural water containing color imparted by organic material tends to be higher in aluminum than would be predicted by pH, silica concentrations, and solubility data for inorganic aluminum species.

INTRODUCTION

Dissolved aluminum is involved in the important processes of rock weathering and soil development. Studies of the structure of aluminum hydroxide, the factors that affect concentrations of dissolved aluminum and its inorganic complexes, and the processes of formation of clay minerals have been described in earlier papers in this series by Hem and Roberson (1967), Hem (1968), Roberson and Hem

(1969), Smith and Hem (1972), and Hem, Roberson, Lind, and Polzer (1973).

The effect of organic solutes on the geochemistry of aluminum is generally minimal owing to the normally low concentrations of organic matter, but under certain conditions, where concentrations are higher, it can be significant. Some examples are the strong complexes formed by humic acid and aluminum described by Pauli (1966), the overall transformation of crop soil by aluminum pictured by Fiskell (1969), and the possible binding of a sizable amount of dissolved aluminum to dissolved organic matter, in soil water in the normal pH range, demonstrated by Kaurichev, Nozdrunova, and Yevseyeva (1969). In fact, Hoefs (1969) went so far as to say "that many geological model cases which have been treated as pure inorganic systems are not realistic at all, because, especially in sedimentary geology, there are no pure systems without organic matter or micro-organisms." Also, Schnitzer (1971) stated that there is increasing evidence that the most important component of "soil solution" is fulvic acid, as it likely affects practically all reactions occurring in soils.

The association of aluminum with water-soluble organic matter raises questions concerning its possible relationship to biota. Aluminum is believed by some investigators quoted by Bowen (1966, p. 174) to be an essential element for certain plants. The aluminum concentration in the sap of plants that grow well in acid soils may be very high; according to Chenery (1948) the sap of such plants may have a pH as low as 3.9. Because of the increased solubility of aluminum at acid pH's, it can be taken more easily into these plants. The silky oak, *Orites excelsa,* a plant native to Australia, is reported to exude aluminum succinate (Hem, 1970). Excessive amounts of aluminum have been shown to be toxic to some plants, such as cotton seedlings (Huck, 1972), potatoes (Lee, 1971a and 1971b), sugarcane (Sumner and Meyer, 1971), and alfalfa and barley (Hutchinson and Hunter, 1970).

This paper considers the influence of dissolved organic matter on the processes of solution and precipitation of aluminum and aluminosilicates. The potential for increased concentration of aluminum due to the presence of low molecular weight natural organic compounds at possible concentrations is shown. A naturally occurring organic pigment, quercetin, which is a large molecule having many of the properties of the more soluble humic substance, fulvic acid, is used as a model compound of higher molecular weight organic matter. This compound is shown to react with aluminum, forming complexes and precipitates and altering the process of formation of aluminum hydroxides by retarding the crystallization and by facilitating the formation of an intermediate material prior to establishing a final solid product. It also is shown to aid in the development of crystalline kaolinite from aluminum silicate solutions.

WATER SOLUBLE ORGANIC MATTER

The amount and character of organic matter in natural water varies widely. These variations are caused by conditions influencing biological activity such as source, season, and climate and by the chemical, physical, and biological conditions existing between the time of initial formation and the time of sampling.

CONCENTRATION IN NATURAL WATERS

A detailed and accurate picture of the forms and amount of dissolved organic material in natural water is not presently available. However, some indication of the amount can be obtained from the reported concentrations in different types of water from various localities. Filtered surface and bottom waters in the Rybinsk Reservoir, U.S.S.R., had concentrations ranging throughout the year from 4 to 12 mg/l (milligrams per litre) of carbon as organic carbon (Skopintsev and Bakulina, 1966). (This reservoir impounds 8 rivers and is located 200 miles (320 kilometres) north of Moscow.) Some relatively organic-rich surface waters of the United States, studied by Christman and Ghassemi (1966) and Gjessing and Lee (1967), contained from 7 to 27 mg/l. Birge and Juday (1934) found from 1.2 to 28.5 mg/l, with a mean of 7.7 mg/l,in a study of 529 lakes. Public water supplies from wells in the southwestern United States contained 0.7 to 1.6 mg/l, whereas those from surface waters in southwestern United States and along the Pacific Coast contained 1.1–7.7 mg/l (Nelson and Lysyj, 1968). Kaurichev, Nozdrunova, and Yevseyeva (1969) tested some soils for organic carbon during May, July, and October and found that after ultrafiltration the soil waters at the surface contained from 24 to 616 mg/l and those at roughly 45–60 centimetres in depth contained from 2 to 73 mg/l.

GENERAL CHARACTER OF ORGANIC SOLUTES

The ever-present naturally produced organic substances in water are the materials of principal interest for this discussion. The manmade organics generally represent only a small fraction of the soluble colloidal organic matter present in natural waters (Christman and Minear, 1971), and the current emphasis on pollution abatement hopefully will decrease their concentrations still further. According to Degens (1965, p. 204) more than 500 organic constituents have been extracted from sediments, soils, and natural waters.

Reactions with aluminum can occur in living matter and during its decomposition even before the organic matter becomes a dissolved species within the water body itself. Thus, the source of dissolved organic matter and the concentrations at its sources are of significance. Christman and Minear (1971) stated that color in water is derived from aqueous extractable material of living woody tissue, from the dissolution of decomposition products of decaying wood and of soil organic material, or from some combination of these processes. Although these may be the more obvious sources, certainly algal colonies also make some contribution. Kroes (1972) showed that filtrates from two types of green algae were nearly 1×10^{-5} molar in steam-volatile acids and, assuming his suggested minimum of 100 as a molecular weight, $1.1–1.6\times10^{-6}$ molar with regard to the phenolic, yellow, water-soluble pigments. (In addition the filtrates contained 7.5–9.0 mg/l high molecular weight substances and 0.2–0.5 mg/l lipophilic substances also with phenolic character.) Suggestive evidence of a flavonol or catechin-type of tannin has been found in excretes of certain marine algae (Craigie and McLachlan, 1964).

Many plant pigments are known to be strong complexers of metals. One of their basic structures frequently is the benzo-γ-pyrone unit. This unit can also be found, as kojic acid, among the metabolic products of the decomposition of pentoses and hexoses by mold. (Besides being found in plants, sugars having the basic structure of pentose and hexose are known to be a large part of the less stable fraction of soluble organic matter in natural waters.)

Catechol-related structures are common in organic materials such as tannin, and a large variety of phenolic units is known to be included in the structure of organic compounds from living substances and their decomposition products. Under the right conditions, the phenols have a capacity to oxidize to quinones, which in turn may form semiquinones and dimers. A review of the sedimentary organics and their source materials was given by Degens (1965). (Sedimentary organics may be precursors to dissolved organics and (or) the result of precipitation of them.)

Colored organic solutes derived from soil are frequently described by the terms "fulvic" and "humic" acids. The terms are indicative only of the methods used for extracting and separating the materials and do not denote any definite chemical composition. All such materials are known to be complicated mixtures. The three groups of compounds considered to be the starting point for the development of humic substances are phenolics and quinones, breakdown products of proteins (possibly in combination with quinones or phenols), and breakdown products of carbohydrates (Duursma, 1965). Black and Christman (1963) found indication that fulvic acids, the more water soluble of the humic substances, are high molecular weight aromatic polyhydroxy methoxy carboxylic acids. Six years later, Schnitzer and Skinner (1969) still considered that the nature of free radicals in humic compounds is a matter of speculation and that the most likely possibilities are semi-quinone radicals associated with a condensed ring system. Schnitzer (1971) noted that 61 percent of the weight of a typical fulvic acid molecule and all of the oxygen is in its functional groups, largely COOH, OH, and C=O. He found that the major type of reaction with metal ions involved both the acidic COOH groups and the phenolic groups and that there was none with alcoholic OH groups. Rashid (1972) listed the carboxyl, hydroxyl, quinone, other carbonyls, and the amino groups on the periphery of the humic acid molecules as the functional groups responsible for the higher metal solubility in the presence of humic acid as compared with other organic structures.

Lamar and Goerlitz (1966) observed that the predominant organic materials in naturally colored surface waters are a mixture of organic carboxylic acids or salts of these acids. They concluded that the natural organic acids are predominantly nonvolatile polymeric carboxylic acids having aromatic and olefinic unsaturation, some of which could have been polymerized in aqueous solution. The aromatic-polyphenolic nature of colored substances in natural water is firmly established by oxidative and reductive degradation studies (Christman and Minear, 1971).

Color intensity is one mode of defining the amount of organic matter present in natural water. However, the amount indicated to be present by this method is only suggestive, as not all species even have color and those that do vary in intensity under similar concentrations. Gjessing and Lee (1967) found that slightly colored waters contain principally the low molecular weight organics, while moderately or highly colored waters have a greater amount of high molecular weight species. Some of these species were found to have molecular weights as great as 200,000.

INFLUENCE OF SIMPLE ORGANIC LIGANDS ON AQUEOUS ALUMINUM SPECIES

The degree of complexing of aluminum by organic ligands derived from the simpler low molecular weight acids can be estimated from published data on the stability of such complexes. In evaluating this influence it seems appropriate to consider first the circumstances of occurrence, the specific identity, and the concentrations of a few substances of this type.

OCCURRENCE AND FORM OF SIMPLE ORGANIC LIGANDS

The nature of these substances can more easily be grasped by an examination of the many more common individual organic ligands in the source materials, such as plant debris and other material in or on soils, than by viewing them at high dulution in large water bodies. Bruckert (1970) found that malic, citric, and oxalic acids were the principal organic acids in oak, beech, fescue, fir, pine, and callune litter; as much as 6,560, 1,310, and 630 parts per million, respectively, were present in samples of litter dried at 105°C. Other organic acids present were succinic, lactic, glucoronic, quinic, vanillic, p-hydroxybenzoic, p-coumaric, cafeic, gentisic (2,6-hydroxybenzoic acid), gallic, chlorogenic, ferulic, and protocatechic (pyrocatechic) acid. Kaurichev, Nozdrunova, and Yevseyeva (1969) identified the simpler soluble organic acids in a soil extract as citric, fumaric, glycolic, and tartaric acids. These soil solutions contained from 2.12 to 69.7 mg/l carbon as organic acid, and this amounted to 0.88–65 percent of the total carbon present. In another soil solution, p-hydroxybenzoic, vanillic, p-coumaric, and ferulic acids were identified and measured (Whitehead, 1964). The concentrations of these acids were from 0.07×10^{-5} to 4.9×10^{-5} molar. For example, p-hydroxybenzoic acid was present in concentrations of 0.67–3.3 mg/l carbon. The soils tested were calcareous loam (with rough grassland vegetation), sand (with bracken), clay with flints (with beechwood), and clay loam (with black currants and cultivated). Extracts from a mor site (forest humus with a layer of largely organic matter abruptly distinct from the mineral soil beneath) was found to contain 1.28×10^{-5} molar citric acid, 3.62×10^{-5} molar malic acid, 8.6×10^{-5} molar oxalic acid, 1.0×10^{-5} molar malonic acid, 2.4×10^{-5} molar acetic acid, and somewhere between 5.0 and 6.6×10^{-5} molar succinic and lactic acid combined (Bruckert, 1970). This adds up to a total of about 2.2×10^{-4} molar identified acids for this soil solution. Stevenson (1972) mentioned values for aliphatic acids of even as high as 1×10^{-3} to 4×10^{-3} molar in soil solutions.

Acids recovered from the more volatile 10 percent of the organic acids in naturally colored surface waters were identified as acetic, adipic, butyric, caproic, fumaric, lactic, maleic, malonic, oxalic, phthalic, propionic, succinic, and valeric acids (Lamar and Goerlitz, 1963, 1966). They found the concentrations of these acids to range from traces (4 μg/l (micrograms per litre)) to 592 μg/l (valeric acid). The presence of carboxyl and in many cases phenolic hydroxyl groups is characteristic of these identified acids, and like fulvic acids, these groups play an important part in organometallic reactions.

MECHANISMS OF ORGANOALUMINUM INTERACTIONS

Aluminum minerals are moderately soluble at pH's of 5 or less; the resulting Al^{3+} species reacts strongly with the negative organic ligands. Aluminum concentrations again increase above pH 7 with the production of $Al(OH)_4^-$. This anion, of course, will not be inclined to react with the predominantly negatively charged organic ligands. Complexing of aluminum by dissolved organic ligands would also be a function of pH in another way. Because most such ligands are only weakly acidic, potential attachment sites for cations will be occupied by H^+ and will not be readily available at low pH. Aluminum complexes should be most readily formed with rather strongly acid organic species that are considerably dissociated with regard to H^+ at pH's less than 5. Some types of naturally occurring organic materials showing this behavior are oxalic acid and some of the similar aliphatic carboxylic acids such as malonic and succinic acids. Some aromatic acids such as salicylic (ortho-hydroxybenzoic acid) release carboxylic H^+ at pH's below 5. This may be of particular significance because many naturally occurring colored organics in river and lake water are stated by various investigators to be polymeric aromatic acids with carboxyl and phenol groups. Salicylic acid is a highly simplified monomeric structure of this type. Data in Sillén and Martell (1964) show that aluminum forms strong complexes with salicylic, oxalic, malonic, and kojic acid. Also, Huang and Keller (1972) observed that more aluminum was brought into solution by the action of citric, tartaric, and salicylic acids on bauxite than could be accounted for simply by the lowering of the pH by these acids. Table 1 presents the theoretical amount of aluminum possible due to pH decrease along with the amount reported by Huang and Keller (1972). Complexing effects for many of the simple acids with aluminum have apparently not been evaluated. It might be interesting to note here that Chenery (1948) reported that the sap of aluminum-accumulating plants had a pH range from 3.9 to 5.2.

Phenolic sites alone are not favorable for attachment of aluminum cations because the phenolic hydrogen is not dissociated significantly at pH's where aluminum cations can exist in important proportions. However, the phenolic site is not to be completely ignored. For example, when this site is located such that it is favorable for hydrogen

TABLE 1.—*Concentrations of aluminum dissolved from bauxite by 0.01 molar organic acids compared with that which could theoretically be dissolved in their absence at the same pH*

Organic acid	pH	Aluminum in presence of complexing acid (mg/l)[1]	Aluminum in absence of complexing acid (mg/l)
Citric	3.14	68.4	51.6
Tartaric	3.13	81.0	55.3
Salicylic	3.35	84.4	12.1

[1] Huang and Keller (1972).

bonding with another functional group, the capacity for the molecule to dissociate is enhanced. This is shown by salicylic acid, o-hydroxybenzoic acid, whose dissociation constant is $10^{-3.00}$, as opposed to p-hydroxybenzoic acid with a constant of $10^{-4.53}$ and to m-hydroxybenzoic acid with a constant of $10^{-5.85}$ (Sillén and Martell, 1964).

The strong binding of metals by chelation (involving more than one point of attachment on a single organic molecule) should be acknowledged. Here again salicylic acid and also kojic acid are examples. The dissociation of kojic acid is small at neutral pH ($K_1=10^{-7.85}$) and of the monovalent salicylate ion is extremely small ($K_2=10^{-13.4}$), and yet the total complexing effect on aluminum is sizeable as shown later in figures 5 through 8. Martell (1971) stated each metal chelate ring formed increases the stability constant by a factor of about 100. He said that the tight binding of the metal ion by chelation prevents it from dissociating to any degree even at high dilutions, while similar complexes with quite high stability constants are well dissociated in dilute solutions.

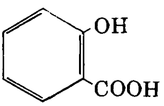
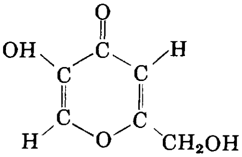
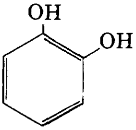
THEORETICAL EVALUATION OF COMPLEXING EFFECTS

Some indications of the potential importance of organic complexing in aluminum chemistry is provided by the theoretical evaluation of the influence of various organic ligands on the solubility of aluminum at equilibrium with solid aluminum hydroxide and the more soluble aluminum silicates and the comparison of this influence with that of fluoride. The selected organic compounds were oxalic, malonic, salicylic, and kojic acids, and the dihydroxy phenolic compound catechol. The structural formulas of these compounds and the total organic carbon concentrations represented by 10^{-5} molar solutions of each are given in table 2. Fluoride concentration is 0.19 mg/l when 10^{-5} molar.

Acidity constants and stability constants for the organoaluminum complexes are given with the appropriate mass-law equations in table 3. Where necessary, the constants were adjusted to zero ionic strength using the Davies equation (Butler, 1964). The activity coefficients used are listed in table 4. Also given are solubility equilibria and equilibrium constants for microcrystalline gibbsite, gibbsite, bayerite, synthetic halloysite, and kaolinite. In additon, the equilibria and stability constants needed for computing activities of hydroxide and fluoride complexes of aluminum are given in table 3. In all these equilibria, the activity of water and the solid phases is assumed to be equal to 1.

The effects of each of the five organic compounds on aluminum solubility and the amount of the organic complexes as compared with inorganic ones are shown graphically in figures 1–10. The solubility

TABLE 2.—*Structure of complexing ligands and their content of organic carbon at 1 × 10^{-5} molal*

Name	Structure	Organic carbon (mg/l)
Oxalic acid	COOH COOH	0.24
Malonic acid	COOH CH_2 COOH	.36
Salicylic acid		.84
Kojic acid		.72
Catechol		.72

plots (figs. 1, 3, 5, 7,9) show the total of aluminum species in solution from pH 4.0 to 9.0, assuming equilibrium at standard temperature and pressure, with synthetic halloysite. A concentration of $10^{-3.48}$ mole/l (mole per litre) or 20 mg/l as SiO_2 of dissolved silicic acid was assigned, but other species in solution were assumed to be low enough to permit using unit activity coefficients. The calculations also carry the inherent assumption that the organic aluminum compounds that might be formed are more soluble than halloysite throughout the pH range considered.

The solubility calculations involve three principal steps. First, the total equilibrium activity of monomeric aluminum ions (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$, and $Al(OH)_4{}^{-}$) was calculated from the halloysite solubility expression for a selected silica concentration and pH value. Second, the total activity of the organoaluminum complexes was calculated for that pH and the corresponding calculated Al^{3+} activity, using the summation of the organic species concentration.

TABLE 3.—*Chemical equilibria used for solubility calculations*

[Activity in moles per litre is represented by [ ] and concentration in moles per litre by ( ). Constants for standard conditions and zero ionic strength unless otherwise indicated]

Mass-action equations	Source
Microcrystalline gibbsite solubility product	
(1) $[Al^{3+}][OH^-]^3=10^{-32.65}$	Hem and Roberson (1967, p. 46).
Hydroxide complexes of aluminum	
(2) $[AlOH^{2+}][H^+]=10^{-5.00}[Al^{3+}]$	Smith and Hem (1972).
(3) $[Al(OH)_2{}^+][H^+]^2=10^{-9.76}[Al^{3+}]$	Do.
(4) $[Al(OH)_4\ ][H^+]^4=10^{-22.07}[Al^{3+}]$	Hem, Roberson, Lind, and Polzer (1973).
Gibbsite solubility product	
(5) $[Al^{3+}]=10^{8.22}[H^+]^3$	Smith (1971).
Bayerite solubility product	
(6) $[Al(OH)_4{}^-][H^+]=10^{-13.95}$	Hem and Roberson (1967).
Dissociation of water	
(7) $[H^+][OH^-]=10^{-14.00}$	Harned and Hamer (1933, p. 2198).

Synthetic halloysite solubility	
(8) $[Al^{3+}]^2[H_4SiO_4^0]^2=10^{11.28}[H^+]^6$	Hem, Roberson, Lind, and Polzer (1973).
(9) $[Al(OH)_4^-]^2[H_4SiO_4^0]^2[H^+]^2=10^{32.98}$	Do.
Kaolinite solubility	
(10) $[Al^{3+}]^2[H_4SiO_4^0]^2=10^{6.73}[H^+]^6$	Calculated from free energies given by Hem, Roberson, Lind, and Polzer (1973).
(11) $[Al(OH)_4^-]^2[H_4SiO_4^0]^2[H^+]^2=10^{-37.34}$	Do.
Dissociation of silicic acid	
(12) $[H_3SiO_4^-][H^+]=10^{-9.77}[H_4SiO_4^0]$	Greenberg and Price (1957).
Oxalic acid dissociation and oxalate complexes (L_o^{2-}=oxalate ion=$C_2O_4^{2-}$)	
(13) $[HL_o^-]=10^{4.14}[H^+][L_o^{2-}]$	Sillén and Martell (1964).
(14) $[H_2L_o]=10^{1.25}[H^+][HL_o^-]$	Do.
(15) $(Al(L_o)_2^-)=10^{5.45}(AlL_o^+)(L_o^{2-})$ (32°C, $I=1$)	Dutt and Sur (1957).
(16) $[Al(L_o)_2^-]=10^{6.09}[AlL_o^+][L_o^{2-}]$ (32°C)	Calculated from equation 15 and activity coefficients in table 4 at $I=1$ ionic strength.
(17) $[Al(L_o)_2^-]=10^{13}[Al^{3+}][L_o^{2-}]^2$ (18°C)	Sillén and Martell (1964).
(18) $[AlL_o^+]=10^{6.91}[Al^{3+}][L_o^{2-}]$	Calculated from equations 16 and 17 assuming no temperature effect between 18 and 32°C.

TABLE 3.—*Chemical equilibria used for solubility calculations*—Continued

Mass-action equations	Source
(19) $[Al(L_o)_3{}^{3-}]=10^{16.3}[Al^{3+}][L_o{}^{2-}]^3$ (18°C)	Sillén and Martell (1964).
(20) $[Al(L_o)_3{}^{3-}]=10^{3.3}[Al(L_o)_2{}^{-}][L_o{}^{2-}]$ (18°C)	Calculated by dividing equation 19 by equation 17.
Malonic acid dissociation and malonate complexes ($L_m{}^{2-}$ = malonate ion = $C_3H_2O_4{}^{2-}$)	
(21) $[HL_m{}^{-}]=10^{5.67}[H^+][L_m{}^{2-}]$	Sillén and Martell (1964).
(22) $[HL_m{}^{-}]=10^{5.72}[H^+][L_m{}^{2-}]$ (35°C)	Do.
(23) $[H_2L_m]=10^{2.85}[H^+][HL_m{}^{-}]$	Do.
(24) $[H_2L_m]=10^{2.84}[H^+][HL_m{}^{-}]$ (35°C)	Do.
(25) $[Al(L_m)_3{}^{3-}]=10^{4.06}[Al(L_m)_2{}^{-}][L_m{}^{2-}]$ (35°C, I=?)*	Do.
(26) $[Al(L_m)_3{}^{3-}]=10^{15.84}[Al^{3+}][L_m{}^{2-}]^3$ (35°C, I=?)*	Do.
(27) $[Al(L_m)_2{}^{-}]=10^{11.78}[Al^{3+}][L_m{}^{2-}]^2$ (35°C, I=?)*	Calculated by dividing equation 26 by 25.
Salicylic acid dissociation and salicylate complexes ($L_s{}^{2-}$ = salicylate ion = $C_7H_4O_3{}^{2-}$)	
(28) $[HL_s{}^{-}]=10^{13.4}[H^+][L_s{}^{2-}]$	Sillén and Martell (1964).
(29) $[H_2L_s]=10^{3}[H^+][HL^{-}]$	Do.
(30) $[AlL_s{}^{+}]=10^{14.11}[Al^{3+}][L_s{}^{2-}]$(26–28°C)	Das and Aditya (1959).

Kojic acid dissociation and complexes (L_k =dissociated kojic acid ion=$C_6H_5O_4^-$)	
(31) $(HL_k)=10^{7.75}[H^+](L_k^-)$ (20–23°C, 0.1M KCl)	Sillén and Martell (1964).
(32) $(AlL_k^{2+})=10^{7.7}(Al^{3+})(L_k^-)$ (20–23°C, 0.1M KCl)	Do.
(33) $(Al(L_k)_2^+)=10^{6.5}(AlL_k^{2+})(L_k^-)$ (20–23°C, 0.1M KCl)	Do.
(34) $(Al(L_k)_3)=10^{5.3}(Al(L_k)_2^+)(L_k^-)$ (20–23°, 0.1M KCl)	Do.
(35) $[HL_k]=10^{7.85}[H^+][L_k^-]$ (20–23°C)	Calculated by applying activity coefficients to equation 31.
(36) $[AlL_k^{2+}]=10^{7.81}[Al^{3+}][L_k^-]$ (20–23°C)	Calculated by applying activity coefficients to equation 32.
(37) $[Al(L_k)_2^+]=10^{6.86}[AlL_k^{2+}][L_k^-]$ (20–23°C)	Calculated by applying activity coefficients to equation 33.
(38) $[Al(L_k)_3]=10^{5.48}[Al(L_k)_2^+][L_k^-]$ (20 –23°C)	Calculated by applying activity coefficients to equation 34.
Catechol dissociation and complexes (L_{py}^{2} =dissociated catechol ion=$C_6H_4O_2^{2-}$)	
(39) $[HL_{py}]=10^{12.8}[H^+][L_{py}^{2-}]$	Sillén and Martell (1964).
(40) $[H_2L_{py}]=10^{9.45}[H^+][HL_{py}^-]$	Do.
(41) $(AlL_{py}^+)=10^{16.27}(HL_{py}^-)(Al^{3+})(OH^-)$ (I=0.2)	Goina, Olariu, and Bocaniciu (1970).
(42) $(Al(L_{py})_2^-)=10^{13.48}(AlL_{py}^+)(HL_{py}^-)(OH^-)$ (I=0.2)	Do.
(43) $(Al(L_{py})_3^{3-})=10^{9.00}(Al(L_{py})_2^-)(HL_{py}^-)(OH^-)$ (I=0.2)	Do.

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*Because I=? and these figures were the only ones listed, it is assumed I=0.

TABLE 3.—*Chemical equilibria used for solubility calculations*—Continued

Mass-action equations	Source
Catechol dissociation and complexes (L_{py}^{2-} =dissociated catechol ion=$C_6H_4O_2^{2-}$)—Continued	
(44) $[AlL_{py}^{+}]=10^{17.63}[HL_{py}^{-}][Al^{3+}][OH^{-}]$	Calculated by applying activity coefficients to equation 41.
(45) $[Al(L_{py})_2^{-}]=10^{13.76}[AlL_{py}^{+}][HL_{py}^{-}][OH^{-}]$	Calculated by applying activity coefficients to equation 42.
(46) $[Al(L_{py})_3^{3-}]=10^{8.20}[Al(L_{py})_2^{-}][HL_{py}^{-}][OH^{-}]$	Calculated by applying activity coefficients to equation 43.
Hydrofluoric acid dissociation and fluoride complexing	
(47) $[HF^0]=10^{3.17}[H^+][F^-]$	Butler (1964, p. 113).
(48) $[AlF^{2+}]=10^{7.01}[Al^{3+}][F^-]$	Hem (1968, p. 8).
(49) $[AlF_2^{+}]=10^{12.75}[Al^{3+}][F^-]^2$	Do.
(50) $[AlF_3^{0}]=10^{17.02}[Al^{3+}][F^-]^3$	Do.
(51) $[AlF_4^{-}]=10^{19.72}[Al^{3+}][F^-]^4$	Do.
(52) $[AlF_5^{2-}]=10^{20.91}[Al^{3+}][F^-]^5$	Do.
(53) $[AlF_6^{3-}]=10^{20.86}[Al^{3+}][F^-]^6$	Do.
Sulfate complexing	
(54) $[AlSO_4^{+}]=10^{3.2}[Al^{3+}][SO_4^{2-}]$	Behr and Wendt (1962).
(55) $[Al(SO_4)_2^{-}]=10^{5.1}[Al^{3+}][SO_4^{2-}]^2$	Do.

TABLE 4.—*Activity coefficients, γ, at designated ionic strengths*

[Reference columns: 1, from Butler (1964, p. 435); 2, presumed from data in Butler (1964, p. 435); 3, presumed from data in Garrels and Christ (1965, p. 103); 4, presumed from Butler (1964, p. 438)]

Ion	A parameter	Charge	Ionic strength	Activity coefficient	Reference	Ionic strength	Activity coefficient	Reference
OH^-	3	−1	0.01	0.899	1	0.2	0.72	4
H^+	1	+1	.01	.914	1	----	----	----
$H_3SiO_4^-$	4	−1	.01	.901	2	----	----	----
HL_o^-	3	−1	.01	.899	2	----	----	----
L_o^{2-}	5	−2	.01	.670	1	1	.23	4
HL_m^-	3	−1	.01	.899	2	----	----	----
L_m^{2-}	5	−2	.01	.670	1	----	----	----
HL_s^-	6	−1	.01	.907	1	----	----	----
L_s^{2-}	6	−2	.01	.675	2	----	----	----
L_k^-	6	−1	.01	.907	1	.1	.80	2
HL_{py}^-	6	−1	.01	.907	2	.2	.72	4
L_{py}^{2-}	6	−2	.01	.675	2	.2	.28	4
F^-	3	−1	.01	.899	2	----	----	----
Al^{3+}	9	+3	.01	.445	1	1	.06	4
$Al(OH)^{2+}$	4	+2	.01	.660	2	----	----	----
$Al(OH)_2^+$	4	+1	.01	.901	2	----	----	----
$Al(OH)_4^-$	4	−1	.01	.901	2	----	----	----
AlL_o^+	4	+1	.01	.901	2	1	.68	3
$Al(L_o)_2^-$	4	−1	.01	.901	2	1	.68	3
$Al(L_o)_3^{3-}$	9	−3	.01	.445	2	1	.03	4
$Al(L_m)_2^-$	4	−1	.01	.901	2	----	----	----
$Al(L_m)_3^{3-}$	9	−3	.01	.445	2	----	----	----
AlL_s^+	4	+1	.01	.901	2	----	----	----
AlL_k^{2+}	7	+2	.01	.685	2	.1	.43	2
$Al(L_k)_2^+$	9	+1	.01	.914	2	.1	.83	2
AlL_{py}^+	4	+1	.01	.901	2	.2	.72	4
$Al(L_{py})_2^-$	4	−1	.01	.901	2	.2	.72	4
$Al(L_{py})_3^{3-}$	9	−3	.01	.445	2	.2	.06	4
AlF^{2+}	4	+2	.01	.660	2	----	----	----
AlF_2^+	4	+1	.01	.901	2	----	----	----
AlF_4^-	4	−1	.01	.901	2	----	----	----
AlF_5^{2-}	4	−2	.01	.660	2	----	----	----

The third step involved the summation of the aluminum species. The calculations were simplified by expressing the summation equations in terms of Al^{3+} and H^+ activities. The calculation is repeated for as many values of pH and total organic concentration as may be needed to outline the curves for total organic contents of 0, $10^{-4.00}$, and $10^{-5.00}$ molar.

A second type of graph was prepared for each of the organic compounds to compare the organic complexing effect with that of fluoride and hydroxide, the two inorganic ions common in natural water that complex aluminum most strongly. These graphs (figs. 2, 4, 6, 8, 10) are based on the same relationships that were used to compute solubility, with added equilibria and summations for aluminum fluoride complex species from table 3. The regression lines on each graph represent conditions under which the total complexed aluminum is equally divided between fluoride and organic aluminum species.

In the preparation of these latter graphs, it was first specified that aluminum solubility was controlled by equilibrium with synthetic halloysite, at a silica concentration of 20 mg/l SiO_2 ($10^{-3.48}$ molar). A summation of organic complex species, in terms of the free ligand and uncomplexed aluminum activities (and of pH if necessary), was then

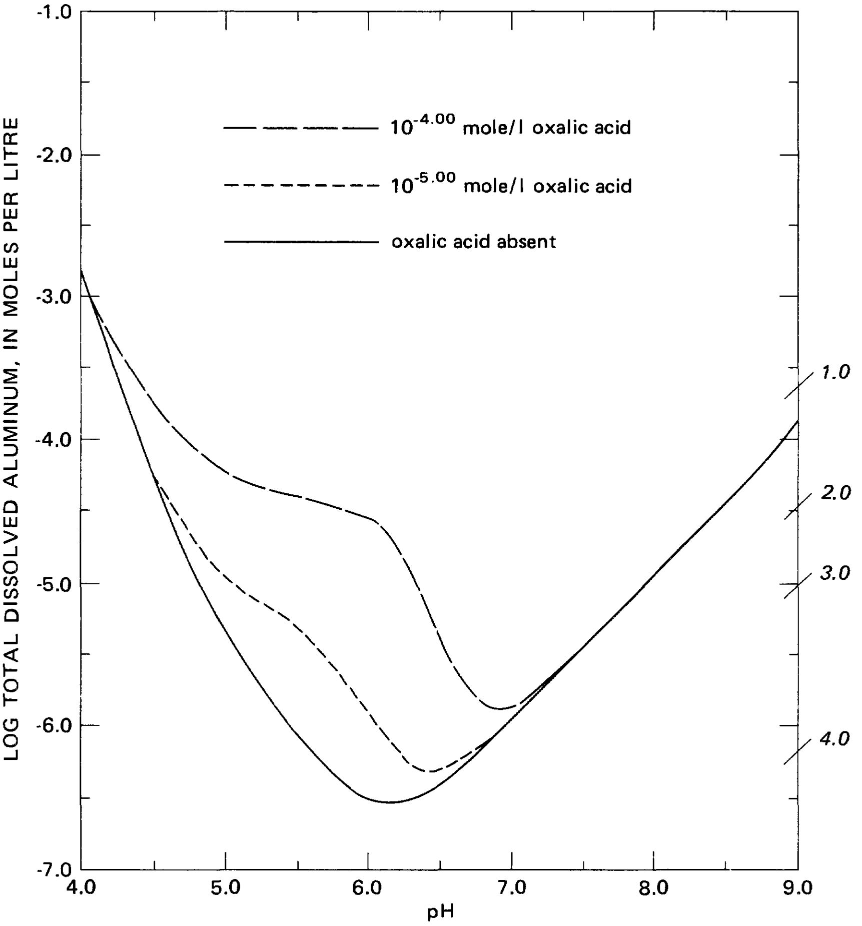


FIGURE 1.—Effects of oxalate complexes on equilibrium solubility of aluminum in the presence of synthetic halloysite. Dissolved silicic acid $10^{-3.48}$ mole/l (20 mg/l as SiO_2). Position of solubility intercepts for four other solids shown by numbers at right (see text).

equated to a summation of fluoride complex species in terms of free fluoride and aluminum activities. A pH is specified, along with a convenient value for activity of the free organic ligand, and a value for $[F^-]$ can then be obtained which satisfies the equation. The pH that was specified earlier in this manipulation fixes the activity of free aluminum. From the activities of the free ligands and the other information, it is possible to calculate equilibrium totals of dissolved fluoride species and of the organic compound. The graphs use these totals as ordinate and abscissa. The final result of the calculation is one point on a curve for the pH selected. The whole calculation is repeated

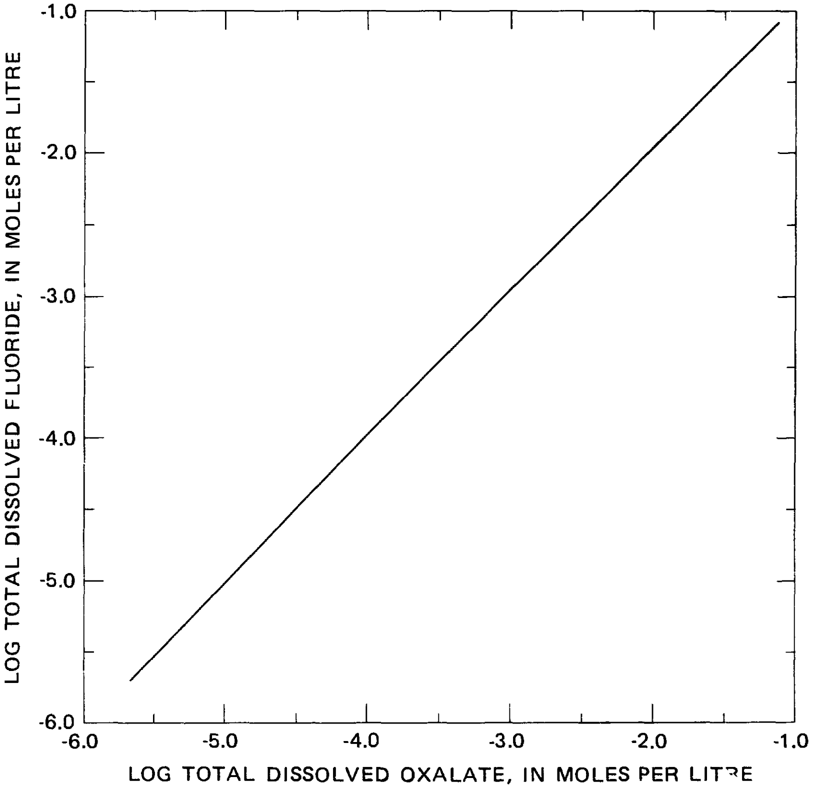


FIGURE 2.—Line separating fluoride and oxalate complexing domains, pH 4.5–7.0; aluminum concentration controlled by solubility of synthetic halloysite.

for additional pH and free ligand values to give enough points for plotting of curves.

Some of the organic compounds showed no important pH effects between pH 4.5 and 6.0, and one regression line can be used to show the specified relationship. For other compounds, however, there is a strong pH effect, and several curves are required to demonstrate this. Figure 1 shows a substantial increase in aluminum solubility, especially near pH 6, when the higher oxalate concentration is present. Figure 2 shows that the oxalate ion is comparable with fluoride in strength of complexing with aluminum. Neither species is able to compete very effectively with hydroxide in alkaline solutions, however, as shown by the convergence of solubility lines in figure 1 above pH 7.

The shape of the solubility traces in figure 1 is the same for any aluminum mineral whose solubility products in acid and alkaline solutions involve $[H^+]/[Al^{3+}]$ or $[H^+]/[Al(OH)_4^-]$ ratios the same as those of microcrystalline gibbsite. This permits a broader use of the

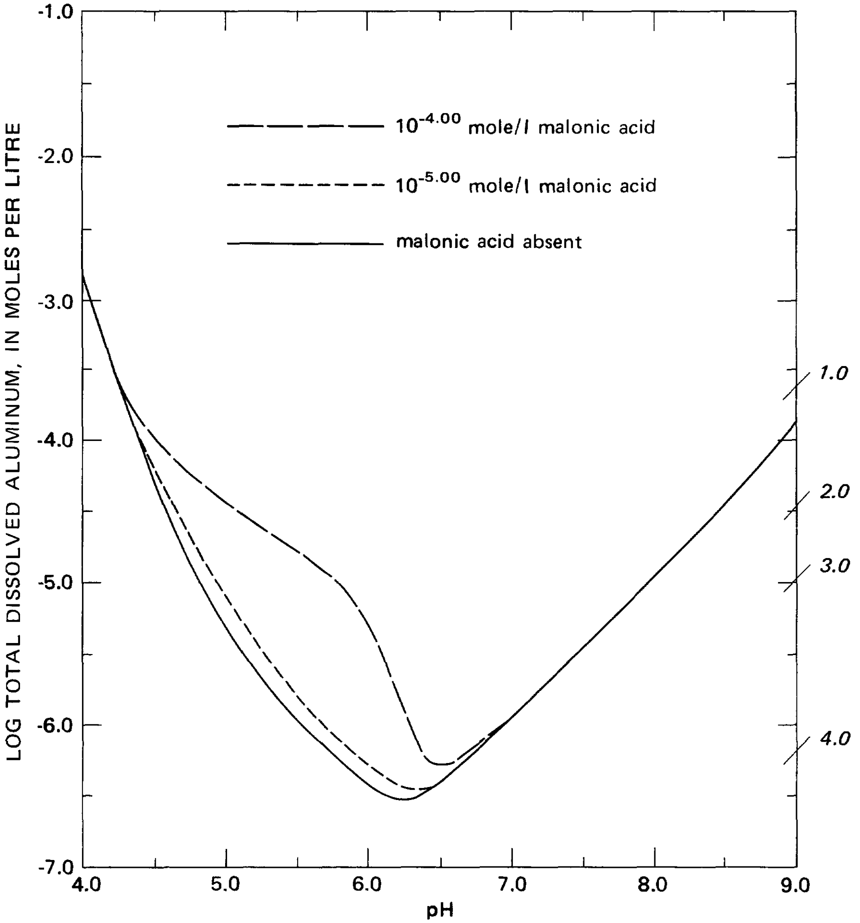


FIGURE 3.—Effects of malonate complexes on equilibrium solubility of aluminum in the presence of synthetic halloysite. Dissolved silicic acid $10^{-3.48}$ mole/l (20 mg/l as SiO_2). Position of solubility intercepts for four other solids shown by numbers at right (see text).

diagram. By displacing the curves up or down, equivalent to shifting the vertical scale, the same drawing will represent the solubility of various forms of gibbsite or of 1:1 clay minerals such as halloysite and kaolinite. The amount the scale should be shifted can be determined from the difference in the molar free energies of the solids when their formulas are the same, as in the gibbsite or in the kaolinite species. The clay mineral solubilities also are a function of the amount of silica in solution, but the appropriate shift of the vertical scale can be readily computed for any H_4SiO_4 activity that is compatible with the assumed solid.

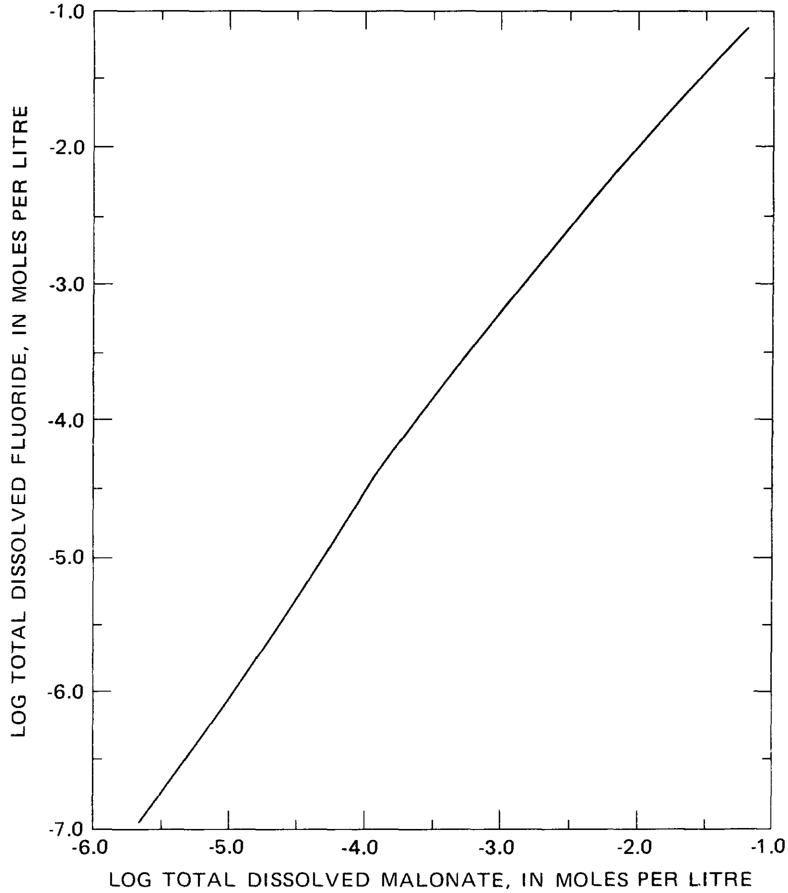


FIGURE 4.—Line separating fluoride from malonate complexing domains, pH 4.5–7.0. Aluminum concentration controlled by solubility of synthetic halloysite.

The intercepts at the pH 9.0 axis, by the right limb of the solubility plot, are for different sets of conditions, as follows:

1. Fresh $Al(OH)_3$ precipitate at alkaline pH, microcrystalline gibbsite in acid, no silica.
2. Synthetic halloysite, dissolved silica, 60 mg/l as SiO_2.
3. Well-crystallized bayerite at high pH, gibbsite at low pH, no silica.
4. Well-crystallized kaolinite with $\Delta G° = -903$ kilocalories/mole, dissolved silica, 20 mg/l as SiO_2.

The wide spread of solubility implied by these conditions (nearly three log units) points up very clearly the importance of knowing the type of solid one deals with when attempting to predict aluminum solubility.

Increasing ionic strength also will increase the apparent solubility

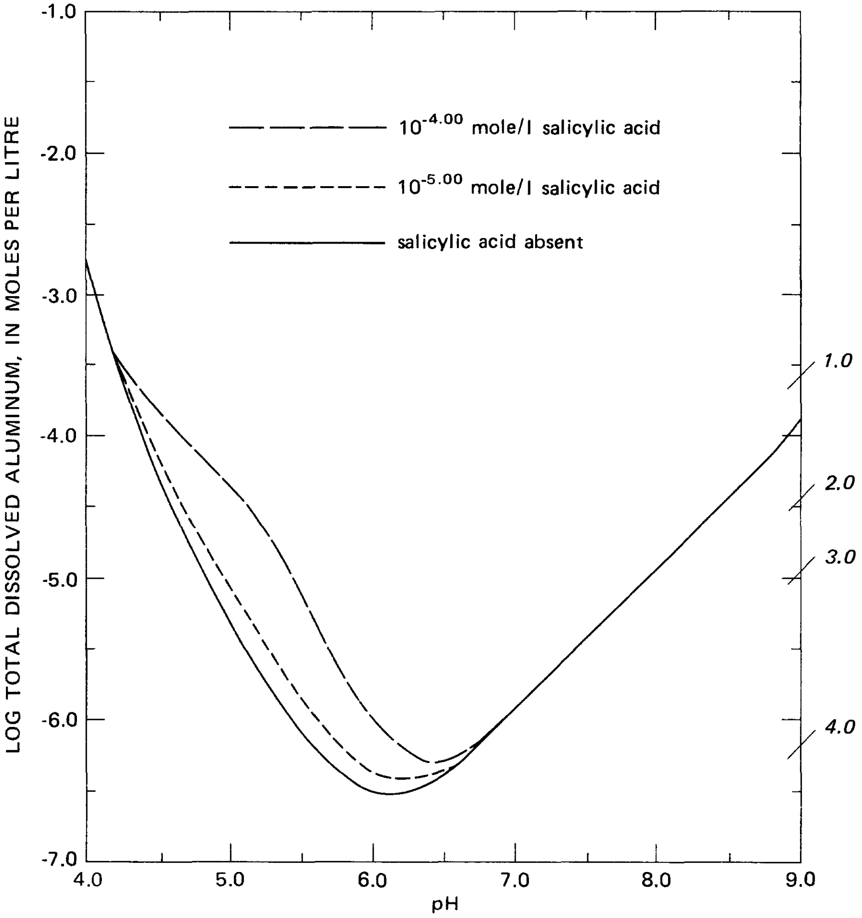


FIGURE 5.—Effects of salicylate complexes on equilibrium solubility of aluminum in the presence of synthetic halloysite. Dissolved silicic acid $10^{-3.48}$ mole/l (20 mg/l as SiO_2). Position of solubility intercepts for four other solids shown by numbers at right (see text).

of aluminum, but not to the same extent at all pH levels; hence a simple shift of scale will not show ionic strength effects accurately. A recalculation taking ionic strength effects into account can be made using activity coefficients in table 4. The effect is strongest at low pH where multivalent ionic species predominate.

Figure 3 shows the solubility of synthetic halloysite in the presence of malonic acid and $10^{-3.48}$ mole/l of silica. Malonic acid is similar to oxalic acid in having two carboxyl groups, but it has one more carbon atom than oxalic and is a somewhat weaker acid. The complexing action of malonic acid toward aluminum is significantly weaker than

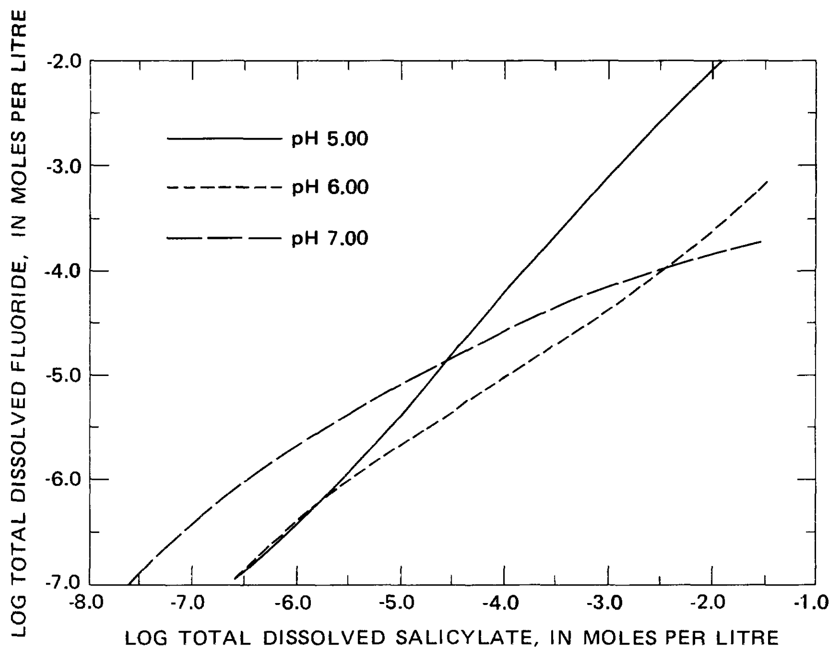


FIGURE 6.—Lines separating fluoride from salicylate complexing domains at pH 5.00, 6.00, and 7.00. Aluminum concentration controlled by solubility of synthetic halloysite.

that of oxalic acid. Its action is also weaker than that of fluoride, as indicated by figure 4.

Salicylic acid has a benzene ring structure, with one phenolic and one carboxylic hydrogen. The influence of this ligand on aluminum solubility is indicated in figure 5. This complex species does not influence aluminum solubility to a significant extent above about pH 6.5.

Unlike the oxalate and malonate complexes, the strength of the salicylate complex seems to vary with pH in the pH 5–7 range. In figure 6 the three lines representing equal totals of fluoride and salicylate species each have different trajectories.

Kojic acid has a rather substantial complexing effect at pH 7.00, as shown by figures 7 and 8. Here the complexing is less influenced by pH than in the case of the other organic compounds studies. This acid does not possess a carboxyl group like so many of the common low molecular weight organic acids. Instead it has a benzo-γ-pyrone structure, and because of resonance, the carbonyl and adjacent OH groups present a chelation site.

The complexing effects of catechol on aluminum are relatively weak

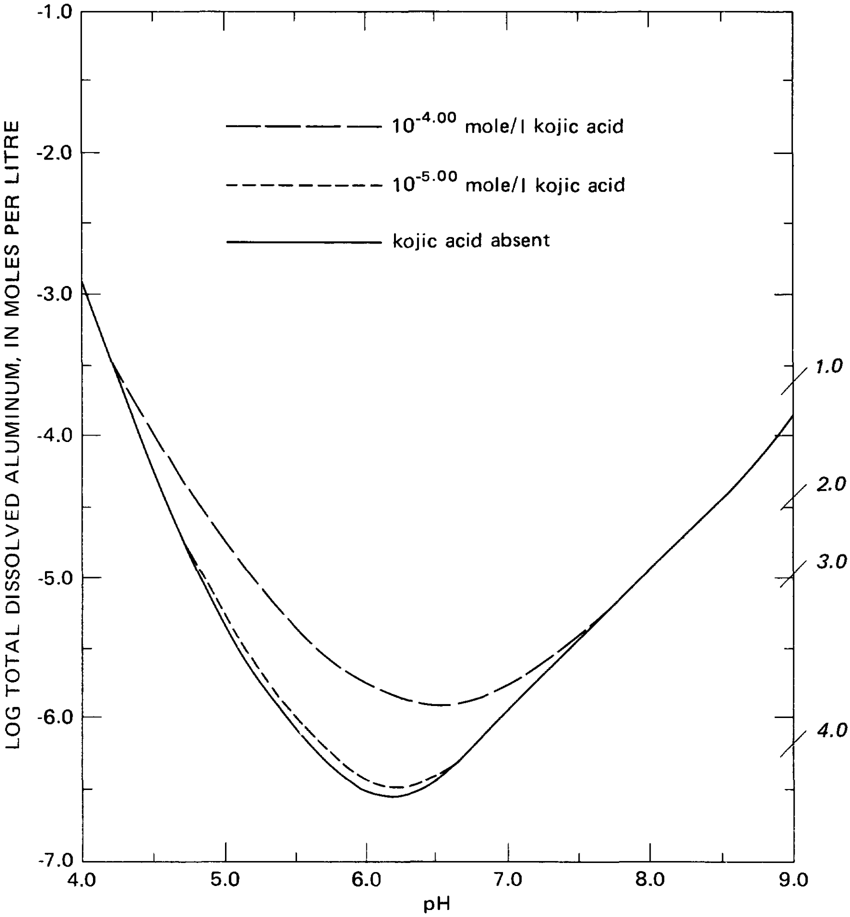


FIGURE 7.—Effects of complexes with kojic acid on the equilibrium solubility of aluminum in the presence of synthetic halloysite. Dissolved silicic acid $10^{-3.48}$ mole/l (20 mg/l as SiO_2). Positions of solubility intercept for four other solids shown by numbers at right (see text).

and summarized in figures 9 and 10. Like salicylic acid the strength of the catechol complexes is influenced by pH.

As noted earlier, it was assumed for the preparations of figures 1–10 that organic aluminum species would be more soluble than aluminum hydroxide or clay minerals and that the influence of organic complexing on aluminum solubility would, therefore, always be in a positive direction. Data on actual solubilities of organic compounds of aluminum are not readily available. Some of these compounds, however, may have solubilities low enough to act as effective controls over aluminum concentration in solution, and the complexing action of

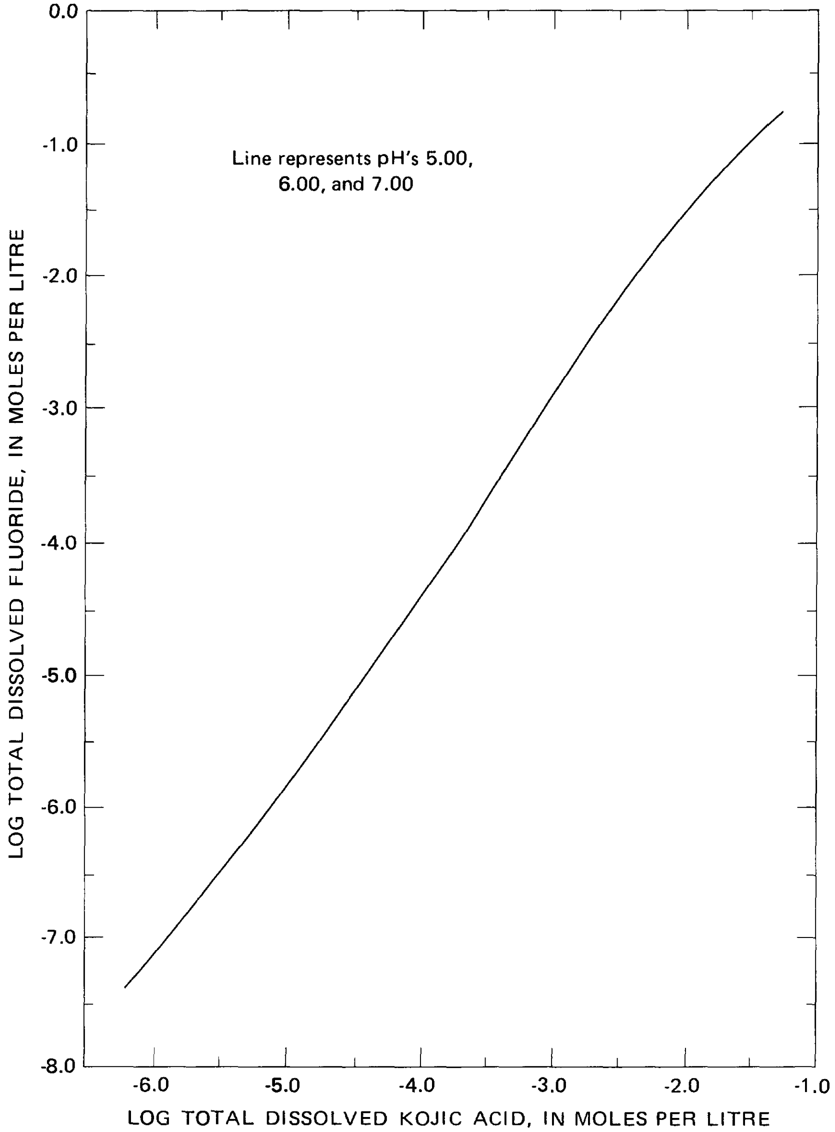


FIGURE 8.—Line separating fluoride from kojic acid complexing domains for pH 5.00—7.00. Aluminum concentration controlled by solubility of synthetic halloysite.

such species could depress the solubility of aluminum rather than enhance it. The ligands of organic species with this kind of potential effect are themselves generally of rather low solubility in water, and their effect is commonly considered to be a type of chemisorption reaction.

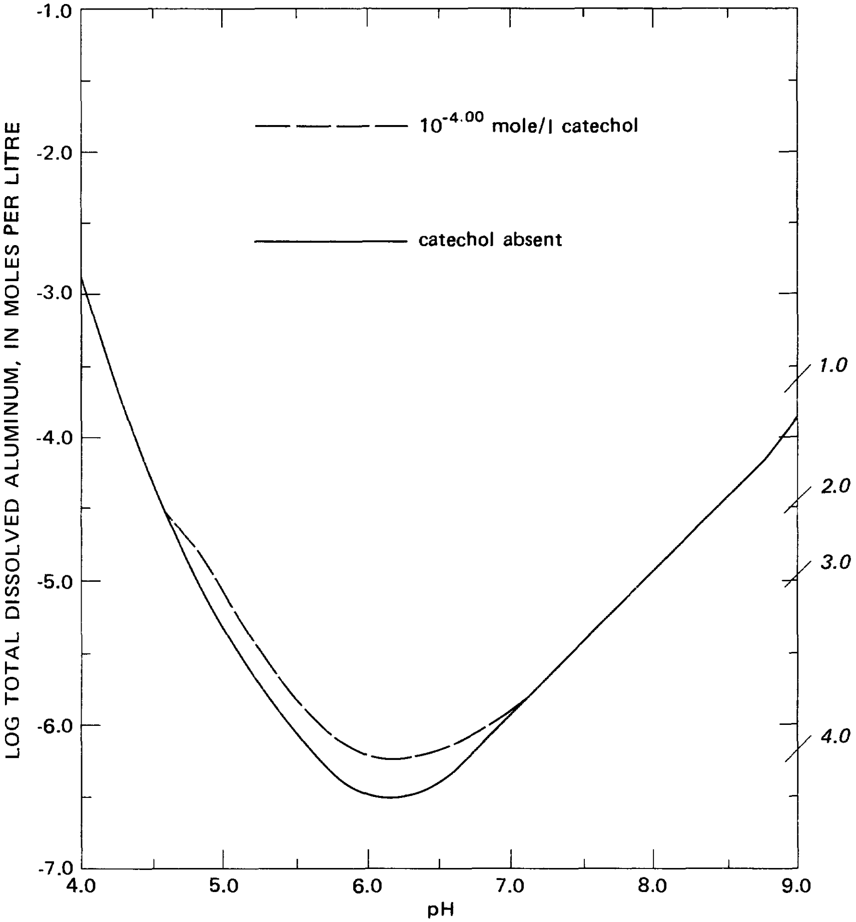


FIGURE 9.—Effects of complexes with catechol on the equilibrium solubility of aluminum in the presence of synthetic halloysite. Dissolved silicic acid $10^{-3.48}$ mole/l (20 mg/l as SiO_2). Positions of solubility intercept for four other solids shown by numbers at right (see text).

Besides these simple organic ligands, many others are possible in natural systems owing to substitution by other functional groups. These, too, are capable of complexing aluminum. A comparison of the stability constants of the simplest aromatic structures of several of them with those of salicylic acid will demonstrate the potential towards complexing that they offer. (See table 5.) Some of these structures might also be found as part of the fulvic and humic acid molecular structures.

In summation, it can be said that over much of the pH range of minimum solubility of synthetic halloysite and microcrystalline

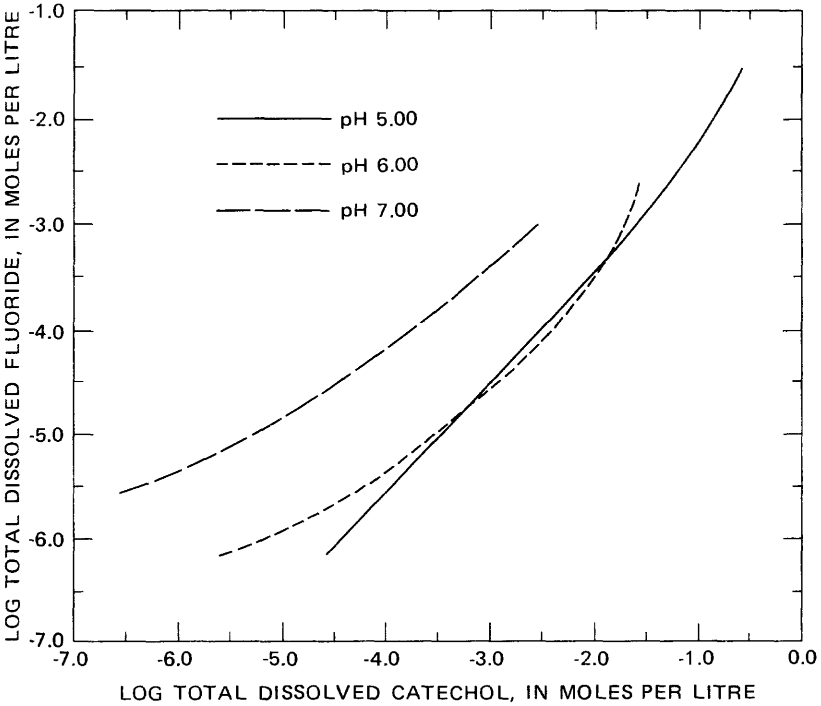


FIGURE 10.—Lines separating fluoride from catechol complexing domains at pH 5.00, 6.00, and 7.00. Aluminum concentration controlled by solubility of synthetic halloysite.

gibbsite, complexing of aluminum by organic ligands of low molecular weight can be at least as important as that due to the strong inorganic complexes with fluoride or hydroxide ligands.

INFLUENCE OF LARGER ORGANIC MOLECULES ON THE BEHAVIOR OF DISSOLVED ALUMINUM

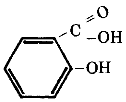
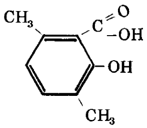
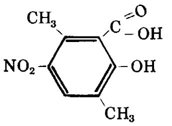
Large organic molecules associated with natural coloring material in water may approach or even exceed colloidal dimensions. Combinations of aluminum with these organic species may change aluminum solubility or interfere with or alter mechanisms of formation of aluminum hydroxide or aluminosilicates.

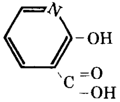
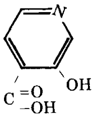
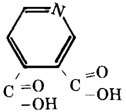
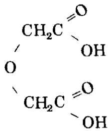
CHOICE OF A REPRESENTATIVE COMPOUND

To study the behavior of large organic ligands toward aluminum, a series of experiments was performed using a single well-defined compound, associated with macromolecular structures, that possesses many of the characteristics discussed so far. Besides the lignins,

Table 5.—*Potential for complexing by other functional groups*

[Reference columns: 1, Sillén and Martell (1964); 2, Foye, Baum, and Williams (1967); 3, Pecci and Foye (1960); 4, Das and Aditya (1959); 5, Napoli (1972)]

Ligand	Structure	H+					Al^{3-}					
		Solvent and temperature	log K_1	log K_{12}	log K_{13}	Reference	Solvent and temperature	log K_1'	log K_2'	log K_3'	logβ_3'	Reference
2-Hydroxybenzoic acid (salicylic acid)		H_2O, 25°C	13.4	3.00	----	1	0.1 M KCl, 25°C	14.00	10.7	8.6	33.3	3
							H_2O, 26–28°C	14.11	----	----	----	4
2-Hydroxy-3, 6-dimethylbenzoic acid		H_2O, 25°C	12.32	3.23	----	2	0.1 M KCl, 25°C	11.62	11.06	----	----	2
2-Hydroxy-5-nitro-3, 6-dimethylbenzoic acid		H_2O, 25°C	8.54	2.78	----	2	0.1 M KCl, 25°C	8.64	6.64	4.62	19.90	2

2-Hydroxpyridine-3-carboxylic acid		H_2O, 25°C	5.33	3.28	----	2	0.1 M KCl, 25°C	16.97	14.90	---	----	----
3-Hydroxypyridine-4-carboxylic acid		H_2O, 25°C	4.83	0.10	----	2	0.1 M KCl, 25°C	12.00	8.01	7.39	27.40	2
3,4-Pyridinedicarboxylic acid		H_2O, 25°C	5.07	2.95	1.50	2	0.1 M KCl 25°C	4.06 ----	4.02 ----	3.73 ----	11.81 ----	2
Oxydiacetic acid (diglycollic acid)		0.5 M $NaClO_4$, 25°C	3.76	2.80	---	5	0.5 M $NaClO_4$, 25°C	----	----	----	$3.16=\beta_1$ $5.25=\beta_2$	5 5

flavan-3,4-diols and flavan-3-ols may be among the sources of colored macromolecules, as they undergo condensation polymerization reactions (Christman and Minear, 1971). The biosynthetic formation of a tannin polymer is by means of flavanone to flavan-3,4-diol to flavan-4-ol (Harborne, 1972). Thus, a structurally related compound could be considered. (See figure 11*A*.) The flavonoids are the largest group of naturally occurring phenols (Seikel, 1964); of the some 600 flavonoids that have been isolated and fully characterized, quercetin, kaempferol, and flavadiol are the most common (Harborne, 1972; Bate-Smith, 1969). Quercetin, whose complexing capacity is well known, was chosen for the study. The structure of quercetin and the rearrangement of a flavonol to the quinoid structure in an alkaline medium are given in figures 11*B* and *C*. (It might be noted that the benzo-γ-pyrone structure and adjacent OH's on a benzene ring are both found in the quercetin molecule. The complexing by each of these structural components alone has already been discussed.)

PREPARATION OF QUERCETIN STOCK SOLUTION

A stock solution of purified quercetin was prepared and used at various dilutions for tests described in this text. A commercially obtained material was purified by the method described by Johnston, Stern, and Waiss (1968), by separation in a methanol solution on a column of Sephadex LH–20. The elution aliquots to be saved were identified by measuring their absorbance by means of a spectrophotometer. Measurements were made at 370 nm (nanometres), as mentioned by Porter and Markham (1970b). The quercetin was then crystallized from the methanol, dried in a vacuum dessicator, and further dried for 1 hour at 120°C with no loss of weight. (The quercetin dihydrate loses its two water molecules at 95–98°C and decomposes at 314°C, Strecher and others, 1960.) The purified quercetin is sparingly soluble at neutral pH. To prepare a sufficiently concentrated stock solution, a finely ground weighed amount was dissolved in distilled, demineralized water by adding dilute sodium hydroxide by drops with constant stirring. The pH was kept below 8.65 during the preparation of the first stock solution and below 8.50 for later preparations. According to Robinson (1967), the oxidation of flavonols in alkaline solutions, open to the air, is slow enough that mildly alkaline solutions may be used in their preparation. Aeration of the solution was kept at a minimum. When the solid was completely dissolved, the excess base was neutralized with standardized perchloric acid, and the final solution thus contained some sodium perchlorate.

PRECIPITATION IN ALUMINUM-QUERCETIN SOLUTIONS

Aluminum may combine chemically with quercetin in the lower pH

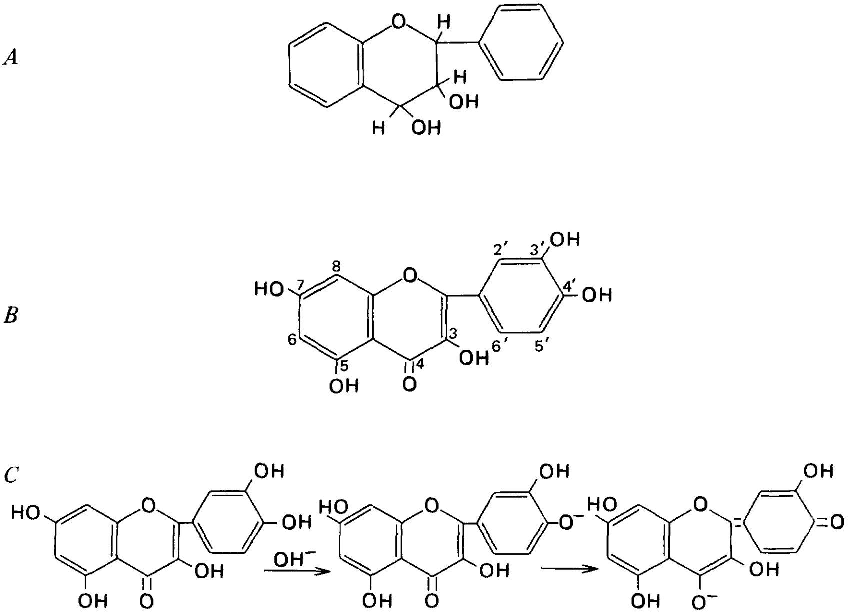


FIGURE 11.—Structural representations: *A*. Flavan-3,4-diol structure, *B*. Quercetin molecule, *C*. Rearrangement of flavonol to quinoid structure in alkaline solution (after Robinson 1967).

ranges to form a material of low solubility. Also, some types of large organic molecules may form relatively stable colloidal or larger aggregates with aluminum hydroxide. The potential importance of such effects was examined by a series of preliminary experiments.

Five equimolar solutions of aluminum and quercetin were prepared. The solutions had concentrations of 1×10^{-5}, 1.5×10^{-5}, 3.5×10^{-5}, 5×10^{-5}, and 8×10^{-5} molar with regard to each constituent and were 0.01 molar in sodium perchlorate. These solutions were placed in 125-millilitre boron-free glass bottles, having moisture-tight seal caps, and allowed to stand at 25°C. From time to time determinations were made of turbidity, aluminum concentration, fluorescence emission, and pH. So as not to alter the process of precipitation by agitation, a new bottle was opened at the time of each check, leaving the remainder of the solution undisturbed. The pH of these solutions was near 4.50 at first but increased to values near 5.00 during the aging period.

By the end of the 2-month aging period, the solutions with the two higher aluminum and quercetin concentrations had developed a substantial turbidity and had lost much of their original dissolved aluminum. These changes can probably be ascribed to the formation and precipitation of some chemical compound of aluminum with quercetin. However, the dissolved aluminum remaining at the end of 2 months is nearly the same as would be predicted for equilibrium with microcrystalline gibbsite. The polymerization process for production of gibbsite ordinarily entails a decreasing pH, but the quercetin in these solutions might have reacted with H^+. No detailed study of the precipitates was made, but electron micrographs showed almost no gibbsite crystals were present.

Upon excitation by light, derivatives of benzo-γ-pyrone emit fluorescence at specific wavelengths, depending on the structure involved. In the case of quercetin, the addition of aluminum to the structure changed the number of emissions from one to two, and they were at wavelengths different from that of the pure quercetin structure itself. Emission for these two centered at 490 and 565 nm and was observed throughout the aging period.

The behavior of the aluminum-quercetin solutions can be briefly summarized as follows:

1. All solutions emitted fluorescence at 565 and 490 nm, about in proportion to the initial aluminum and quercetin concentrations, but the fluorescence intensity decreased with time.
2. The loss of fluorescence was generally associated with development of turbidity and precipitation.
3. During the 2-month aging period, a decrease in dissolved aluminum and an increase in pH occurred in all the solutions, but it was observed after shorter aging periods in the solutions with the higher initial concentrations of reactants.
4. The precipitate was mostly an aluminum-quercetin compound, perhaps with a small admixture of gibbsite.

ALUMINUM-QUERCETIN COMPLEXES

The nature of the reacting species at the time of preparing the solutions can be deduced readily. The pH of the aluminum perchlorate solution was below 3.00, and that of the sodium quercetin above 5.00 (5.90 for 1×10^{-5}M to 5.03 for 8×10^{-5}M); both were 0.01 molar in sodium perchlorate. At the low pH of the aluminum solution, the aluminum is all in the $Al(H_2O)_6{}^{+3}$ state, but at the adjusted pH of the mixture (4.50), about 16 percent is in the $Al(H_2O)_5(OH)^{+2}$ state and about 6 percent in the $Al(H_2O)_4(OH)_2{}^{+1}$ state. Titrations of 1×10^{-3} molar sodium quercetin solutions with standard acid and base gave indication of one inflection point below pH 7.00, and this was at pH 5.56. The quercetin anion probably has one negative charge site available on most units, and in the mixing process aluminum cations or protons might become attached there. To evaluate the complexing reaction more closely, the properties of prepared solutions were measured over a period of time to establish the final complexing ratios and to determine if these ratios represented relatively stable soluble complexes or if the slowly precipitating solid that formed had a well-defined composition.

Several conclusions can be made from Porter and Markham (1970a, b, c). The amount of complexing and the ratio of aluminum to quercetin complexed depends on conditions such as pH, nature of the solvent, and the structure and concentrations of the reacting substances. From figure 11 it is evident the quercetin molecule has three places where oxygen and (or) phenolic OH are located at adjacent sites. Sites of this type might constitute favorable locations for aluminum ion attachment. In other words, aluminum might be attached at the 3′–4′ position, the 5-hydroxy-4-keto-position, and the 3-hydroxy-4-keto-position, the latter probably being the most preferred site.

COMPOSITION OF COMPLEXES

Two approaches were tried in an attempt to identify the ratios of aluminum to quercetin in the complexes and precipitates. The first was the method of Job (1928), where the total of the two constituents is held constant in a series of solutions but the metal to ligand ratios differ, and the second method was a modification involving a series of solutions in which one constituent was held constant and the other varied. Fluorescence was measured at 565 and 490 nm for each solution.

The sum of the concentrations studied using Job's method was 2×10^{-5} molar in aluminum plus quercetin. The fluorescence emissions at 565 and 490 nm were measured after 1, 6, and 19 days of aging. The mole ratios of aluminum to quercetin examined were 0:10, 1:9, 1:4, 3:7, 1:2, 2:3, 1:1, 3:2, 2:1, 7:3, 4:1, 9:1, and 10:0. The maximum in fluorescence should be observed at the ratio corresponding to the composition of the complex causing the fluorescence. The pH's of the solutions increased somewhat during the experiment, but the turbidity even through the 19th day was in the range of pure water, indicating no significant precipitation. A small amount of fluorescence is given off by quercetin itself at the wavelengths observed for the fluorescence of complexes. Consequently, to assist in interpreting the fluorescence due to complexes, the readings were corrected for the effect of quercetin according to the method of Vosburgh and Cooper (1941). The final results are shown in figures 12 and 13. Fluorescence intensities are represented in arbitrary units on a linear scale of 0–100 and are not directly convertible to ion concentrations. However, the conditions of measurement were the same for all samples, and the intensity values, therefore, indicate relative concentrations of complexes and are a valid measure of changes or differences. The

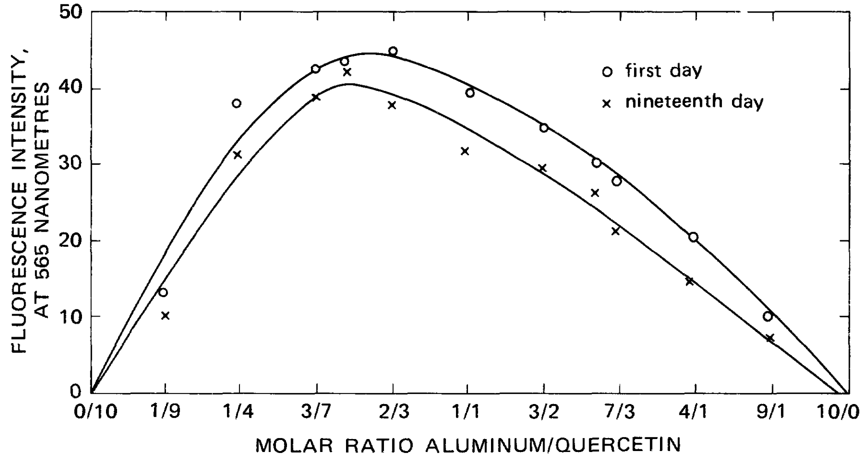


FIGURE 12.—Intensity of fluorescence at 565 nm in solutions having various aluminum to quercetin molar ratios. Total solute concentration constant.

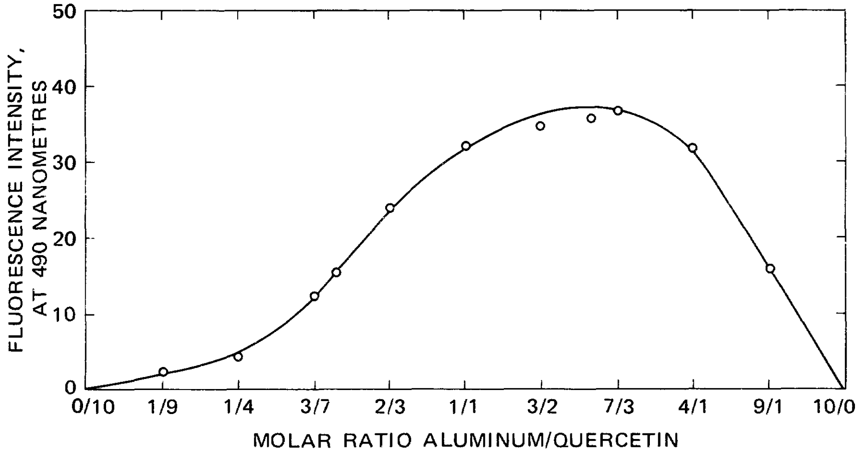


FIGURE 13.—Intensity of fluorescence at 490 nm in solutions having various aluminum to quercetin molar ratios after 1 day. Total solute concentration constant.

565-nm curve had a maximum near an aluminum to quercetin ratio of 2:3 on the 1st and 6th day and became sharper, centering around 1:2 by the 19th day. The intensity of fluorescence did not change greatly during the 19 days. The 490-nm curve had a maximum near 7:3 when the solutions were aged 1 day, 3:2 when aged 6 days, and became sharper at 3:2 after 19 days aging. The intensity of this fluorescence was noticeably greater at the first measurement than it was in later measurements, and the later two sets of data points are not shown in figure 13.

The attempt at the method where one component is held constant was done with the quercetin concentration held at 1×10^{-5} molar. The soluble complexes were measured immediately after mixing and after 6 and 14 days of aging. The ratios of aluminum to quercetin measured were 0:10, 1:4, 1:3, 2:5, 9:20, 1:2, 3:5, 2:3, 3:4, 1:1, between 6:5 and 5:4, 4:3, 3:2, about 5:3, 2:1, 9:4, and 5:2. A plot of fluorescence intensity versus the aluminum-quercetin mole ratio should give a curve with a change in slope at the composition of the complex causing the fluorescence. The pH's of the solutions immediately after mixing ranged from 4.49 to 4.51, on the 6th day from 4.49 to 4.60, and on the 14th day 4.56 to 4.75. The turbidity of all the solutions at each of these times was well within the range of pure water. Because the quercetin concentration was held constant, no correction was applied for its presence. The 565-nm plot, figure 14, had a smooth curve when aged only 1 day. By the 6th day, however, the plot had a sharp break at the 1:2 ratio. Measurements made at 14 days are not shown and gave more scatter; however, they also indicated a 1:2 ratio. The fluorescence at this wavelength did show some decrease with time, particularly at the higher ratios. The 490-nm readings did not give interpretable results. The intensity of the fluorescence at the 490-nm wavelength decreased substantially during the 14-day aging period. In conclusion, it can be said that quite likely the 565-nm fluorescence peak represents a

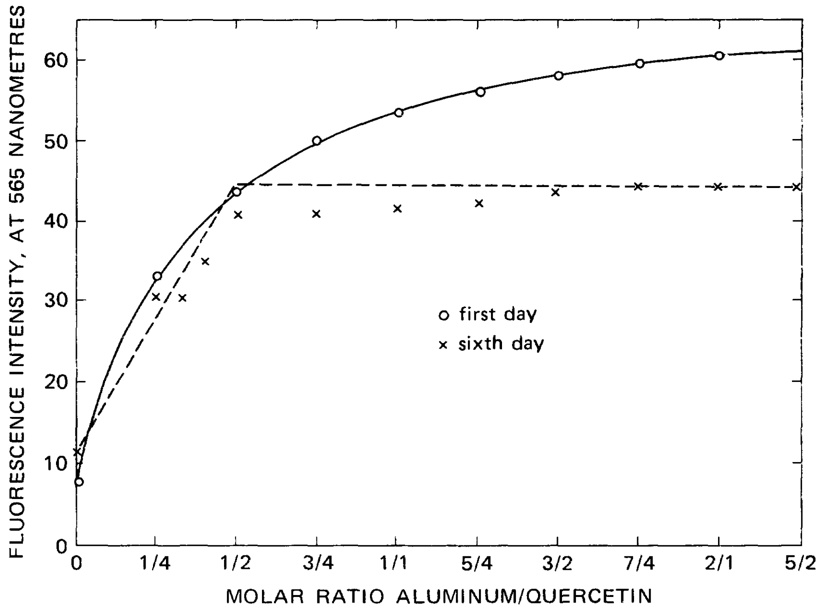


FIGURE 14.—Intensity of fluorescence at 565 nm in solutions having various aluminum to quercetin molar ratios. Quercetin concentration constant.

complex with an aluminum to quercetin ratio of 1:2 and the 490-nm peak a complex, richer in aluminum, with a 3:2 ratio.

Observations during these tests indicate that the high aluminum to quercetin ratio complex, represented by the 490-nm fluorescence, is the less stable and may be a precursor of solid material. The basis for this statement is that this complex is the one that loses fluorescence when the turbidity becomes greater than that of pure water and also that the peak is decreased when these test solutions are filtered. The loss of fluorescence may be explained by polymerization to macromolecules and subsequently to particles large enough to precipitate.

Even though it is recognized that Job's method is strictly applicable only to systems simpler than the one investigated here and cannot be used to determine accurate stability constants for these complexes, the qualitative indication that the method gives of complex composition is probably useful.

A second series of tests was made using Job's method with somewhat more concentrated solutions. The sum of the concentrations of the initial solutions was 4×10^{-5} molar in aluminum plus quercetin. Before this experiment was completed, a noticeable amount of precipitate had formed in most of the solutions, and the fluorescence had largely disappeared. However, the results again indicated molar ratios of 1:2 and 3:2 aluminum to quercetin for the two complexes. From consideration of the results of Porter and Markham (1970c), who studied quercetin complexing and dissociation in a nonaqueous system, one can picture the more soluble 1:2 complex with quercetin in water at pH 4.5 as the structure represented by figure 15*A*. The second aqueous complex ratio, 3:2, might be represented by figure 15*B*. The complexes appear to be unstable or at best sparingly soluble, however, and one might question the significance of any effort to specify exact values of thermodynamic stability constants.The amount of ionization of quercetin is small in the final aqueous solutions. Taking the pK_a of 5.56±0.08 (K_a is the quercetin acid dissociation constant) and a final pH of 4.55 and assuming the total concentrations of quercetin as 1×10^{-5} and 2×10^{-5} molar, the calculated concentrations of H_4L^- would be 1×10^{-6} and 2×10^{-6} molar, respectively, or only about 10 percent of the total quercetin. (The activity coefficient used, 0.912, was that for dibenzyl acetic acid (Butler, 1964), and the 0.01 ionic strength of the solution was considered.) However, there may be other factors influencing quercetin complex formation besides the previously discussed acid dissociation. Martell (1971) gave a rather thorough description of chelation and references for further pursuit of the subject. He indicated that the combination of a ligand with a metal ion

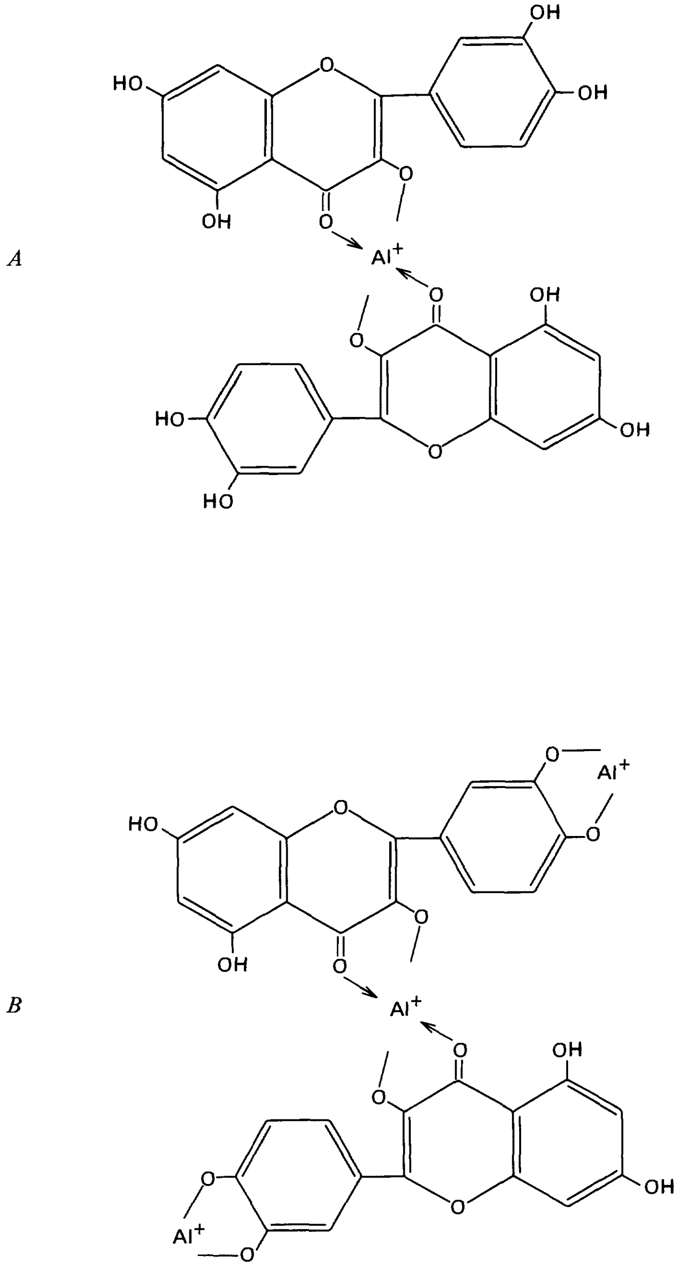


FIGURE 15.—Possible structures of aluminum-quercetin complexes. *A*, Aluminum to quercetin 1:2. *B*, Aluminum to quercetin 3:2.

involves the displacement by the ligand of one of the water molecules from the fully coordinated metal ion hydration shell. The nature and size of the coordinated donor groups of the solvent and attached ligands determine the coordination numbers of the metal ions. If the number of donor groups matches the coordination number of the metal, the chelate or complex is stable, but if not, and the relatively active "aquo" form exists, several types of reactions can occur. Strong polarization of the donor atoms and adjacent parts of the organic molecules results when the metal and ligand combine, shifting electrons toward the metal ion. This change of electron distribution can lead to solvolysis, rearrangement of the organic molecule, and even decomposition reactions. Thus, an accurate understanding of the final precipitation process and probably even the complex development requires more information than we have been able to obtain in our experiments.

Attachment of the aluminum ions at the keto and hydroxyl positions is somewhat similar to that of complexing by kojic acid and at the phenolic hydroxide positions to that of complexing by catechol, represented in figures 7 and 9 respectively. The low solubility of the product formed with quercetin, however, implies that the influence of quercetin on aluminum behavior might differ from the solubility enhancement predicted for the other organic ligands. It seems likely, for example, that a concentration of 10^{-4} molar for quercetin cannot be reached at pH 5 when the concentration of aluminum is of a near order of magnitude.

Figures 12 and 14 can be used as a basis for estimating the strength of the 1:2 aluminum-quercetin complex which fluoresces at 565 nm. At the maximum fluorescence reached, the quercetin may, as a first approximation, be assigned entirely to the complex AlQ_2 (where Q stands for quercetin). From the stoichiometry a concentration of uncomplexed aluminum can be assigned. The concentration of uncomplexed quercetin, however, can only be said to be small compared with the total amount and cannot be assigned any specific value. Nevertheless, one may now select a point lower on the fluorescence curve that represents an intensity less than the maximum by some specific factor and calculate from this the amount of quercetin complexed at that point. The amounts of free aluminum and quercetin can be approximately calculated from stoichiometry applied to the aluminum quercetin ratio indicated on the X axis of the graph.

Several repetitions of this calculation give values for β_2 for the formation of AlQ_2,

$$Al^{+3}+2Q^{-}=AlQ_2^{+},$$

of about 10^{12}, which is applicable at the pH of the test solutions (4.5–5.5). This approach ignores possible effects from the other aluminum-quercetin complex that fluoresces at 490 nm, but this complex appears to be too unstable to treat as an equilibrium species. The method of estimation is subject to many uncertainties, and the value of β_2 for the quercetin complex given here is only a rough approximation.

Although the effect of quercetin on equilibrium solubility of aluminum near pH 5.00 probably is similar in magnitude to the effect of malonate shown in figure 3, there are important differences. Low solubility of quercetin and the tendency to form higher complexes that are even less soluble are important. Also, the chemistry of the quercetin complexes is not fully evaluated. The influence of pH, for example, is uncertain, and the tendency for the pH of solutions containing quercetin and aluminum to increase during aging is not fully explained.

MODIFICATION OF ALUMINUM HYDROXIDE PRECIPITATE BY TRACES OF QUERCETIN

Organic complexes of aluminum may influence the chemical behavior of the element in other ways, besides their effect on equilibrium solubility. Where concentrations of the oganic ligand are too small to form complexes with a major part of the dissolved aluminum, there may still be threshold effects that can influence the mechanisms whereby aluminum hydroxide and related species are precipitated, and the form of the precipitate can be substantially influenced by such effects. The influence of small concentrations of quercetin on reactions of aluminum was studied, and results will be presented in the following sections of this report.

Solutions that precipitated aluminum hydroxide in previous studies by Hem and Roberson (1967), Roberson and Hem (1969), Schoen and Roberson (1970), and Smith and Hem (1972) were duplicated with the addition of quercetin as an example of organic material in concentrations that might occur in natural waters. The ratios of aluminum to quercetin, 100:1 and 100:4, were such that aluminum-quercetin complexes themselves could comprise only a very small fraction of the reacting species. In spite of this, there was a definite modification of the rate and possibly the mode of formation of aluminum hydroxides.

Two series of solutions were prepared, one containing 5×10^{-6} mole/l quercetin (0.9 mg/l organic carbon), designated the Q21 and Q22 series, and one containing 2×10^{-5} mole/l quercetin (3.6 mg/l organic carbon), designated the Q23 series. The solutions contained 4.71×10^{-4} mole/l aluminum and were 0.01 in total ionic strength. They were prepared by the method described in Hem and Roberson (1967), except with the addition of the amount of quercetin mentioned to solution I and twice that amount to solution III.

BLOCKAGE OF CRYSTALLIZATION IN ACIDIC SOLUTIONS

The development of gibbsite in acidic solutions is obviously hindered by the presence of quercetin. Table 6 gives results of the procedure for determining the three forms of aluminum, described by Smith and Hem (1972), applied to solutions aged 121, 126, and 127 days and also to those aged 310, 311, and 312 days. Solutions containing quercetin had substantially higher pH and greater concentrations of the unstable Al_b polymer than did the comparable solutions where quercetin was absent. Figure 16 shows graphically that monomeric aluminum was produced in lower concentration in the presence of quercetin. The process of conversion of Al_b to crystalline gibbsite released protons, and inhibition of the process by quercetin appears to be the logical explanation of the observed differences. The "apparent solubility" of Al_c species after 310 days is represented in figure 17 as circles designating the monomeric aluminum concentration. In earlier studies where quercetin was absent, the solubilities after comparable aging times were substantially lower.

In the work of Hem and Roberson (1967), the solid formed during relatively short aging periods (1 to about 60 days) was described as

TABLE 6.—*Effect of quercetin on stability of aluminum species*

Aluminum-quercetin solutions							Aluminum only						
Sample	Age (days)	pH	r_n ((OH):(Al))	Al_a	Al_b	Al_c	Sample	Age (days)	pH	r_n ((OH):(Al))	Al_a	Al_b	Al_c
				(moles/l ×10^4)							(moles/l ×10^4)		
Q21D	0	4.65	1.02	----	----	----	C	0	4.52	0.94	3.40	0.65	0.49
	127	4.51	----	1.81	2.30	0.59		82	4.48	----	3.20	.97	.37
	312	4.49	----	1.92	1.90	.89		121	4.47	----	3.23	.79	.52
Q21E	0	4.72	1.28	----	----	----	D	0	4.66	1.36	2.84	1.06	.64
	127	4.56	----	1.55	2.38	.78		82	4.26	----	2.34	.34	1.86
	312	4.53	----	1.74	1.93	1.03		121	4.23	----	2.39	.06	2.09
								259	4.12	----	2.30	.02	2.22
Q21F	0	4.76	1.47	----	----	----		----	----	----	----	----	----
	127	4.59	----	1.54	2.47	.71		----	----	----	----	----	----
	312	4.57	----	1.49	1.94	1.28		----	----	----	----	----	----
Q23A	0	4.79	1.53	----	----	----		----	----	----	----	----	----
	121	4.68	----	1.15	1.95	1.61		----	----	----	----	----	----
	310	4.65	----	1.13	1.55	2.03		----	----	----	----	----	----
Q21G	0	4.78	1.79	----	----	----	E	0	4.79	1.84	2.24	1.50	.50
	127	4.65	----	.92	2.82	.96		77	4.54	----	1.53	1.45	1.56
	312	4.64	----	1.10	2.20	1.40		116	4.52	----	1.60	1.20	1.74
	----	----	----	----	----	----		254	4.32	----	1.50	.12	2.92
Q22A	0	4.86	1.89	----	----	----	F	0	4.88	2.13	1.46	1.78	1.30
	126	4.68	----	.75	2.44	1.51		82	4.30	----	1.20	.26	3.08
	311	4.63	----	.90	1.58	2.23		121	4.28	----	1.21	.10	3.23
	----	----	----	----	----	----		259	4.20	----	1.02	.02	3.50
Q22B	0	5.06	2.42	----	----	----	G	0	5.02	2.47	1.17	1.97	1.40
	126	4.74	----	.36	.67	3.68		77	4.40	----	.68	.13	3.63
	311	4.66	----	.31	.44	3.96		116	4.35	----	.66	.043	3.84
	----	----	----	----	----	----		254	4.28	----	.62	.007	3.91
Q23B	0	5.16	2.72	----	----	----	H	0	5.23	2.76	.78	1.36	3.40
	121	4.90	----	.23	.34	4.14		82	4.51	----	.29	.05	4.20
	310	4.81	----	.22	.11	4.38		121	4.49	----	.284	.011	4.24
	----	----	----	----	----	----		259	4.45	----	.235	----	4.30

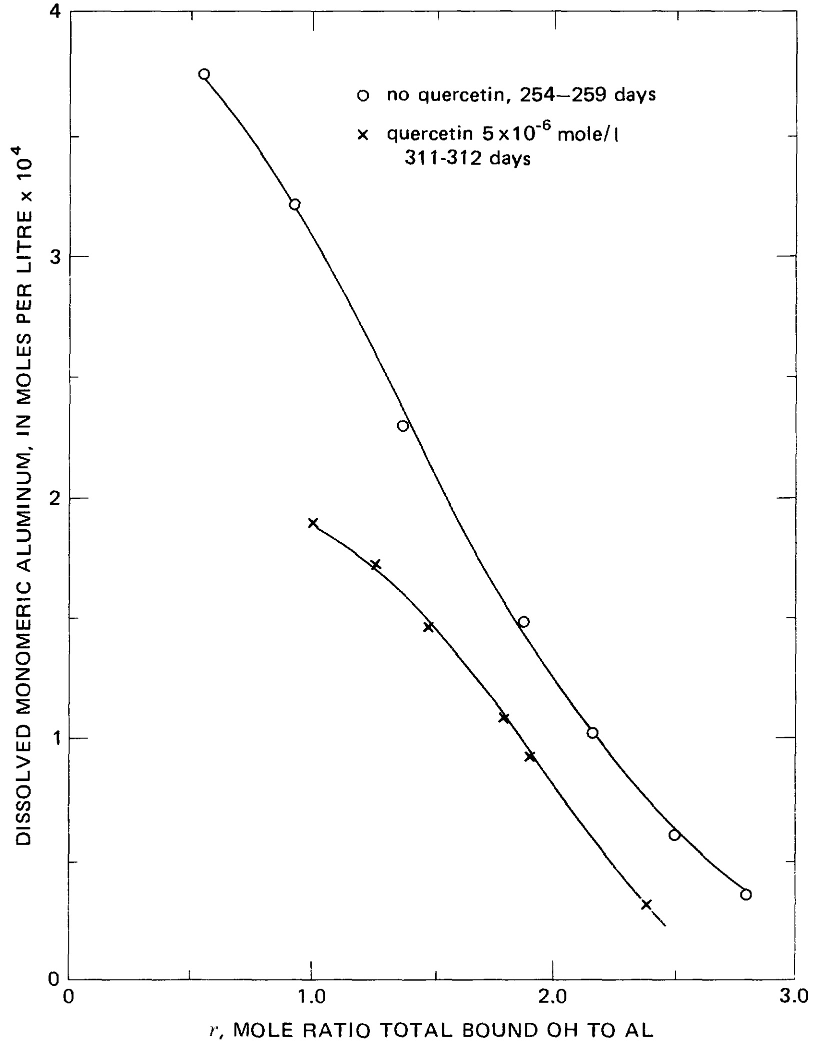


FIGURE 16.—Effect of small amounts of dissolved quercetin on the concentrations of monomeric aluminum species in aged solutions.

microcrystalline gibbsite, and its solubility product ($*K_{s0}$) in the reaction

$$Al(OH)_{3(c)}+3H^{+}=Al^{3+}+3H_2O$$

was determined to be $10^{9.35}$. The better crystallized material obtained by Smith and Hem (1972) after much longer aging had a $^{*}K_{s0}$ value of $10^{8.22}$. Data in table 7 indicate that in the presence of small amounts of quercetin the calculated solubility product for $Al(OH)_3$ is near the microcrystalline gibbsite value even after 312 days of aging.

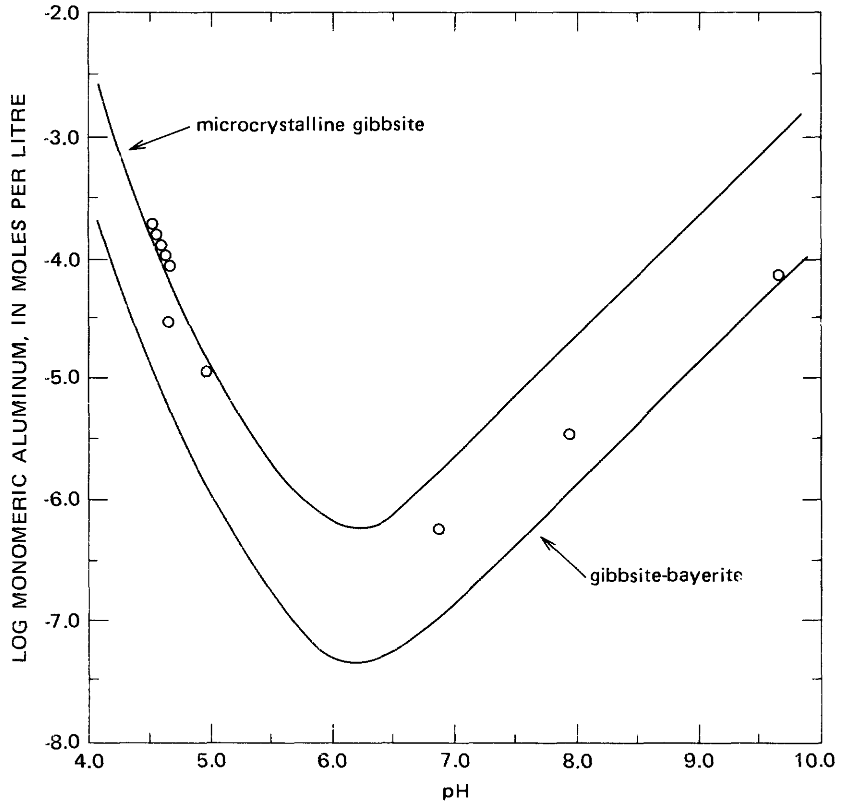


FIGURE 17.—Monomeric aluminum concentrations in solutions containing $10^{-5.30}$ mole/l of quercetin (circles) after 310 days aging compared with equilibrium values for microcrystalline gibbsite and well-crystallized gibbsite or bayerite.

Smith and Hem (1972) attributed the decrease in pH observed during aging to a process of polymerization whereby Al_b was converted to Al_c and protons were released. The presence of quercetin evidently slows down this process. The pH of solutions containing quercetin only decreased slightly during 1 year of aging. The concentrations of the organic ligand were too small to have a direct influence; rather there must have been a "threshold" effect, whereby the quercetin interfered with nucleation and growth of aluminum hydroxide particles.

AVERAGE SIZE OF ALUMINUM HYDROXIDE POLYMERIC IONS

The process of polymerization of aluminum hydroxide ionic species to form gibbsite has been described by Hem and Roberson (1967) and Smith and Hem (1972) as the formation of a network of double hydroxide bridges linking aluminum ions together in a geometric

TABLE 7.— $^*K_{s0}$ *values of aged acidic solutions containing quercetin*

Solution	Age (days)	r_n value	log $^*K_{s0}$
Q21D	127	1.02	9.32
	312	----	9.29
Q21E	127	1.28	9.39
	312	----	9.36
Q21F	127	1.47	9.46
	312	----	9.40
Q21G	127	1.79	9.39
	312	----	9.45
Q22A	126	1.89	9.38
	311	----	9.33
			(mean)9.38
Q22B	126	2.42	9.21
	311	----	8.95
Q23A	121	1.53	9.57
	310	----	9.48
Q23B	121	2.72	9.39
	310	----	9.15

pattern of coalesced hexagonal rings. Bridging hydroxide is essentially unreactive, and its change of status in the solution frees protons and lowers the pH. Aluminum hydroxide polynuclear ionic species have been postulated by some investigators, usually with no definite structural consideration being given. It seems evident, however, that the aluminum ions in such species would necessarily be linked by the double hydroxide bridges. The determination of Al_b is by a kinetic procedure that depends on the slow rate of disruption of this bridged structure. It is possible to make some inferences about the relative size of Al_b units in the presence of traces of quercetin from data in table 6 and from structural considerations.

Amounts of Al_b in some of the aluminum-quercetin solutions were initially larger than in the similar solutions of Smith and Hem (1972), given in table 6 for comparison, but this is not considered particularly significant. The initial concentration of Al_b is in part a function of the way the solutions are mixed.

The ratio of bound hydroxide to aluminum in the Al_b fraction was calculated from stoichiometry of the solutions. This value ranged from 1.4 to 1.9 and did not get as high as 2.0 in any quercetin solutions even after more than 300 days of aging. In the comparable solutions of Smith and Hem (1972), the OH:Al ratio in the Al_b fraction was greater than 2.0 after only 1 day. If all the bound OH is in bridging positions, the minimum value of the ratio for a six-membered hexagonal ring is 2.0. At least some of the bound OH in the Al_b units is likely to be held in nonbridging positions. In any event, the low values of the ratio indicate that most of the Al_b units do not become large enough to include even one ring and thus do not attain the gibbsite structure during the 300 days of aging.

The net effect of quercetin would appear to be one of slowing the polymerization process. Some Al_b does disappear, but at the rate indicated for the solutions cited in table 6, many years would be needed to complete the process. Only a few of the centers of polymer growth formed when the solutions are mixed are large enough to sustain growth toward a crystalline state. The smaller polynuclear ions may attain a considerable degree of metastability in such a solution, but such species still are not thermodynamically stable.

IDENTIFICATION OF CRYSTALLINE SPECIES

Principal evidence as to the crystalline nature of the gibbsite obtained in studies by Hem and Roberson (1967) and Schoen and Roberson (1970) included X-ray diffraction patterns and electron micrographs. The material characteristically formed thin hexagonal platelets 0.1μm (micrometre) or less in diameter with a distinctive appearance in electron micrographs, and aggregates of these particles gave X-ray diffraction scans with sharp peaks characteristic of gibbsite (fig. 18).

The X-ray diffraction procedure may fail to detect crystallinity if the crystals are very small or form less than about 10 percent of the total of solid material. The electron micrographs permit examination of very small fractions of the total precipitate and small amounts of crystalline material in an amorphous matrix could thus be overlooked by either procedure. The identification of crystalline material by either procedure, however, is definite evidence of important amounts of such material being present.

Of all the solutions containing quercetin, only one (Q22B) yielded material that could be identified as gibbsite by X-ray diffraction. The pattern for this material is shown in figure 19. Other solutions having similar concentrations of quercetin did not show this peak. Those solutions where the initial OH:Al molar ratio was below 1.89 showed no peaks at all. Those having higher ratios and some of the solutions having higher quercetin contents contained material that gave a broad and intense peak for a *d*-spacing between about 6 and 8 A (angstroms). No positive assignment of structure of composition can be made from this evidence; however, a broad ill-defined bulge in the pattern was observed in some earlier work where quercetin was absent, at about this *d*-spacing. Material of this kind has been called boehmite or

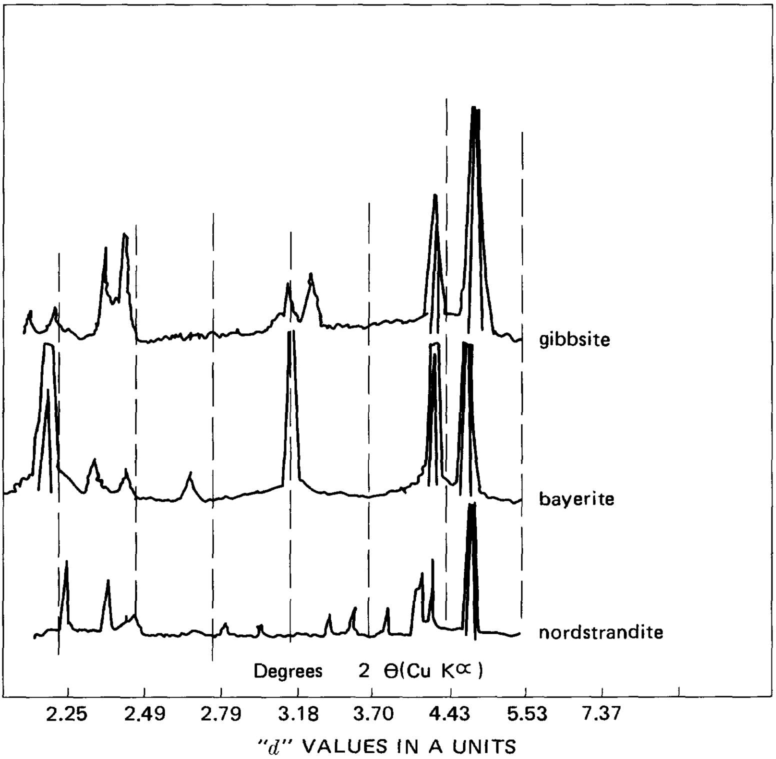


FIGURE 18.—X-ray diffraction patterns of gibbsite, bayerite, and nordstrandite (Schoen and Roberson, 1970).

pseudo-boehmite by some workers, as boehmite has a major peak in this general range.

Electron micrographs of solids recovered from solution Q22B show small quantities of poorly formed gibbsite crystals. The other solutions which had OH:Al ratios below 3 did not appear to contain any gibbsite crystals, but several had aggregates of layered material without well-defined crystal form, which might have produced the 6–8 A peaks just noted.

The presence of minute amounts of quercetin in acidic solutions evidently hinders the formation of gibbsite and seems to encourage the formation of significant quantities of poorly crystallized $Al(OH)_3$ with a different structure. The material that is ultimately precipitated is relatively stable and is not amorphous to X-rays, but it has large, definite ranges of structural dimensions. Considering that the quercetin solutions were studied over a period of 310–312 days without producing well-formed gibbsite, they are a sharp contrast to those of Hem and Roberson (1967), who found microcrystalline gibbsite

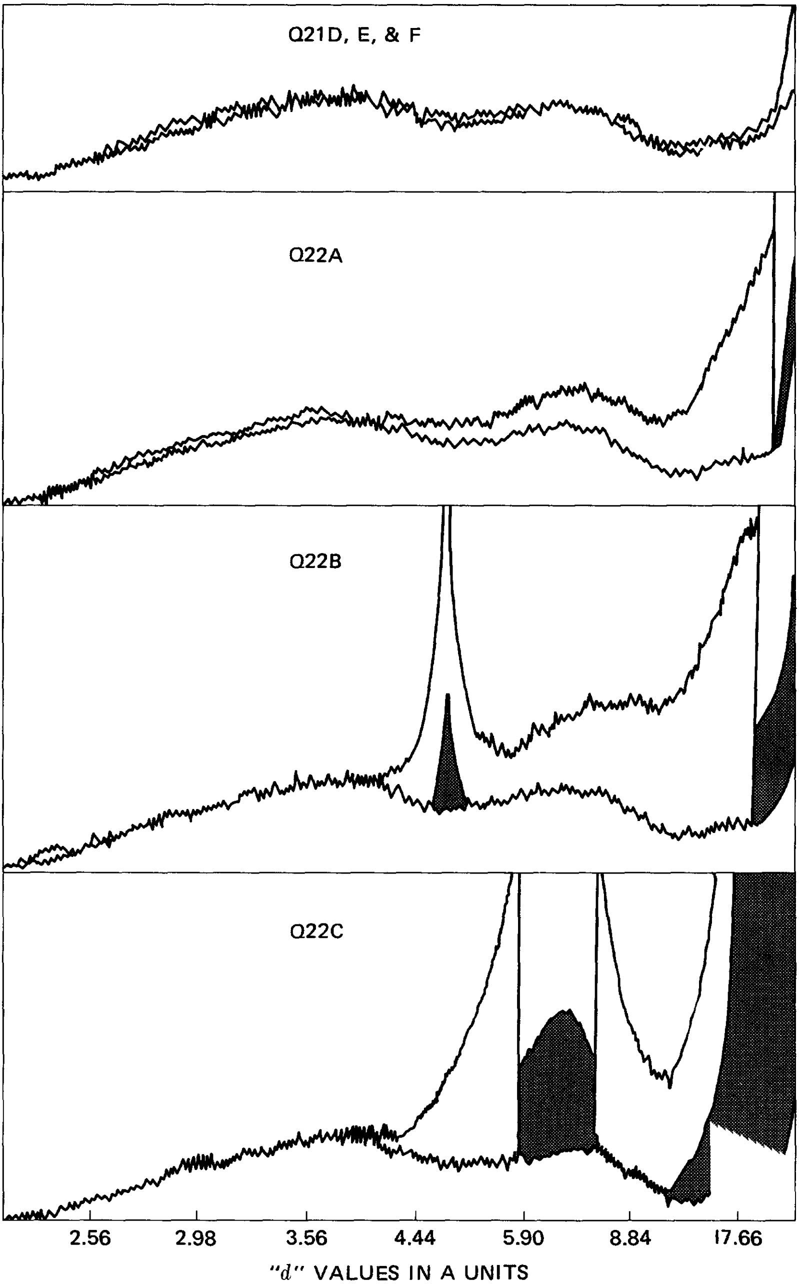


FIGURE 19.—X-ray diffraction patterns for solid material recovered from solutions Q21D–F and Q22A–C aged 311 and 312 days. (The lower line on each graph is the pattern given by the empty glass slide. The darkened areas are where the pattern went off scale and the peak was diminished in size by one-half.)

particles in solutions with r_n's ((OH):(Al)) from 2.0 to 3.0 within 2–10 days of aging at 25°C, and to those of Smith and Hem (1972), who achieved a solubility value of well-formed gibbsite for their solutions within 254–259 days.

BLOCKAGE OF CRYSTALLIZATION IN BASIC SOLUTIONS

The formation of bayerite which normally occurs when aluminum is precipitated in an alkaline solution is also retarded by the presence of quercetin. An inspection of the $^*K_{s4}$ values, represented by the equation

$$Al(OH)_{3(c)}+H_2O=Al(OH)_4{}^-+H^+,$$

will illustrate this. Hem and Roberson (1967) found a solubility product of $10^{-12.71}$ in their day-old solutions of pH 7.5–9.5, but the material was amorphous to X-rays. Within 10 days, the solubility product reached that of bayerite, $10^{-13.95}$. The solid present at that time had an X-ray pattern of bayerite. In the aluminum-quercetin solutions, with the lesser amount of quercetin and with a pH greater than the minimum solubility of gibbsite and bayerite (well above pH of 6.0), the $^*K_{s4}$ values were higher than that of bayerite from age 3 to 311 days. With the solution of r_n of 4.42, the $^*K_{s4}$ eventually closely approached that of bayerite; the period of most marked decrease in $^*K_{s4}$ in this solution was between ages 40 and 126 days. In the series with more quercetin, the $^*K_{s4}$ values were close to the amorphous material value even though aged 121 days, and by age 509 days the value for Q23G, the most basic solution in this series, was still only midway between that of the amorphous material and that of bayerite. (See table 8.)

DEVELOPMENT OF BAYERITE

Some stages in the development of bayerite crystals can be traced by means of the electron micrographs of precipitates from Q22E, r_n of 3.65. (See figs. 20–24.) Early in the aging period, a sheetlike mesh of interlaced crystals is formed. On further aging this mesh assumes a "jackstraw" pattern, and a few scattered bayerite crystals appear (fig. 20). At this time a general view of this material indicates no widespread crystallinity. Upon additional aging, better ordered bayerite crystals appear (fig. 21). A general view of this material indicates an occasional well-formed crystal shape but mostly still poorly defined fragments (fig. 22). The 126-day-old solid still had a mixture of free and enmeshed crystals. The micrographs seem to indicate that where the interlaced mesh is absent the bayerite particles themselves once again have only the fine pebbly texture brought out by coating with platinum (fig. 23), but some of the bayerite crystals leave the impression that the mesh is part of the crystal itself.

TABLE 8.—*Composition during aging of solutions having* r_n *values greater than 2.75*

Solution	r_n ((OH):(Al))	Age (days)	pH	p(Al)[1]	log*K_{S4}	Solution	r_n ((OH):(Al))	Age (days)	pH	p(Al)[1]	log*K_{S4}
Q22C	2.76	0	5.62	----	----	Q23C	2.85	0	5.31	----	----
		4	5.50	3.40	----			3	5.19	4.36	----
		19	5.29	4.50	----			21	5.07	4.42	----
		40	5.16	4.63	----			41	5.01	4.47	----
		126	5.03	4.97	----			121	4.96	4.68	----
		311	4.89	4.98	----			310	4.86	4.70	----
Q22D	2.99	0	7.75	----	----	Q23D	2.93	0	5.79	----	----
		4	7.62	5.43	−13.10			3	5.71	5.09	----
		19	7.09	5.53	−12.67			21	5.44	5.09	----
		40	6.87	----	----			41	5.34	5.59	----
		126	6.70	6.43	−13.18			121	5.20	5.65	----
		311	7.03	6.43	−13.51			310	5.12	6.43	----
		514	6.87	6.23	−13.15			509	5.07	6.23	----
						Q23E	3.02	0	6.11	----	----
								21	6.51	----	----
								41	6.62	----	----
								121	6.75	6 13	−12.93
						Q23F	3.27	0	8.00	----	----
								3	7.94	4.51	−12.56
								21	7.63	5 25	−12.93
								41	7.32	----	----
								121	7.29	5 59	−12.93
Q22E	3.65	0	8.63	----	----	Q23G	3.46	0	8.85	----	----
		4	9.39	3.67	−13.11			3	8.69	3 74	−12.48
		19	9.43	3.77	−13.25			21	8.57	3 68	−12.30
		40	9.31	3.81	−13.17			41	8.82	3 60	−12.47
		126	9.31	4.20	−13.56			121	9.02	3 81	−12.88
		311	7.93	5.43	−13.41			310	8.97	4 06	−13.08
								509	8.45	4.74	−13.24
Q22F	4.42	0	10.05	----	----						
		4	9.92	3.37	−13.34						
		19	9.76	3.43	−13.24						
		40	9.68	3.39	−13.12						
		126	9.90	3.78	−13.73						
		311	9.63	4.13	−13.81						

[1] Aluminum determined by the regular ferron method.

Figure 24 shows that even at age 311 days there still were bayerite crystals forming. This micrograph also is a pronounced demonstration of the pyramid shape that the bayerite crystal assumes. The whole series of micrographs gives real visual evidence of the existence of an intermediate material for an extended period of time during the organizational development of aluminum trihydroxides.

A third aluminum trihydroxide, nordstrandite, has been synthesized previously also. It has the same free energy as bayerite (Hem and others, 1973). Schoen and Roberson (1970) suggested that nordstrandite forms in solutions of pH 5.8 and more and that the sequence of crystallization in mildly alkaline solutions is from early formed bayerite to nordstrandite. In an attempt to determine the importance of pH in the formation of bayerite and nordstrandite, they found that in solutions near neutral pH these two minerals precipitated simultaneously. Some of both may be present in figure 25. The X-ray pattern for material from this solution (fig. 26) has a peak near the "*d*" spacing of boehmite, but because of uncertainties in the

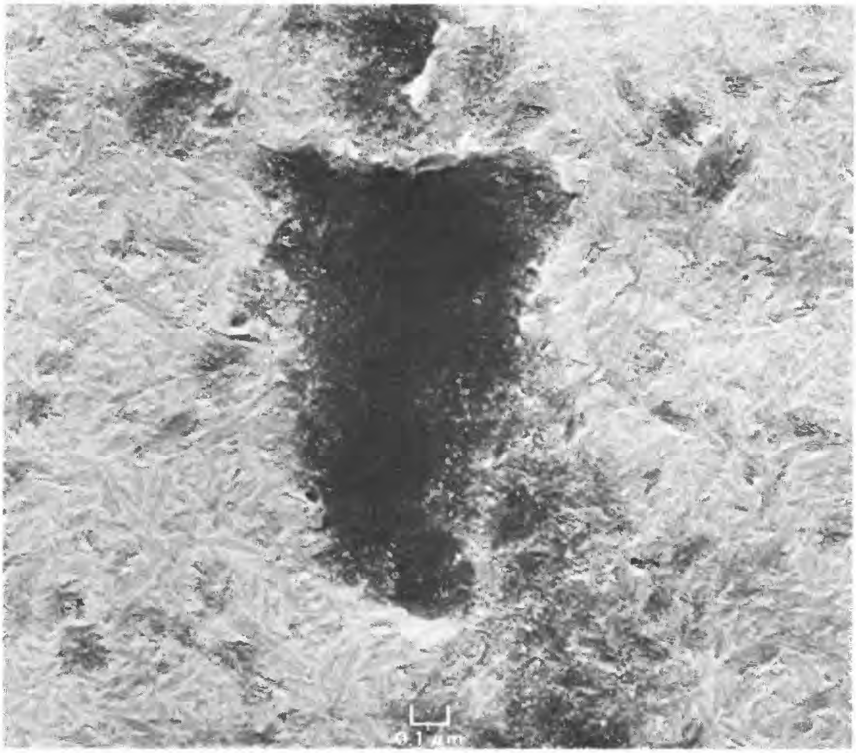


FIGURE 20.—Electron micrograph of solids recovered from solution Q22E aged 40 days. A bayerite crystal beginning to form.

literature regarding identification and solubility of this mineral, it cannot be conclusively assigned.

Solution Q22F, r_n of 4.42, had well-defined crystal shapes characteristic of bayerite and nordstrandite by an age of 126 days. The X-ray diffraction pattern after aging 311 days had peaks characteristic of bayerite (fig. 26). Nordstrandite crystals identified by Schoen and Roberson (1970) were elongated rectangles or parallelograms. Electron micrographs of this sample at a shorter aging time gave no indication of crystallinity and contained filmy amorphous matter having no observable texture.

No crystallinity was observed in electron micrographs of material from any of the Q23 solutions with the exception of Q23G. When aged 310 days, Q23G had the "jackstraw" pattern and, when aged 509 days, in addition showed faint dots that possibly indicated focal points for the initiation of some type of further crystallization. The micrographs of the solids from this series supplement the solubility data in helping to

FIGURE 21.—Electron micrograph of solids recovered from solution Q22E aged 57 days. A more clearly defined bayerite crystal.

substantiate that the crystallization process is even more retarded in the presence of higher concentrations of quercetin.

INTERMEDIATE PRODUCTS

The X-ray diffraction patterns of the quercetin series fit the trend established by the other data, namely, that the formation of bayerite is favored more strongly as the pH becomes more basic and that intermediate products are more prominent in less basic solutions and in those with higher concentrations of quercetin. (See figs. 27, 28.)

By the time all the basic solutions (with the exception of Q22F which was not tested) were aged 121–126 days, they were shown to have indication of a broad peak as pictured in figure 26 for Q22E at age 311 days. The point of this peak suggests a "*d*" spacing range very near that of natural boehmite. The electron micrographs of Q23E and Q23F, age 126 days, did not show any of the precursor crystal mesh, and unfortunately no further crystallization could be traced in these solutions, as they had been used up. The entanglement of the bayerite crystals in the mesh of poorly organized material in figure 29 may

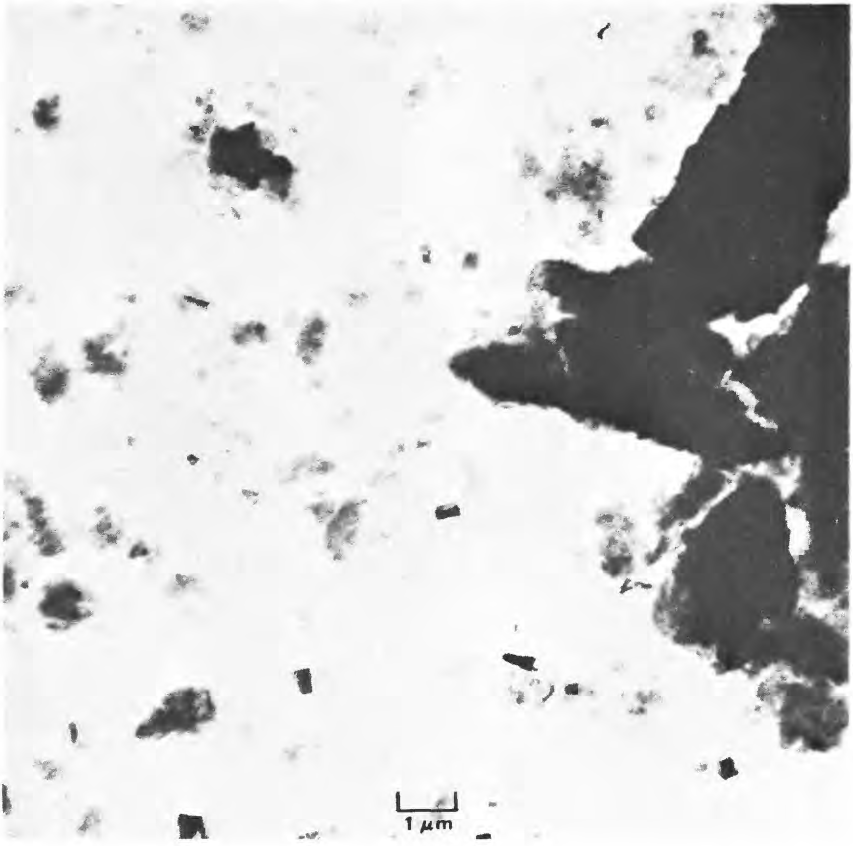


FIGURE 22.—Electron micrograph of solids recovered from solution Q22E aged 57 days. A general view of the solids.

explain why the X-ray diffraction pattern showed only one tiny bayerite peak, representing a "*d*" spacing of 4.34 A, at this age for Q22E. Along with this peak there was the described broad peak which was already pronounced both for it and for Q23G by this time. These same broad high peaks persisted even at age 514 days for Q22D and at age 509 days for Q23D and Q23G, but there was no indication of the development of new peaks as in the case of Q22E.

TOTAL EFFECT

Quercetin definitely slows the precipitation of bayerite and nordstrandite. The result may be described as temporary stabilization of dissolved intermediate substances having some similar properties to those found after very short aging periods in supersaturated solutions containing only aluminum. Also, crystalline material having a solubility near or slightly less than microcrystalline trihydroxide is

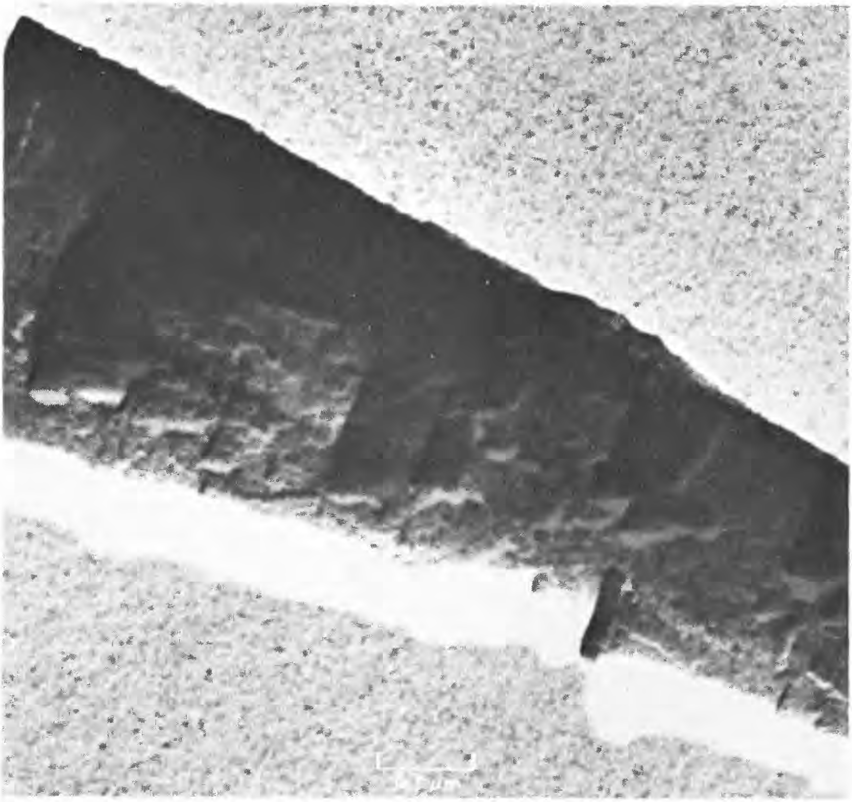


FIGURE 23.—Electron micrograph of solids recovered from solution Q22E aged 126 days.

formed, with an X-ray diffraction peak very near that of natural boehmite. The structural dimensions and possibly the composition of the material evidently depend on the specifications of the test solution. A review of the X-ray diffraction patterns indicates that there is little or no change in the location of the peak points on aging but that the intensities of the peaks increased dramatically with time. This would suggest that the intermediate structures did not convert to new structures with time but became better established.

EFFECTS OF ORGANIC SOLUTES ON ALUMINOSILICATE PRECIPITATION

The presence of aqueous silicic acid (silica) in solutions that are moderately supersaturated with respect to gibbsite or bayerite can cause substantial changes in the nature of the precipitated product and in the chain of chemical events leading to a state of equilibrium. The precipitated material described by Hem, Roberson, Lind, and Polzer

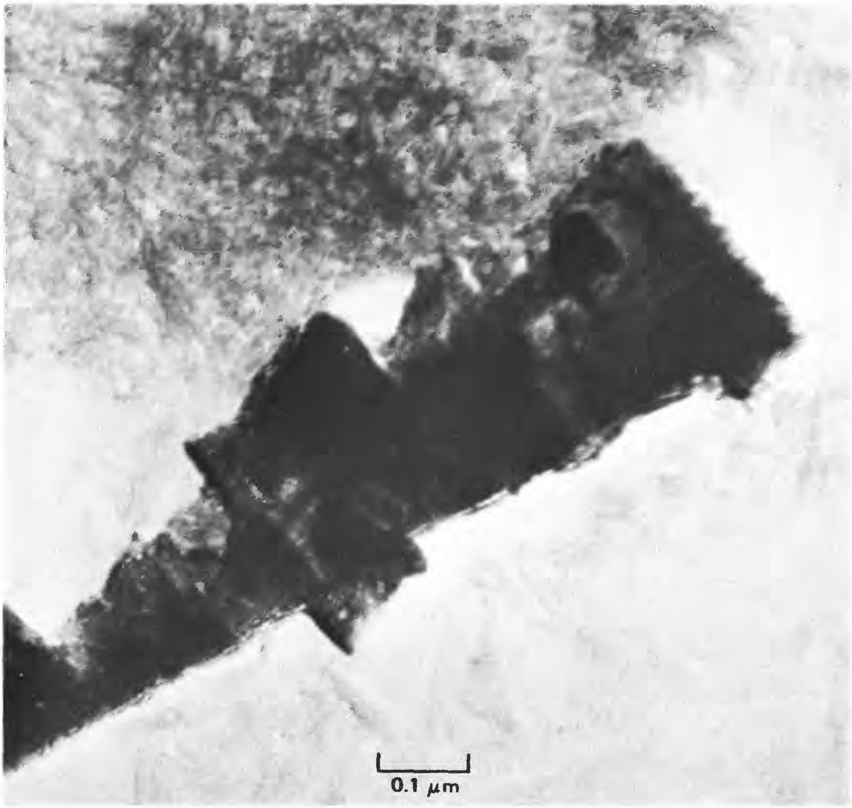


FIGURE 24.—Electron micrograph of solids recovered from solution Q22E aged 311 days. A bayerite crystal and associated mesh.

(1973) commonly was a mixture of amorphous aluminum hydroxide and a 1:1 aluminosilicate with the composition and solubility of halloysite. The optimum conditions for the precipitation of this synthetic halloysite appear from the data published by Hem, Roberson, Lind, and Polzer (1973) to include a substantial excess of silica over that of aluminum in solution and a pH near or a little above neutrality. All solutions are relatively dilute, although perhaps more concentrated than some weathering solutions in well-watered environments. The temperature was near 25°C in all solutions. At pH levels below 5.0 the precipitates were chemically similar but required a very long aging period before they stabilized (several years in some instances).

Research on clay-mineral synthesis has been extensive, and many reports on the results of this work have been cited in our earlier publications. One aspect rather briefly touched upon, however, is the possible influence of organic material on low temperature synthesis of

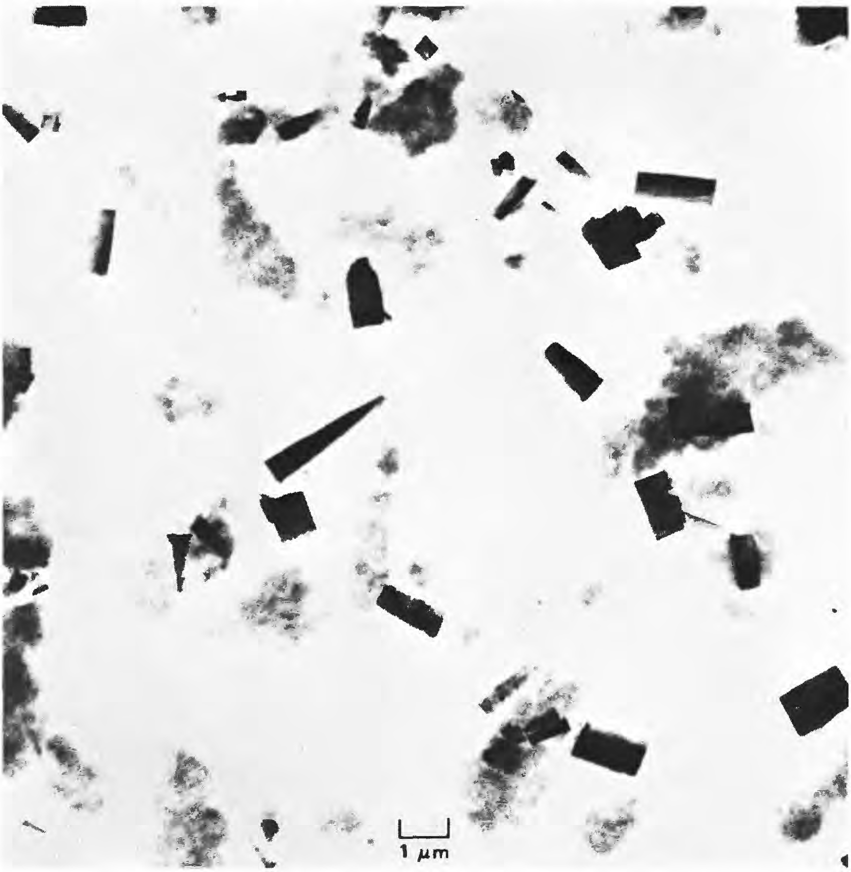
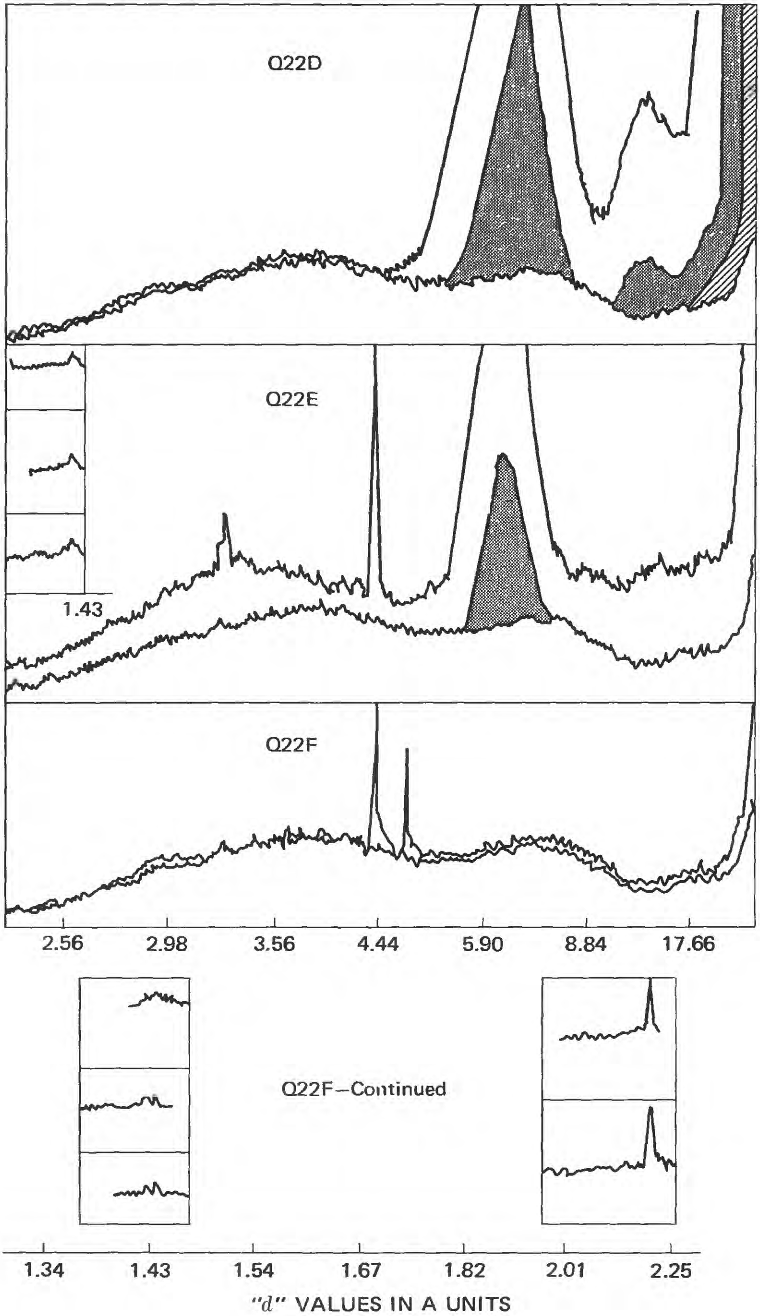


FIGURE 25.—Electron micrograph of solids recovered from solution Q22E aged 311 days. Possible nordstrandite crystals along with bayerite crystals.

clay minerals. Some investigators have prepared a gel, for example, by mixing organically complexed aluminum and silica species and have shown that a 1:1 clay mineral evolves during aging at a higher temperature (DeKimpe, 1967, 1969). Linares and Huertas (1971)

FIGURE 26.—X-ray diffraction patterns for solids recovered from solutions Q22D–F aged 311 days. Darkened areas are where the pattern went off scale and the peak was diminished by one-half. The scratched areas are where the peak was diminished by one-tenth. The lower line of each graph is the pattern given by the empty glass slide. The boxed-in areas are small peaks found far beyond the "*d*" spacings shown for the other test solutions. These small peaks have been repeated to verify their existence.


Q22D
Q22E
1.43
Q22F
2.56
2.98
3.56
4.44
5.90
8.84
17.66
Q22F—Continued
1.34
1.43
1.54
1.67
1.82
2.01
2.25
"*d*" VALUES IN A UNITS

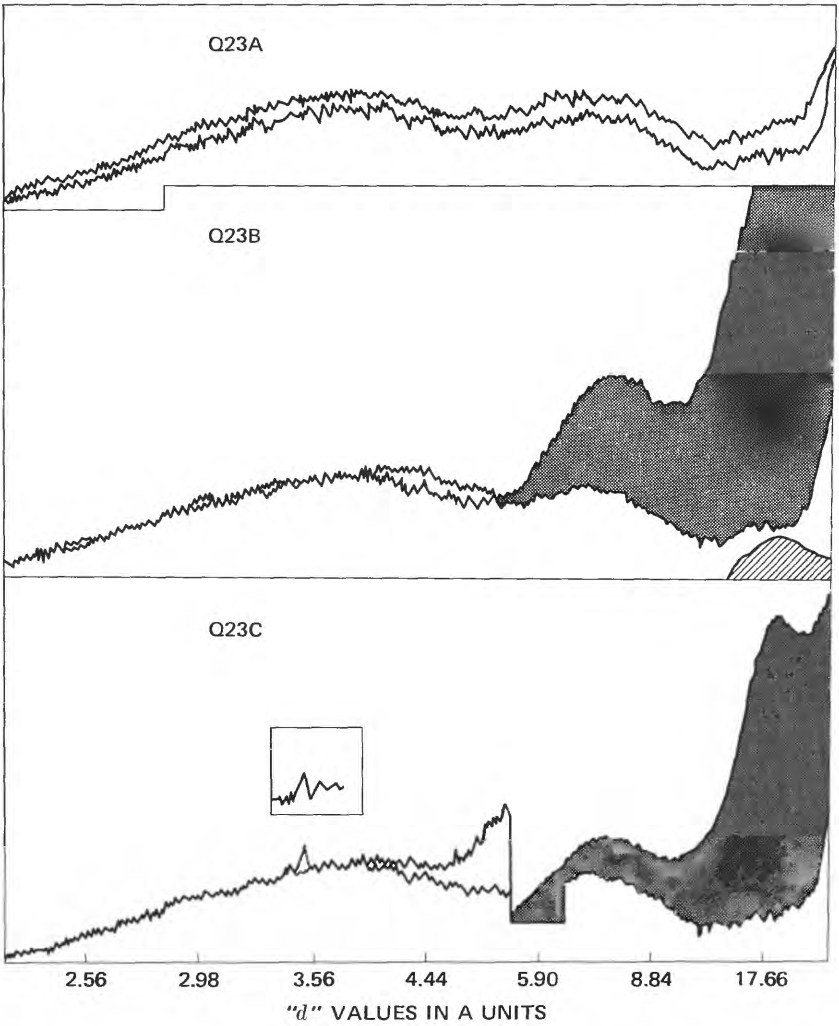


FIGURE 27.—X-ray diffraction patterns for solids recovered from solutions Q23A–C aged 310 days. Darkened areas are where the pattern went off scale and the peak was diminished by one-half. The scratched areas are where the peak was diminished by one-tenth. The lower line on each graph is the pattern given by the empty glass slide. The boxed-in area contains a peak that has been repeated to verify its position and shape.

reported a synthesis of kaolinite at 25°C using what they considered to be a fulvic acid–aluminum complex as one starting material.

The rationale for expecting that organically complexed starting material might expedite the formation of clay may perhaps be related to the structure of aqueous aluminum and silicon hydroxides. An

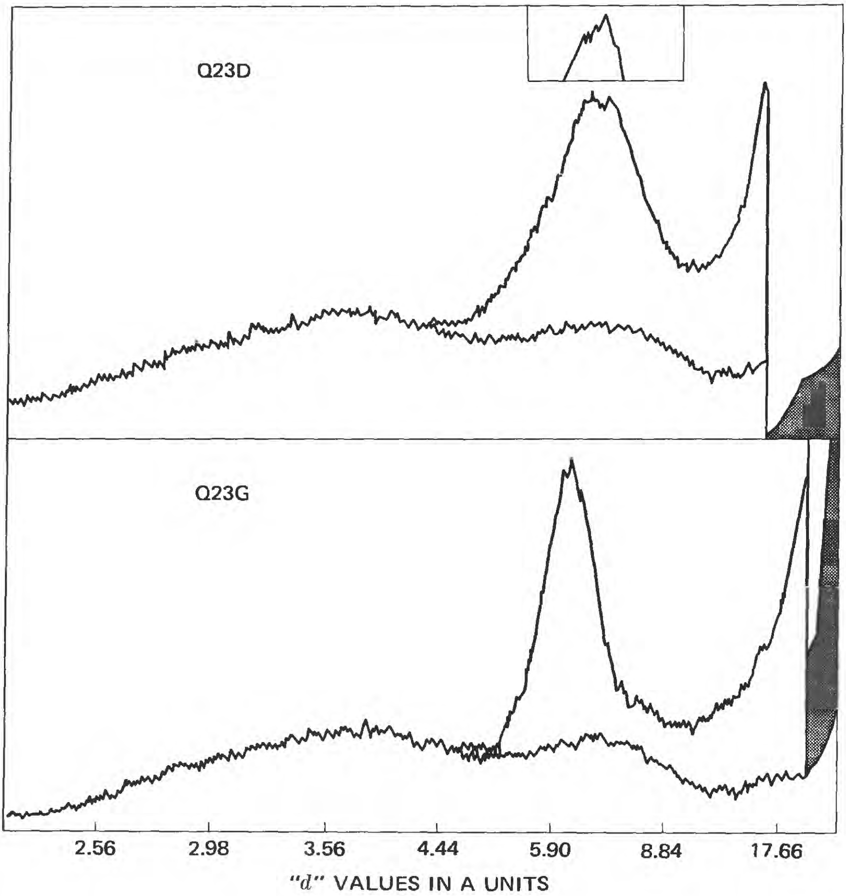


FIGURE 28.—X-ray diffraction patterns for solids recovered from solutions Q23D and Q23G aged 310 days. Darkened areas are where the pattern went off scale and the peak was diminished by one-half. The lower line on each graph is the pattern given by the empty glass slide. The boxed-in area contains a peak that has been repeated to verify its position and shape.

electrically neutral sheet polymer composed of aluminum ions in six-fold coordination with close-packed hydroxide ions constitutes the gibbsite structure, and a somewhat similar but more open sheet composed of silicon ions in fourfold coordination with oxygen constitutes the silica layer of a 1:1 clay. Although such a clay is sometimes described as having gibbsite layers alternating with silica layers, this is an oversimplification that obscures certain important structural factors. Possibly a noncrystalline material could be synthesized by adsorption of a layer of uncharged $Si(OH)_4$ tetrahedra on the surface of a sheet structure of $Al(OH)_3$, followed by

FIGURE 29.—Electron micrograph of solids recovered from solution Q22E aged 126 days.

polymerization and dehydration of the silica layer into an $(Si_2O_5{}^{2-})_n$ sheet. The initial formula for this material would be $Al(OH)_3 \cdot Si(OH)_4$, or $Al_2Si_2(OH)_{14}$. It could be converted to the composition of kaolinite or halloysite by dehydration:

$$Al_2Si_2(OH)_{14} = Al_2Si_2O_5(OH)_4 + 5H_2O.$$

The apparent simplicity of this process is deceiving, for actually each water molecule produced probably involves the transfer of a proton from one OH^- ion to another OH^-, leaving an O^{2-} and converting the second OH^- to a water molecule. To form the complete kaolinite structure, this water molecule would need to be removed from the reaction site. The final product contains an extensive network of Si-O-Al bonding, and each aluminum ion participates in two such bonds. The third unit of charge on each aluminum ion remains shared in a double hydroxide bridge with an adjacent aluminum ion. Because this kind of mechanism is so complicated, it is likely to be slow and difficult, especially if the gibbsite structure has developed extensively.

Most of the more successful kaolinite syntheses have resorted to high temperature and pressure to attain crystallinity (Hemley, 1959). Kittrick (1970) was able to crystallize clay minerals from aqueous solutions by providing previously formed clay minerals as nucleation surfaces. The work of Hem, Roberson, Lind, and Polzer (1973) does indicate that a small yield of crystalline material can be obtained at 25°C, along with a large amount of poorly organized 1:1 clay, during long aging.

A possible advantage in using organically complexed aluminum and (or) silica as starting material is that Al-O bonding may be present in the organic structure and could thus be present as the synthesis reaction begins. Then the crystallization of the clay could proceed, forming Al-O-Si bonds without the need for removing water molecules from their coordination positions in the lattice. Also, the organic material might inhibit the polymerization of aluminum hydroxide and thus provide a less established crystal structure at the start of the synthesis.

MODIFICATION OF THE PRECIPITATION OF ALUMINOSILICATES BY TRACES OF QUERCETIN

To further verify the organoaluminum interactions with clay minerals, comparison of reactions with and without organic matter under controlled laboratory conditions is necessary. Solutions that precipitated a metastable aluminosilicate in previous studies by Hem, Roberson, Lind, and Polzer (1973) were duplicated with the exception of the addition of quercetin as a representative model of organic material. Again the concentration of quercetin used was that to be found for organic matter in natural water. The ratios of aluminum to quercetin, 100:1, were such that aluminum-quercetin complexes themselves were, at most, only small fractions of the reacting species.

Three series of solutions containing 5×10^{-6} mole/l (0.9 mg/l organic carbon) were prepared. The first series was labeled Q19 and Q20, the second Q24, and the third Q25 and Q26. The method described by Hem, Roberson, Lind, and Polzer (1973), where silicic acid reagent was added directly to the basic solution II, was used. The quercetin was added in the amount mentioned to solution I and twice that amount to solution III. The initial and subsequent concentrations of aluminum and silica are listed in tables 9 and 10, with IAP_a (ion-activity product) defined by equation 8, table 3, and IAP_b by equation 9, table 3. The solids from these solutions were compared with well-identified minerals and with a soil sample of natural streambed sediment. The minerals are described as follows:

Halloysite 13, Eureka, Utah, (percent impurities: limonite 2, orthoclase 1–1.5, quartz trace, and alunite trace).[1]

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[1] Occurrence and Micro Examination of Reference Clay Mineral Species, M.S. Main, API project 49, Clay Mineral Standards 1950, Preliminary Report No. 5.

Kaolinite 9, Mesa Alta, N. Mex., (percent impurities: sericite 1–1.5, orthoclase 1.5, limonite 11.5, and leucoxene 1).[1]
Keokuk Geode Kaolinite, Keokuk, Iowa.[2]

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[1] Occurrence and Micro Examination of Reference Clay Mineral Species, M.S. Main, API project 49, Clay Mineral Standards 1950, Preliminary Report No. 5.

[2] A sample of this kaolinite was furnished by Professor W. D. Keller, University of Missouri, and has been described by Keller, Pickett, and Reesman (1966).

TABLE 9.—*Compositions of acidic aluminum-silica-quercetin solutions before and after aging*

Solution	Initial contents Al (mg/l)	Initial contents SiO_2 (mg/l)	Initial contents pH	Aged solutions days	Aged solutions Al (mg/l)	Aged solutions SiO_2 (mg/l)	Aged solutions pH	log IAP_a	Precipitate from solutions Si:Al (mole/mole)
Q19D	12.7	57.8	4.58	332	8.94	54.4	4.14	10.98	0.406
Q19E	12.7	59.4	4.63	332	7.94	55.4	4.18	11.10	.377
Q20A	12.7	38.2	4.63	155	10.8	36.4	4.20	11.12	.425
Q20B	12.7	39.7	4.68	155	9.47	38.3	4.25	11.34	.190
Q20B	12.7	39.7	4.68	332	5.52	37.6	4.17	10.42	.131
Q20C	12.7	41.3	4.76	155	8.08	39.8	4.34	11.76	.146
Q19G	12.7	64.4	4.86	36	7.6	63.6	4.44	12.66	.070
Q20D	12.7	43.9	5.37	155	4.78	40.1	4.67	13.08	.215
Q20D	12.7	43.9	5.37	332	2.91	35.5	4.62	12.32	.385
Q24A	12.2	44.8	5.51	136	.01	29.7	5.44	10.56	.556
Q24A	12.2	44.8	5.51	251	.00	29.4	5.44	10.56	.567

TABLE 10.—*Composition of neutral and basic*

Solution	Initial contents Al (mg/l)	Initial contents SiO_2 (mg/l)	Initial contents pH	Aged solutions Al (mg/l	Aged solutions SiO_2 (mg/l)	Aged solutions pH	log IAP_b	Precipitate Si:Al (moles/mole)	Al (mg/l)	SiO_2 (mg/1)	pH
				Age 155 days					**Age**		
Q20E	12.7	45.2	6.47	0.01	26.6	6.53	−32.71	0.658	----	----	----
Q20F	12.7	46.2	7.91	.09	26.0	7.34	−32.45	.719	0.01	25.4	7.44
Q20G	12.7	46.8	8.62	.19	25.4	7.54	−32.21	.768	----	----	----
Q20H	12.7	48.3	8.96	.54	23.7	7.55	−31.39	.908	.04	23.7	7.87
				Age 136 days					**Age**		
Q24B	12.2	46.4	6.76	0.02	27.3	6.75	−32.53	0.704	0.00	27.4	6.80
Q24C	12.2	47.0	7.58	.04	26.9	7.05	−32.55	.742	.01	26.8	7.00
Q24D	12.2	47.6	7.95	.05	26.5	7.29	−32.83	.780	.03	26.2	7.16
Q24E	12.2	48.2	8.36	.11	26.4	7.44	−32.47	.810	.04	24.8	7.31
Q24F	12.2	48.8	8.64	.26	24.4	7.55	−32.01	.918	.08	23.7	7.36
Q24G	12.2	49.2	8.77	.46	23.3	7.64	−31.73	.995	.25	22.1	7.83
Q24H	12.2	51.4	9.33	3.06	21.4	8.92	−32.65	1.47	1.08	16.1	7.95
				Age 114 days					**Age**		
Q25A	12.2	49.1	8.79	1.36	25.8	7.79	−30.92	0.965	0.37	22.9	7.53
Q25B	12.2	48.2	8.36	.84	27.4	7.74	−31.18	.822	.49	25.0	7.46
Q25C	12.2	49.2	8.89	1.00	25.4	7.95	−31.50	.954	.21	23.7	7.54
Q25D	12.2	48.2	8.81	.48	26.2	8.06	−32.44	.866	.10	24.4	7.40
				Age 115 days							
Q26A	12.2	49.6	8.95	2.16	26.2	8.02	−31.04	1.04	.66	21.7	7.54
Q26B	12.2	48.8	8.68	1.49	25.8	7.94	−31.22	.964	.35	22.5	7.49
Q26C	12.2	49.4	9.04	.81	25.0	7.72	−31.34	.962	.14	23.7	7.38
Q26D	12.2	48.6	8.91	.55	26.0	7.73	−31.66	.871	.14	24.2	7.38

The soil sample was the <200-mesh fraction of bottom sediment taken from Colma Creek at Colma, San Mateo County, Calif., by C. E. Roberson on October 2, 1972.

CRYSTALLINITY OF PRECIPITATES

Electron micrographs of the two standard kaolinites and one of the halloysites are shown in figures 30–32. The characteristic thin layers and sharp straight edges and angles of kaolinite crystals in both large and small units are shown in figures 30 and 31. Surface texture on some of the crystals is the effect of shadowing material used in preparing the sample. The electron micrograph of halloysite (fig. 32) shows some of the flat sheets similar in appearance to kaolinite and rolled up material more typical of halloysite. The thin sheets apparently roll up and sometimes the rolls appear to have been flattened after forming.

Analytical data in table 9 indicate smaller losses of aluminum and silica during aging but a somewhat greater decline in pH than do comparable acidic solutions without quercetin studied by Hem, Roberson, Lind, and Polzer (1973, p. 11). Also, the silica to aluminum

aluminum-silica-quercetin solutions

Aged solutions—Continued											
log IAP_b	Precipitate Si:Al (moles/mole)	Al (mg/l)	SiO_2 (mg/l)	pH	log IAP_b	Precipitate Si:Al (moles/mole)	Al (mg/l)	SiO_2 (mg/l)	pH	log IAP_b	Precipitate Si:Al (moles/mole)
332 days											
----	----	----	----	----	----	----	----	----	----	----	----
−34.57	0.736	----	----	----	----	----	----	----	----	----	----
----	----	----	----	----	----	----	----	----	----	----	----
−34.29	.873	----	----	----	----	----	----	----	----	----	----
251 days				**Age 358 days**					**Age 481 days**		
−33.23	0.699	0.01	26.1	6.28	−32.24	0.748	0.02	26.4	6.77	−32.51	0.737
−33.65	.744	.02	25.9	6.76	−32.60	.778	.05	26.2	7.07	−32.33	.769
−33.03	.790	.05	25.9	7.31	−32.91	.802	.05	25.3	7.27	−32.76	.824
−33.13	.864	.07	24.5	7.39	−32.82	.877	.10	25.0	7.48	−32.58	.861
−32.68	.930	.07	22.9	7.48	−33.06	.959	.14	24.1	7.55	−32.46	.920
−32.68	1.02	.24	21.8	7.63	−32.33	1.03	.17	22.4	7.66	−32.58	1.00
−31.90	1.40	.57	16.2	7.77	−32.12	1.36	.26	16.9	7.55	−32.23	1.30
230 days				**Age 328 days**					**Age 451 days**		
−31.72	0.994	0.37	22.9	7.49	−31.63	0.994	0.16	23.3	7.66	−32.60	0.962
−31.26	.900	.26	24.3	7.48	−31.87	.899	.12	24.7	7.65	−32.78	.873
−32.19	.955	.21	23.3	7.48	−32.09	.970	.09	23.9	7.66	−33.07	.938
−32.50	.883	.12	24.4	7.49	−32.56	.885	.09	25.2	7.65	−33.01	.875
−31.28	1.09	.42	22.9	7.66	−31.86	1.02	.15	21.9	7.4	−32.2	1.03
−31.70	.997	.37	22.2	7.55	−31.78	1.01	.12	23.0	7.4	−32.3	.959
−32.20	.957	.13	23.7	7.54	−32.61	.956	.08	24.6	7.4	−32.6	.919
−32.22	.909	.13	24.0	7.51	−32.54	.915	.08	25.3	7.4	−32.6	.863

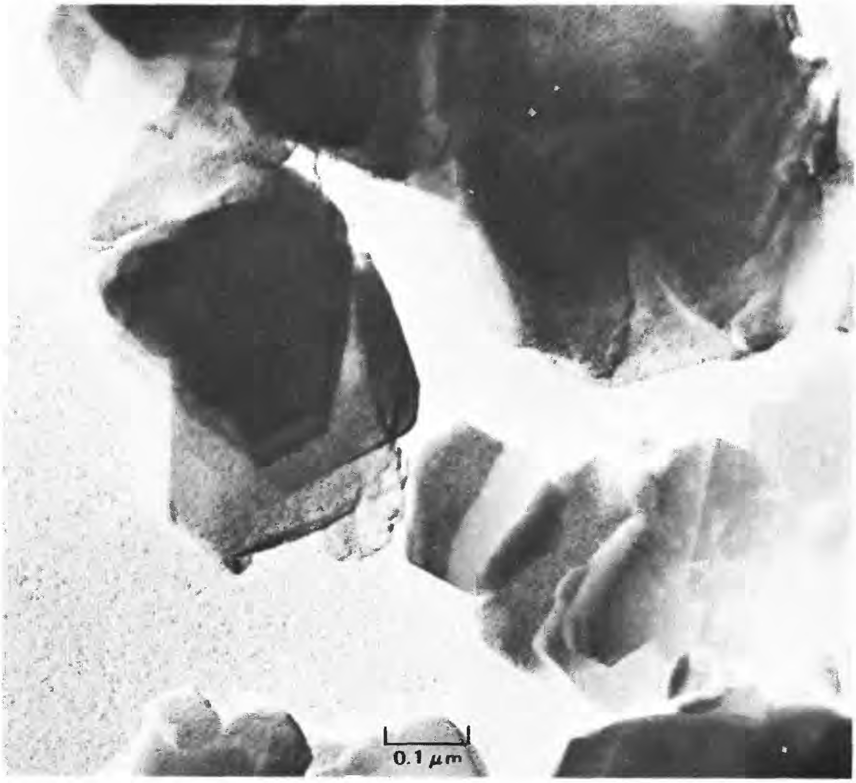

FIGURE 30.—Electron micrograph of kaolinite from Mesa Alta, N. Mex.

mole ratio of the precipitates indicated in table 9 is lower (further from the desired 1:1 ratio) than was found in solutions without quercetin. Possibly these differences could be attributed to the formation of a smaller amount of better ordered material when the organic ligand is present. However, the net solubility as indicated by the ion activity products does not appear to be greatly different, perhaps because the major solubility control in both sets of experiments is the predominating poorly crystallized material.

Neutral and basic solutions that had precipitated aluminosilicate material in the presence of low concentrations of quercetin gave evidence of much better crystallized material than had been obtained by Hem, Roberson, Lind, and Polzer (1973) without organic matter being present. Data in table 10 indicate about the same amount of aluminum and silica precipitation, though, and a similar rather close approach to a 1:1 mole ratio of silica to aluminum. There seems, however, to be a tendency for a more nearly uniform and somewhat lower final pH when quercetin was present. This again may indicate

FIGURE 31.—Electron micrograph of Keokuk geode kaolinite (Keller and others, 1966).

that the product formed is more stable when the organic ligand is available.

As noted in table 10, the ion activity products for Q20E–H were similar to other values for solutions that contained solids identified as synthetic halloysite. Their pH was between 6.53 and 7.55 after 155 days of aging, and they contained numerous small but very sharply defined kaolinitic crystals. Typical electron micrographs are shown in figures 33 and 34. Not enough of the well-crystallized material could be isolated to obtain an X-ray diffraction pattern. However, after aging 332 days the log ion activity products for Q20F and H were more negative than before (approaching that of kaolinite), but no further determinations could be made because the solutions had all been used up.

To verify the results obtained in the Q20 series, another set of experimental solutions was prepared, the Q24 series. All these solutions had pH and solute concentrations in the range covered by the Q20 samples in which the best crystallinity was observed. After aging 251 days, some layered material could be seen, but well-defined

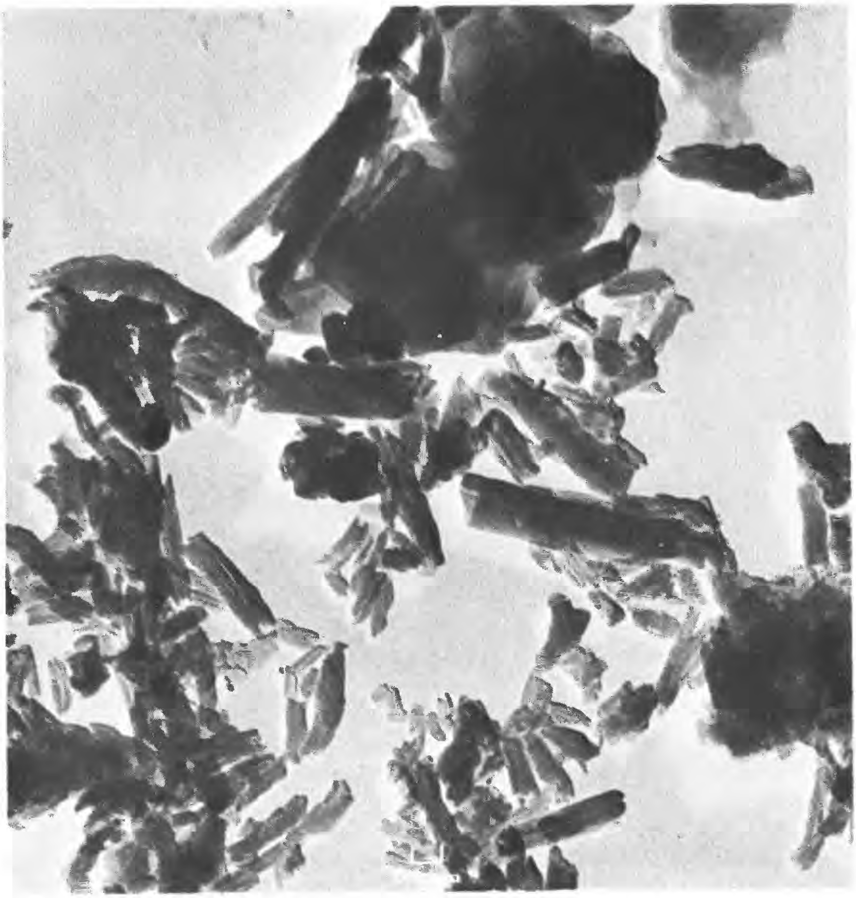

FIGURE 32.—Electron micrograph of halloysite from Eureka, Utah.

crystallinity was lacking (fig. 35). After aging 358 days, rolled structures similar to halloysite (fig. 36) and somewhat more crystalline layered material (fig. 37) were observed.

Finally, after aging 481 days well-crystallized kaolinitic material was found in the precipitates of all solutions in the Q24 series. Four typical electron micrographs are given in figures 38–40.

The X-ray diffractograms for the precipitates still showed no well-defined peaks, presumably because poorly crystallized material still constituted the bulk of the solid. However, there was a general increase in signal above that given by an empty slide covering the "*d*" spacings for the more prominent kaolinite and halloysite peaks. This increase in signal became more pronounced with aging. At age 481 days sample Q24F (dried at 250°C) was scanned several times at

FIGURE 33.—Electron micrograph of solids recovered from solution Q20G aged 155 days (from Hem and Lind, 1974). Copyright 1974 by the American Association for the Advancement of Science.

settings giving an amplified and somewhat noisy signal. Halloysite and metahalloysite have strong peaks near 7.4, 4.4, and 3.6 A. In five scans the signal consistently was high around 7.4 A. In four scans made covering 3.6 A, three had a high signal at this spacing.

The product in the Q24 series is comparable in all respects with that synthesized in the Q20 series. The length of time required to reach crystallinity appears to have been different, but the organic intermediate does seem to offer a feasible path to kaolinite synthesis at 25°C.

SOLUBILITY OF PRECIPITATE

As noted in previous work, the rate at which the basic solution is

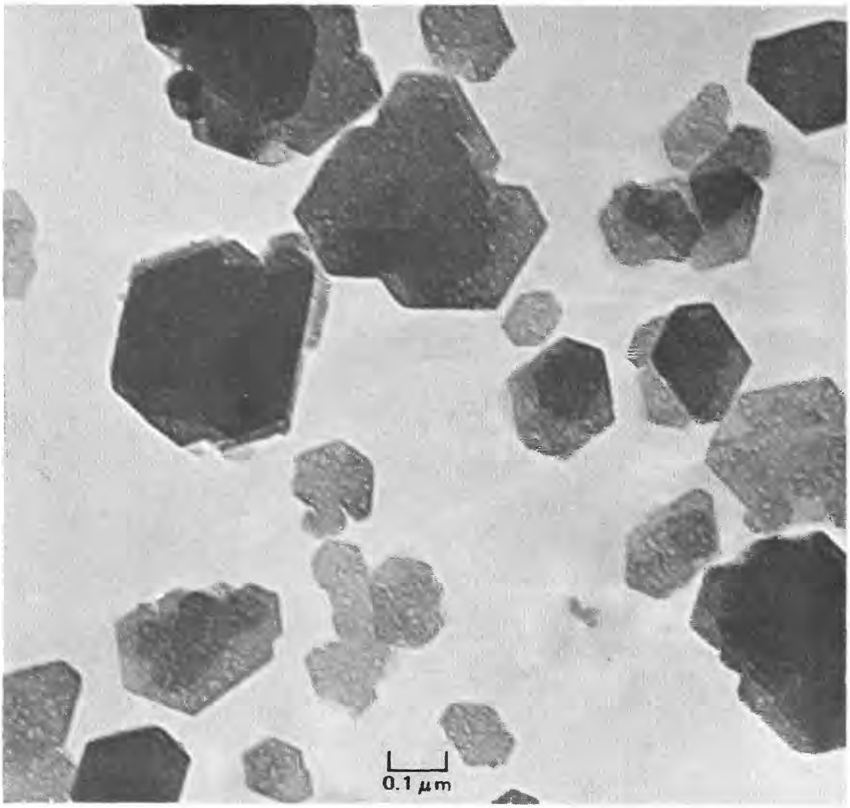

FIGURE 34.—Electron micrograph of solids recovered from solution Q20G aged 155 days (another view) (from Hem and Lind, 1974). Copyright 1974 by the American Association for the Advancement of Science.

added to the other two has an effect on the amounts of unstable aluminum hydroxide species that are formed, at least in those solutions where the pH remains below neutrality. To test the possible importance of this factor, solutions Q25A–D and Q26A–D, having specifications similar to Q20G, were prepared in several different ways, as described in table 11. The stock solutions I, II, and III were prepared in the same manner as described for the earlier aluminosilicate series. These solutions were added in such ratios as to make mixed solutions of two concentrations of aluminum and silica for each mode of addition. (The contents of the mixed solutions initially and after aging are listed in table 10.) In the Q25 series the mixtures of aluminum perchlorate and quercetin were allowed to stand for 3 days, before adding silica and sodium hydroxide, to test the idea that time might promote the formation of the aluminum-quercetin complex. In the Q26 series this preliminary aging step was omitted. Two of the solutions in

FIGURE 35.—Electron micrograph of solids recovered from solution Q24D aged 251 days.

TABLE 11.—*Preparation of solutions Q25A–D and Q26A–D*

Solution	Initial pH	Age of solutions I and III at time of addition of solution II (days)	Time interval over which solution II (basic) was added (minutes)
Q25A	8.79	3	4
Q25B	8.36	3	4
Q25C	8.98	3	60
Q25D	8.81	3	60
Q26A	8.95	0	4
Q26B	8.68	0	4
Q26C	9.04	0	60
Q26D	8.91	0	60

each group were brought to their starting pH by rapid mixing of the stock solutions and two by very slow addition of the basic solution with stirring.

During the preparation of these solutions, the pH passed through the

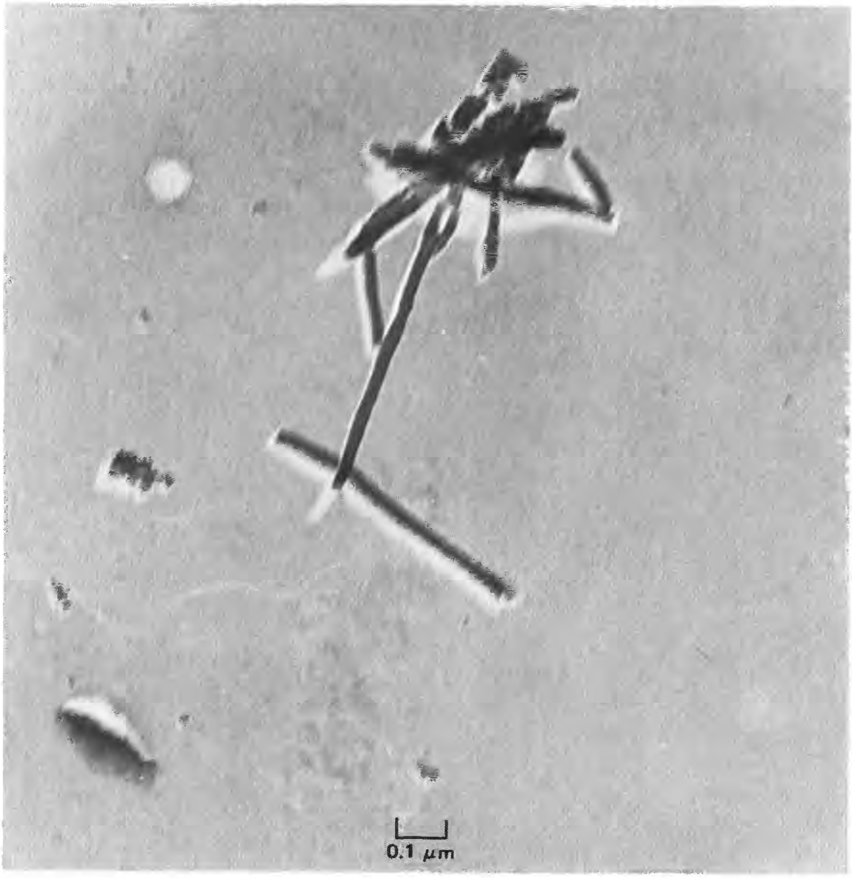

FIGURE 36.—Electron micrograph of solids recovered from solution Q24C aged 358 days.

minimum solubility region for synthetic halloysite, and it seems reasonable that when the pH was in this range (near 6.0) for a relatively long time the precipitation would be more nearly complete and the structure better organized than if the pH were more rapidly increased to its final level. Thus, the solutions with short mixing times would be expected to be further from equilibrium at the start of aging than the ones with long mixing times. That this expectation is realized is indicated by the data in table 10. The ion activity products for short mixing-time solutions are less negative than those for corresponding long mixing-time solutions in every instance. Even after 328 days of aging this difference is discernible. The effect of the additional aging time after preparing solutions I and III before adding solution II is not discernible in any of the later analyses of the solutions.

Crystallization in the Q25 and Q26 solutions appeared to follow the

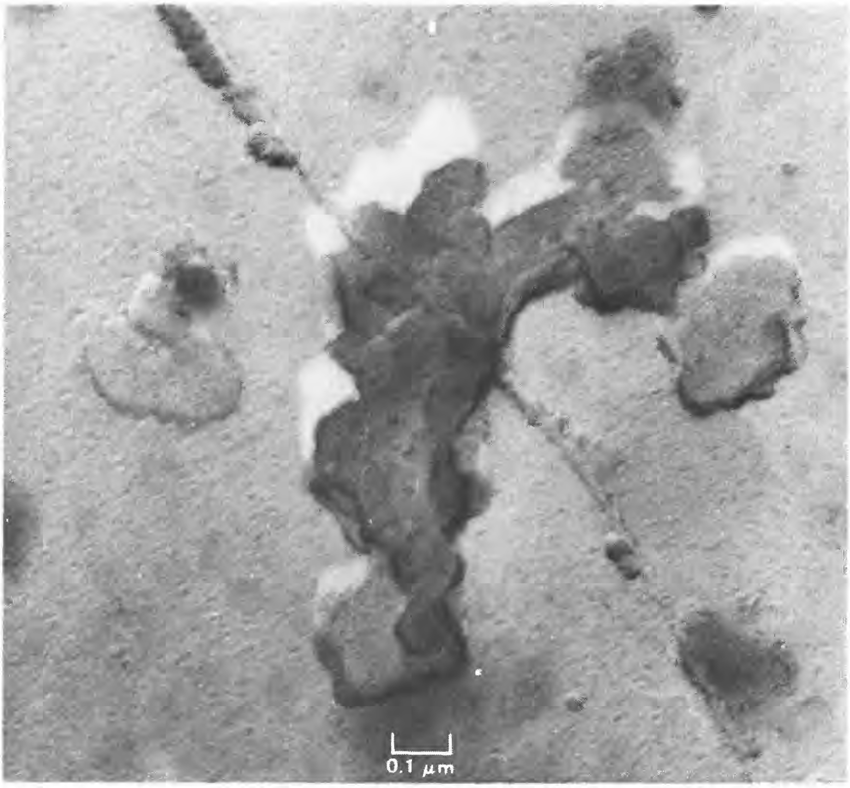

FIGURE 37.—Electron micrograph of solids recovered from solution Q24G aged 358 days.

same path as in Q24 solutions. The final observations of these showed small amounts of well-crystallized kaolinite and halloysite were present in the mass of poorly organized material (fig. 41).

STREAM SEDIMENT

The sample of sediment from Colma Creek contained considerable amounts of quartz and apparently some halloysite, according to its X-ray diffraction pattern. It exhibited the main 3.34-A peak and the 10.1-A peak of hydrated halloysite (endellite), along with suggestions of the 4.42-A and 2.56-A peaks. An electron micrograph of some of the particles is shown in figure 42.

The natural material is of interest because it shows that stream sediments may contain significant amounts of aluminosilicate minerals similar in appearance and probably in other properties to the synthesized halloysite. The chemical behavior of sediments will, therefore, have some traits in common with synthetic halloysite.

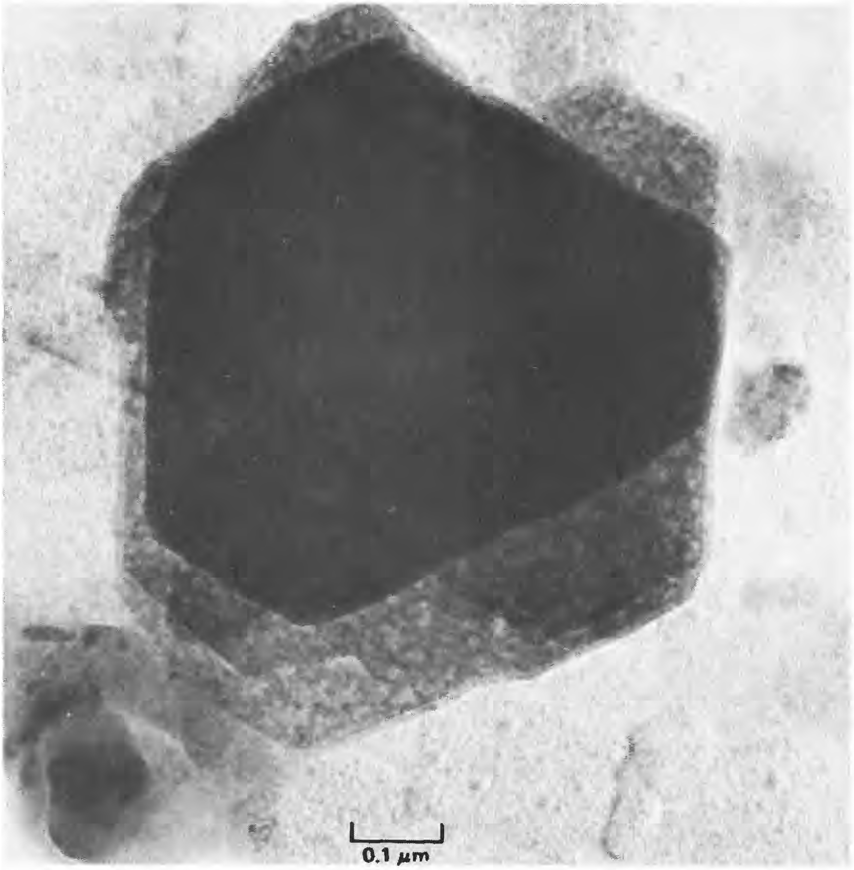

FIGURE 38.—Electron micrograph of solids recovered from solution Q24C aged 481 days.

SUMMARY

Small amounts of quercetin appear to expedite the processes of clay-mineral synthesis at neutral or mildly alkaline pH. At lower pH (<5.0) the quercetin seems to inhibit the process. Well-crystallized kaolinite was obtained in several solutions in one experimental series, and later efforts to repeat these results were successful, although they required a somewhat longer aging time. The weight of evidence, including solubility, stoichiometry, and electron micrography, all supports the formation of a kaolinitic clay mineral. The yield of well-crystallized material obviously is small, but probably the yield could be improved by further refinement of the technique.

Considering these facts and the close interrelationships of organic matter with aluminum and clays in natural systems and of the evidence of changes of composition and structure of minerals by

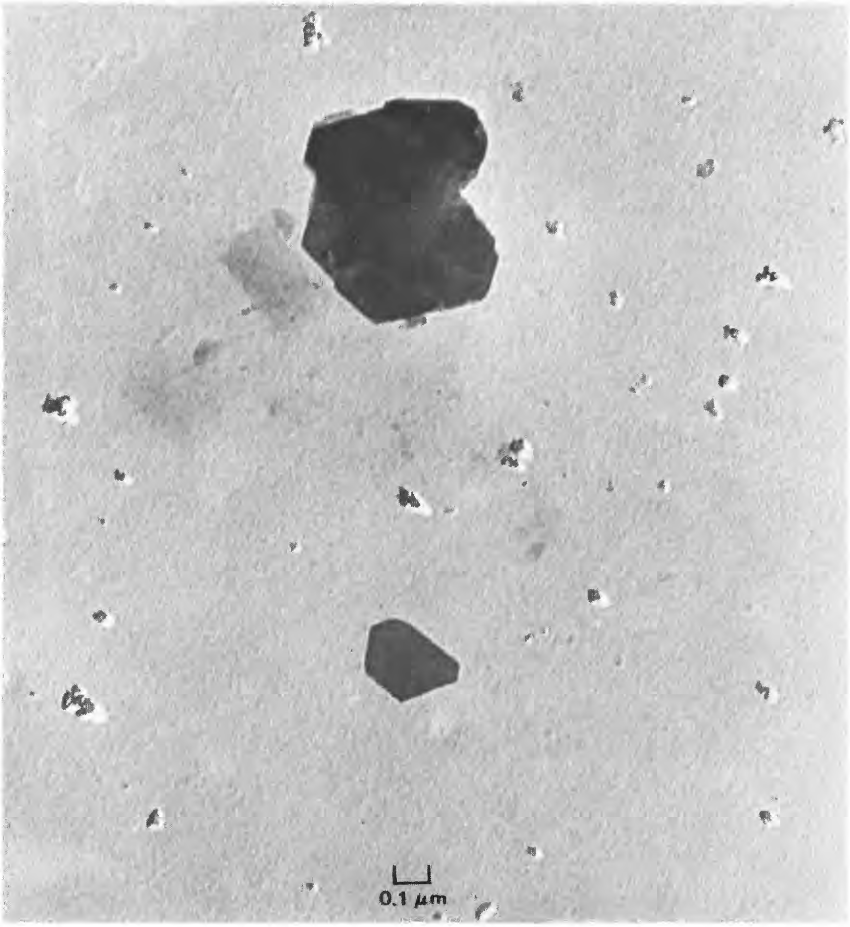

FIGURE 39.—Electron micrograph of solids recovered from solution Q24E aged 481 days.

organic matter, it may be concluded that there is no doubt that water-soluble organic matter can be a vital factor in the ultimate composition and structure of clay minerals in contact with water.

IMPLICATIONS OF ORGANIC COMPLEXING IN ALUMINUM GEOCHEMISTRY

Some indication of the difficulties involved in evaluating natural aluminum solubility controls can be obtained from calculations and graphs given earlier in this report. Certain of the conditions that must be specified for a calculation would normally be known or measurable. These include the total ionic strength of the solution, its content of complexing ligands and other dissolved species of interest, and the temperature and pressure. Existence of specific solids and their purity,

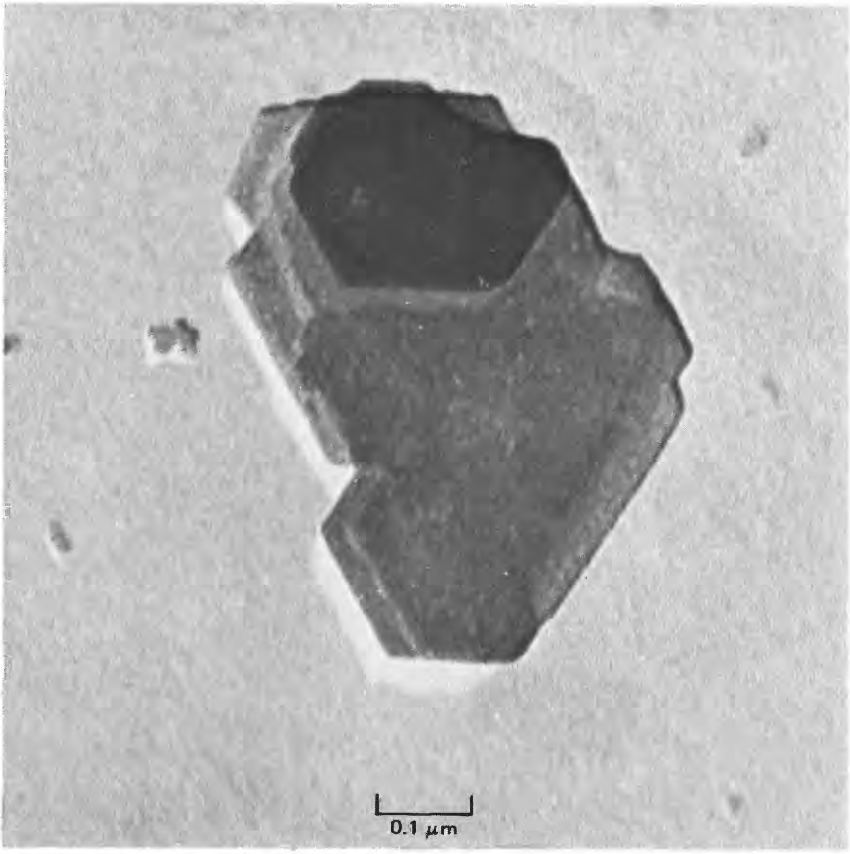

FIGURE 40.—Electron micrograph of solids recovered from solution Q24G aged 481 days (from Hem and Lind, 1974). Copyright 1974 by the American Association for the Advancement of Science.

or stability, is more difficult to ascertain, and the assumption of equilibrium, implying a ready reversibility of the governing reactions, is likely to be unreliable. Even if all the uncertainty were reduced to a question of the stability or crystallinity of the controlling 1:1 clays, it is apparent from figure 1 that the aluminum concentration at equilibrium might have a range of more than two powers of 10.

Considerations of reversibility and form of solid tend to be interrelated. For example, the studies of Hem, Roberson, Lind, and Polzer (1973, p. 15) showed a reversible solubility for their freshly precipitated synthetic halloysite. Better crystallized material has been found to form so slowly in the pH range studied here that a directly reversible solubility for crystalline kaolinite, the least soluble solid considered in figure 1, seems very improbable under these conditions. A more logical mechanism would probably view this form

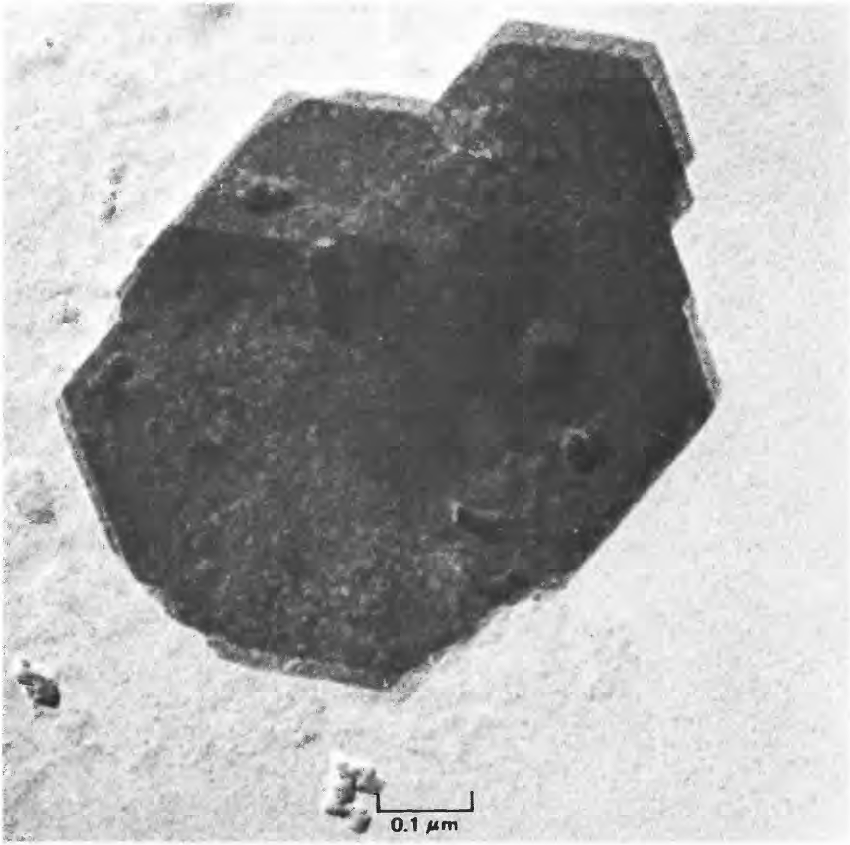

FIGURE 41.—Electron micrograph of solids recovered from solution Q26B aged 451 days.

of kaolinite to be an equilibrium species only at conditions other than 25°C and 1 atmosphere pressure and in solutions differing from the general composition we have studied.

The relationships in Al-Si-H_3O systems might be represented schematically as

$$\begin{tikzcd}
\text{Halloysite} \arrow[d, "-H_2O"'] & + & H^+ \arrow[r, shift left] & Al^{3+} \arrow[l, shift left] \arrow[d, shift left, "+OH^-"'] & +\ SiO_{2(aq)} \arrow[d, shift left] \\
\text{Kaolinite} & + & H^+ \arrow[ur] & \text{Gibbsite or Bayerite} \arrow[u, shift left] & SiO_{2(c)} \arrow[u, shift left]
\end{tikzcd}$$

Equilibrium can be established where reversibility is indicated. Formation of aluminum hydroxide in preference to clays, or alteration

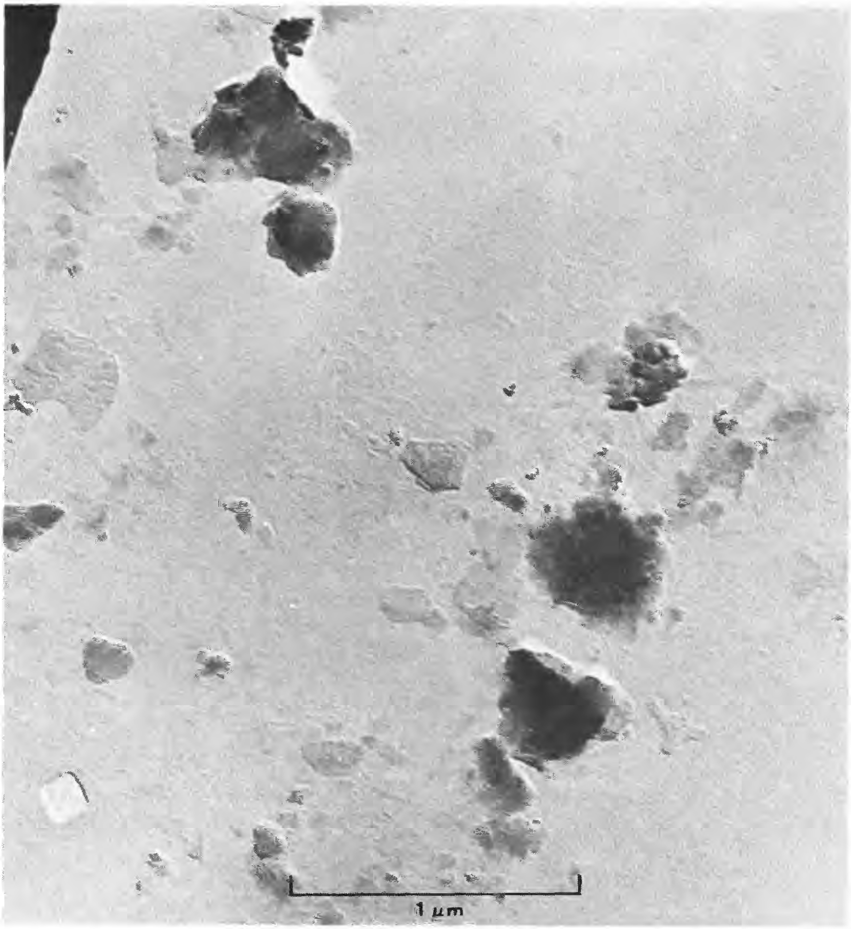

FIGURE 42.—Electron micrograph of fine-grained material separated from Colma Creek bed sediment.

of the latter to aluminum hydroxide, is indicated by this relationship to depend on dissolved activity of silica and hydrogen ions.

Natural weathering regimes capable of direct precipitation of either clay minerals or aluminum hydroxide would require supersaturation with respect to the given mineral in terms of dissolved aluminum and silica, and this probably most commonly happens only very near the mineral surface from which the aluminum and aqueous silica have been derived. Complexing of aluminum or the action of a low pH water can increase aluminum concentrations, but normally one would expect an excess of aqueous silica over aluminum in such systems because silicon normally is present in larger amounts than aluminum in the source materials.

Weathering solutions in which a low concentration of silica is maintained, as might occur in a terrane receiving large amounts of rainfall, could alter clays, previously formed at the surface of weathered primary rock minerals or transported to the area in some way, to aluminum hydroxide. The literature contains many papers suggesting this type of origin for bauxite deposits. The pH in such a system is likely to be in a range favoring gibbsite precipitation, as dilute runoff waters in humid regions commonly have pH's somewhat below neutrality. The critical level for silica concentration probably is not as low as some authors imply from consideration of the stability of kaolinite. In our experiments the less well crystallized precursor, synthetic halloysite, superseded the crystallization of gibbsite only when aqueous silica concentrations exceeded about 9 mg/l as SiO_2. It would seem, therefore, that bauxite might be produced from clays even where the dissolved silica in the associated solutions sometimes reached this level.

The effect of organic complexing in most weathering environments probably would be to increase aluminum solubility and possibly to decrease the availability of reactive species. Such effects would tend to promote removal of aluminum in the effluent solutions and prevent accumulation of aluminum enriched solids. Also, the organic material might interfere in the precipitation of aluminum hydroxide.

For the above reasons, one probably should not expect to find gibbsite accumulations in environments that were rich in accumulated organic debris, such as lake bottom deposits, swamps, or peat bogs. In humid tropical environments much organic matter may be produced, but it tends to be decomposed rapidly, rather than accumulating in the soil.

ANOMALOUS ALUMINUM CONCENTRATIONS IN NATURAL WATER

In the absence of complexing effects, the solubility of aluminum in a dilute river or ground water would normally be in the vicinity of 10^{-6} molar (fig. 17) near pH 7. This is equivalent to about 27 μg/l and is near the limit of detection for the usual methods of determination used in water analysis laboratories. Lower concentrations could be expected for runoff waters that have not reached equilibrium with available solid sources of aluminum, such as the poorly organized clay minerals that commonly occur in soils and streambed sediments. Higher concentrations from 100 to 1,000 μg/l occasionally appear in reports of water analyses published in the literature. Most of these represent water with low pH, but some are near neutral and have a yellow or brown color. It is of interest to examine a few of the analyses to see if they can be readily explained

Before doing this it should be noted that routinely collected and analyzed water samples may not furnish reliable data on minor constituents or on solution parameters that may be unstable. Reported aluminum values may include particulate material that was not separated from solution, and the pH reported may represent a laboratory determination that may not indicate the pH in the water at the time of sampling.

Ground water that has a low pH can be expected to have a much higher concentration of aluminum than the 10^{-6} molar mentioned above. Certain types of thermal springs, analyses for which are cited by White, Hem, and Waring (1963, p. 44–47), show these properties. Generally the aluminum contents of these waters are below saturation with respect to aluminum hydroxide or silicate minerals. There may be other aluminum minerals, however, that are less soluble than these; in the low pH, high sulfate environment, for example, alunite may be the least soluble species (Roberson and Hem, 1969). Water with a low pH may also occur in mine workings as a result of the large scale imposition of an oxidizing regime on fresh sulfide mineral surfaces. In such environments an equilibrium with kaolinite may be reached, if this mineral is readily available. Hem, Roberson, Lind, and Polzer (1973, p. 38–39) were able to demonstrate a near approach to equilibrium with kaolinite in water from flooded coal mines in eastern Pennsylvania.

Water from acid springs, drainage from mines, and various kinds of industrial waste effluent may impart local conditions of low pH and high aluminum concentration to surface streams. Upon mixing with the main flow of water, supersaturation with respect to synthetic halloysite or a similar clay mineral is very probable. However, persistence of equilibrium conditions after precipitation of the solid had taken place would be unlikely because of the influence of dilution and the many other effects that might occur in such an open system.

A system in which greater-than-expected equilibrium concentrations of aluminum might appear to be present would be one having organic material capable of complexing aluminum in solution and a supply of aluminum to be complexed. Perhaps more commonly an aluminum complex is already present in living herbaceous material and becomes available for solution after death or destruction of the plant. One could, therefore, postulate the most likely places and times for finding high aluminum content in runoff. For example, favorable conditions might include low soil pH, abundant vegetation, and a large supply of runoff occurring at a time when fresh organic debris was abundant, as during a rainy period shortly after the annual autumnal leaf fall in a deciduous forest.

Some indication of the amount of organic material in solution in natural water can be gained from the color number determined as a part of the routine chemical analysis. The number is only an index of the color intensity and is far from being a quantitative measurement of organic material, but a highly colored water generally may be considered to represent one that has a relatively large content of organic material. Runoff from swamps and water in lakes and streams of forested regions, especially where topography is relatively flat and streams flow sluggishly, and in regions at high latitudes where tundra constitutes the vegetation may be highly colored.

EFFECT OF FILTRATION

The concentration of aluminum reported may represent not only that part which is in true solution but also colloidal and particulate matter. Many published analyses represent water samples that were not filtered before analysis, although it has been usual practice in Geological Survey laboratories and in other laboratories which are geochemically oriented to perform analyses only on water free from visible turbidity. Clarification commonly was by settling during storage of samples prior to analysis. Some colloidal particles might remain in an apparently clear supernatant, however. The filter pore size necessary for a filtrate to represent a true solution is still under question (V. C. Kennedy and B. F. Jones, written commun., 1971). One can conclude from existing data that a 0.1-μm filter can remove from 0 to 100 percent of the aluminum in a water sample that has passed a 0.45-μm filter.

A classification of material according to particle size will give an idea of the type of material removed by filtration and the composition of the filtrate. Lammers (1968), in his study of fractionation of suspended and colloidal substances in natural water, classified particles smaller than 0.01μm as dissolved, those from 0.01μm to 200μm as insoluble suspended and colloidal particles, and those larger than 200μm as materials that would normally tend to settle out rapidly unless they were free swimming or buoyant organic particles or unless the water was very turbulent.

The removal of aluminum from solution by a 0.1- and 0.45-μm filter was somewhat inadvertently tested on the quercetin solutions. After about 2 months of aging of these solutions, the total aluminum was measured in filtrates that had passed a 0.45-μm filter. (The 0.45-μm filter is the pore size most widely used for filtration prior to a water analysis.) All the other aliquots representing other aging times were filtered through 0.10-μm filters. Only one of the aliquots seemed to contain a significant amount of particulate material between the 0.10 and 0.45-μm diameters.

Kennedy and Jones (written commun., 1971) found that a part of the fine particulates (<0.1–1.5-μm grain size) in the stream samples they analyzed was composed of organic matter containing trace metals. Thus, the finest particles in a river water could be in part organic, and some of the aluminum reported in excess of that attributable to inorganic ions and their complexes could be bound to these organic particles besides being in the form of dissolved organic complexes.

EXAMINATION OF ANALYTICAL DATA

It is recognized that natural waters are not necessarily in a state of chemical equilibrium. However, it would seem logical that metastable solids of the types first observed in aging of laboratory solutions should be the first to appear in natural waters. These species probably would persist until conditions are favorable for a higher state of crystallization. As in other parts of this report, the mineral species considered are microcrystalline gibbsite, microcrystalline trihydroxide (the prebayerite form), and metastable halloysite.

Tables 12 and 13 contain data taken from published sources and compare calculated aluminum solubility, assuming no organic complexing, with actually observed concentrations for 31 water samples. The calculated solubilities assume either an equilibrium with respect to microcrystalline gibbsite or microcrystalline trihydroxide where silica content was less than 9.0 mg/l or with respect to synthetic halloysite where silica concentration was higher. Inorganic complexes are taken into account, but organic ones are not. Thermodynamic data are taken from table 3, and the activity coefficients are taken from the results of a computer output of the program described by Kharaka and Barnes (1973).

The departure from the calculated equilibrium concentration of aluminum is substantial in most of the more highly colored waters in tables 12 and 13. Probably, however, most of the aluminum is associated with particulate matter in these waters and probably could have been removed, for the most part, by filtration. This statement is based partly on the observed tendency for quercetin-aluminum complexes to precipitate at higher concentration and pH and also on our extrapolation of the behavior of quercetin to that of naturally occurring aqueous organic compounds of high molecular weight. Some additional support is available in numerous studies of principles and techniques for removal of organic color in the conditioning and treatment of water supplies. This removal is commonly accomplished by addition of aluminum, pH adjustment to an alkaline condition, and filtration. Most investigators have considered this as a colloidal system (Stumm and O'Melia, 1968).

TABLE 12.—*Analyses of naturally colored water with high aluminum contents* (Fe≤500μg/l)

Location	Date	Reported				Calculated at equilibrium	Reference
		Aluminum (Al) (μg/l)	Silica (SiO_2) (mg/l)	pH	Color number	Aluminum (μg/l)	
Patuxent River at Hardesty, Md	8-26-63	300	12.0	6.50	5	18	U.S. Geological Survey (1967, p. 212).
Partridge River near Aurora, Minn	2-18-65	500	12.0	7.30	40	95	U.S. Geological Survey (1970, p. 355).
Do.	4- 4-65	400	13.0	7.60	50	173	Do.
St. Louis River near Aurora, Minn	9-13-65	600	11.0	7.70	39	256	U.S. Geological Survey (1970, p. 356).
St. Louis River at Scanlon, Minn	7-14-65	300	17.0	7.80	20	211	U.S. Geological Survey (1970, p. 357).
Do.	1-17-65	900	9.7	6.70	100	33	Do.
Redeye River near Aldrich, Minn	10-17-67	400	13.0	7.80	11	278	Lindholm (1970, p. 30).
Partridge River near Aldrich, Minn	10-17-67	400	9.8	7.60	14	36	Do.
Ground water from the Pottsville Group, Monongahela River basin, W. Va	4-28-64	100	5.6	6.30	2	24	Friel, Wilmoth, Ward, and Wark (1967, p. 103)
Leaf River near Verndale, Minn	10-17-67	700	5.7	8.00	11	562	Lindholm (1970, p. 30).
Lehigh River at Walnutport, Pa	4-21-59	200	4.1	5.20	5	129	McCarren and Keighton (1969, p. 35).
Hurricane Creek near Belfast, Ark	8-13-63	38,000	1.4	9.40	30	15,100	Halberg, Bryant, and Hines (1968, p. 41).
Patuxent River at Benedict, Md	6-28-63	800	3.8	6.50	5	127	U.S. Geological Survey (1967, p. 313).
Patuxent River near Laurel, Md	4- 2-64	100	6.8	6.70	3	29	U.S. Geological Survey (1969, p. 352).
Partridge River near Aurora, Minn	7-20-65	600	5.5	7.30	40	110	U.S. Geological Survey (1970, p. 355).
St. Louis River near Aurora, Minn	7-21-65	800	5.5	7.20	120	86	U.S. Geological Survey (1970, p. 356).
St. Louis River at Scanlon, Minn	8-26-65	800	6.3	7.20	110	88	U.S Geological Survey (1970, p. 357).
Cheat River at Rowlesburg, Monongahela River basin, W. Va	5-10-63	100	1.3	7.10	4	68	Friel, Wilmoth, Ward, and Wark (1967, p. 61).
Ground water from the Pottsville Group, Monogahela River basin, W. Va	4-28-64	200	6.6	5.30	2	129	Friel, Wilmoth, Ward, and Wark (1967, p. 103).

TABLE 13.—*Analyses of naturally colored water with high aluminum contents* (Fe=500–1,000$\mu g/l$)

Location	Date	Reported				Calculated at equilibrium	Reference
		Aluminum (Al) (μg/l)	Silica (SiO_2) (mg/l)	pH	Color number	Aluminum (μg/l)	
St. Louis River at Scanlon, Minn	4- 9-65	700	9.9	7.10	160	73	U.S. Geological Survey (1970, p. 357).
Do.	9-30-65	1,300	9.7	7.40	130	144	Do.
Patuxent River at Benedict, Md	10- 4-63	1,000	2.6	6.90	5	65	U.S. Geological Survey (1969, p. 256).
St. Louis River at Scanlon, Minn	10-30-64	700	7.3	6.50	170	31	U.S. Geological Survey (1970, p. 357).
Little Patuxent River near Laurel, Md	6-27-63	100	15.0	6.40	8	27	U.S. Geological Survey (1967, p. 212).
Little Patuxent River at Fort George G. Meade, Md	10- 2-63	400	11.0	6.40	25	17	U.S. Geological Survey (1969, p. 252).
Partridge River near Aurora, Minn	12- 7-64	1,000	13.0	7.20	90	71	U.S. Geological Survey (1970, p. 355).
St. Louis River near Aurora, Minn	12- 4-64	900	13.0	7.10	90	55	U.S. Geological Survey (1970, p. 356).
Do.	1- 7-65	800	12.0	6.80	90	32	Do.
Do.	2-26-65	600	14.0	7.20	130	63	Do.
St. Louis River at Scanlon, Minn	2-26-65	800	10.0	7.40	150	140	U.S. Geological Survey (1970, p. 357).

CONCLUSIONS

Natural waters commonly contain organic material, although amounts and species to be expected cannot be accurately predicted from existing published information. Aluminum may form stable soluble complexes with low molecular weight organic ligands and may be associated with relatively insoluble or colloidal particulate forms of high molecular weight organic compounds. Association of aluminum with high molecular weight organic material present as colloidal particles in river water can increase the apparent dissolved aluminum content if such particles are not removed from the water before analysis.

Concentrations of soluble organic ligands in the vicinity of 10^{-4} molar probably are near the upper limit to be expected in most stream water. The complexing power of such concentrations of organic material for aluminum is comparable to that of strongly complexing inorganic ligands, such as fluoride. Under favorable conditions organic complexes might be capable of increasing aluminum solubility by a factor of 100 in part of the pH range of natural water.

The structure of quercetin is similar to some of the naturally occurring organic coloring material in natural waters. Laboratory experiments with this material show that it forms complexes with aluminum. Besides the simple enhancement of solubility and possible formation of aluminum-enriched colloidal particles, there are significant effects on the previously elucidated processes of polymerization of aluminum hydroxide macroions and the formation of crystalline aluminum hydroxide and aluminosilicates. Such effects can be observed even when the concentration of organic material is so small that it can complex only a minor fraction of the dissolved aluminum. The results of the quercetin experiments may be summarized as follows:

1. Quercetin forms a complex with a 1:2 aluminum to quercetin mole ratio. The stability constant β_2 for the reaction
$$2Q^- + Al^{3+} = AlQ_2^+$$
is near 10^{12}. A complex with the composition $Al_3Q_2^{n+}$ also seemed to be formed but disappeared from solution on aging.
2. Polymerization of dissolved aluminum hydroxide species to form gibbsite, observed in previous studies below pH 6.5, was strongly inhibited by the presence of small amounts of quercetin. In solutions near neutrality and mildly basic, the precipitate formed in the presence of quercetin gave a large X-ray diffraction peak that might indicate the presence of boehmite. The more alkaline solutions ultimately yielded crystalline bayerite. The process of formation of the latter material, however, also is inhibited by the presence of quercetin.

3. Small amounts of quercetin in solutions duplicating those used earlier for synthesis of relatively amorphous clay minerals with 1:1 aluminum to silica ratios ("synthetic halloysite") improved the yield of well-organized small crystals of kaolinite. The bulk of the material remained amorphous to X-rays, however, during aging periods of 6 months or more at 25°C. Probably in these solutions the quercetin inhibited aluminum hydroxide crystallization and by so doing made it possible for the formation of Al-O-Si bonding to keep pace with the other aspect of the crystallization process.

The aluminum concentrations in a selected group of water analyses that reported organic color were in excess of calculated equilibrium saturation, considering only inorganic species. These waters probably contained aluminum associated with organic matter.

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