Influence of Citric Acid on the Crystallization of Aluminum Hydroxides

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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 of non-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. Acids may interfere with the formation of crystalline aluminum hydroxides in the system. The hydroxides formed in the presence of citric acid and aluminum influence the formation of crystalline aluminum hydroxides in the system. The hydroxides formed from the solution containing 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 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
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 at the surfaces of the adjacent layers. Related layer silicates which do not have 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 at the surfaces of the adjacent layers. Related layer silicates which do not have ionic bonding have been assumed to be purely van der Waals (Ward and Phillips, 1971).

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/m² for both minerals and 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 gibraltar and diter 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 in the concentration of citric acid:aluminum ratio. Moreover, the X-ray diffraction data show that the hydrolys 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 hydrolys 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 10⁻⁴ 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 aqeous 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

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