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INFLUENCE OF CITRIC ACID ON THE CRYSTALLIZATION OF ALUMINUM HYDROXIDES

(Received 27 May 1974)

Numerous studies have been carried out on the hydrolytic reactions of aluminum at room temperature and pressure in partially neutralized aluminum solutions. These studies have shown that the ionic environment in the system is important in influencing the formation or nonformation of crystalline aluminum hydroxides. Chloride (Hsu, 1966; Turner and Ross, 1970) and SO_4^{-2} (Hsu, 1973) at high concentration and silicic acid (Luciuk and Huang, 1974) will inhibit the formation of crystalline aluminum hydroxides. In soil solutions and natural waters, organic acids form part of the environment and though their concentrations may be low, many of them, e.g. oxalic and citric acids, have strong complexing or chelating properties towards aluminum. It has been reported that non-crystalline hydrous oxides and hydroxides of aluminum are quite frequently present in slightly acid and acid soils (Mitchell *et al.*, 1964). Bruckert (1966) and other workers reported that it is exactly under these acid conditions that the organic acids reactive towards aluminum are persistent in soils. These findings lead one to suspect that organic acids may interfere with the formation of crystalline aluminum hydroxides.

In order to ascertain the influence of the organic acids on the formation of crystalline aluminum hydroxides in the natural environment, where the concentrations of both organic acids and aluminum are low ($1·10 \times 10^{-4}$ M and $1·10 \times 10^{-3}$ M), $AlCl_3$ solutions containing citric acid ranging in concentration of 0, 10^{-6} and 10^{-4} M, respectively, were titrated to OH/Al molar ratio of 3·0 with 0·1 M NaOH solution. The suspensions were aged for varying periods. The precipitate was collected by ultrafiltration at a pressure of 40 psi (Huang and Luciuk, 1974). The reaction products collected were examined by X-ray powder diffraction with CuK_α radiation and replica electron microscopy. Citric acid, a strong chelating acid commonly occuring in soils, natural waters, and biological systems was chosen to reflect the similar behaviour towards aluminum of other low molecular weight organic acids common in natural systems.

Examination of the aluminum hydroxides formed at various aging periods leads to the conclusion that both the level of citric acid and the initial concentration of aluminum influence the formation of crystalline aluminum hydroxides in the system. The hydroxides formed in the absence of citric acid are essentially well crystallized bayerite at the end of a 40-day aging period (Fig. 1A). The hydroxides formed from the solution containing 10^{-3} M

Al in the presence of 10^{-6} M citric acid are initially amorphous to X-rays but with time crystallinity develops. As shown in Fig. 1B, with a hydroxide aged for 40 days, well-defined peaks of gibbsite are visible on the X-ray diffraction pattern. Since an acid environment favors the crystallization of aluminum hydroxide into gibbsite relative to bayerite (Barnhisel and Rich, 1965), the acidity of citric acid apparently has helped to promote the formation of
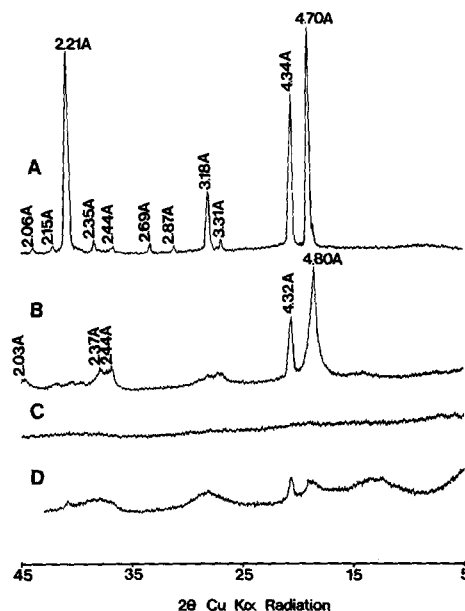

Fig. 1. X-ray diffraction patterns of hydrolytic reaction products of Al at the initial OH/Al molar ratio of 3 and (A) Al concentration of $1·10 \times 10^{-3}$ M in the absence of citric acid collected after 40 day ageing at room temperature, (B) Al concentration of $1·10 \times 10^{-3}$ M in the presence of 10^{-6} M citric acid collected after 40 day ageing at room temperature, (C) Al concentration of $1·10 \times 10^{-3}$ M in the presence of 10^{-4} M citric acid collected after 40 day ageing at room temperature followed by 3 day ageing at 80°C and (D) Al concentration of $1·10 \times 10^{-4}$ M in the presence of 10^{-6} M citric acid collected after 40 day ageing at room temperature.

gibbsite and deter the formation of bayerite. However, at the same concentration of citric acid, the corresponding hydroxides precipitated from 10^{-4} M Al give only poorly defined patterns (Fig. 1D). This is evidently due to the increase of the citric acid:aluminum ratio. Moreover, the X-ray diffraction data show that the hydrolytic products of aluminum can be completely amorphous to X-rays if the citric acid concentration is sufficiently high (Fig. 1C). The crystallization of aluminum hydroxides is hindered or delayed by citric acid apparently because coordination of carboxylate groups with aluminum hampers the hydrolysis of the terminal groups of aluminum ions. Though the chemistry of Fe and that of Al are not the same, it is interesting to note that Schwertmann et al. (1968) observed a delay in the crystallization of iron oxides and a shift in the nature of the products formed in the presence of citric acid.

The inhibition or delay in the formation of crystalline aluminum hydroxides caused by the citric acid is further reflected in the electron micrographs of the hydrolytic reaction products of aluminum. In Fig. 2, for instance, the surface features of the reaction products aged 40 days in the absence and in the presence of 10^{-6} M citric acid are significantly different. In the absence of citric acid, the crystals formed are well-defined (Fig. 2A). The product in the presence of citric acid possesses a rather fluffy, rough surface (Fig. 2B).

The results of this investigation provide direct evidence to the effect that the hydrolytic reaction of aluminum and the surface features of the reaction products in the aqueous system are greatly influenced by the presence of citric acid. This is of basic importance in understanding the solution and colloid chemistry of Al, as well as the behaviour of aluminum in soil solutions and natural waters.

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INTERLAYER BONDING IN TALC AND PYROPHYLLITE

The bonding between the silicate layers of micas such as muscovite consists of ionic, van der Waals, and repulsion components (Bailey and Daniels, 1973). The origin of the ionic bonding has been supposed to originate in the partial substitution of aluminum for silicon in the tetrahedra which gives the silicate layers a negative electrostatic charge and attracts the positively charged potassium ions situated between the layers. Related layer silicates which do not have a net charge on the layer and no interlayer cation are of two types: the 1:1 phyllosilicates such as the kaolin and serpentine minerals, and the 2:1 phyllosilicates such as talc and pyrophyllite. The interlayer bonding of the 1:1 structures is known to involve long hydrogen bonds between the hydroxyls which form one of the surfaces of the 1:1 layer and the oxygens which form the adjacent surface of the next layer (Giese, 1973; Cruz et al., 1972). The interlayer bonding in talc and pyrophyllite, which lack surface hydroxyls, has been assumed to be purely van der Waals (Ward and Phillips, 1971).

Ward and Phillips (1971) have calculated the specific surface energy of talc and pyrophyllite using the Lennard–Jones potential function to describe the van der Waals bonding between the oxygens on either side of the cleavage plane, (001). The force constants in the potential function were determined from the bulk modulus value of pyrophyllite (Bridgeman, 1924) and the calculated specific surface energies are 490 mJ/m^2 for both minerals or 17·1 kcal/mole for talc and 16·7 kcal/mole for pyrophyllite.

The assumption that there is no ionic contribution to the interlayer bonding and therefore there are only van der Waals interactions can be examined by a technique described elsewhere (Giese, 1974). In brief, the specific electrostatic surface energy of a layer structure can be determined by calculating the electrostatic energy for the normal structure and for a series of related, hypothetical structures which contain the same rigid silicate layers but have increasing distances between the layers. The plot of electrostatic energy vs the increase in interlayer distance is a simple curve which rapidly approaches a constant value for large separations. The numerical difference between the energy of the expanded structures and that of the normal mineral is the surface energy.

Such calculations have been done for talc and pyrophyllite using the most recent crystal structure refinements of