

SIZE AND SHAPE OF ALLOPHANE PARTICLES IN DISPERSED AQUEOUS SYSTEMS

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Abstract—Aqueous suspensions of allophane show relatively high viscosity, presumably because of strong particle interaction between the unit particles. To test this hypothesis, we measured the particle weight and particle size of allophane during a dispersion using the light scattering method. The particle weight was more than several hundred times larger than that of the unit particle, and the size was 100–400 nm, whereas the Stokes' diameter of the particles in the sample was less than 50 nm. Particle weight and size varied with the pH of the sample. Particle sizes were cross-checked by ultrafiltration through membrane filters. The experimental findings show that the unit particles of allophane within dilute dispersions appear to be associated like strings of beads, forming domains (primary floccules) about 100 nm in diameter. When these domains coagulate under certain conditions, they do not grow analogously but form clusters, such as secondary floccules, then precipitate. Formation of secondary flocculation of loose structure accounts for the maximum relative viscosity at the transition pH between dispersion and coagulation.

Key Words—Allophane, Cluster, Colloid, Domain, Light Scattering, Shape, Size, Ultrafiltration, Viscosity.

INTRODUCTION

Volcanic ash soils, especially those widely distributed throughout Japan, characteristically have porous and relatively stable natural structures, but once disturbed or dried out, their physical properties change markedly (Maeda et al. 1977; Wada 1989). These properties are mainly due to the key clay mineral of the soils, allophane. Since allophane consists of unit spherical particles 3.5–5.5 nm diameter (Kitagawa 1971; Wada and Wada 1977), we investigated how the unit particles of allophane assemble to form the macro structure of the soils.

The shape of allophane within aqueous dispersed systems has been discussed by Egashira (1977), based on the relationship of the relative viscosity and the axis ratio of the suspended particles computed by Mehl et al. (1940). He concluded that allophane is dispersed as disc-shaped particles several tens of nanometers in diameter. Wada et al. (1981) and Nitawaki et al. (1981) using a modified Robinson equation, showed that the high relative viscosity of allophane may be due to the thick hydration layer around the particles. Hall et al. (1985) used neutron scattering to determine the size of the unit particle of aqueous suspensions and found that the diameter of this particle is about 5 nm, the same as found by electron microscopy. Because the applicable particle size range of the neutron scattering method is 2–35 nm, floccules of allophane beyond that range could not be measured.

Karube (1982a, 1982b) measured the size of dispersed allophane particles by light scattering and ul-

trafiltration, and found that they are associated like strings of beads and dispersed as domains several hundreds of nanometers in diameter. However, some of the allophane samples used during Karube's research were later found to contain small quantities of imogolite. If allophane is contaminated by imogolite, even at a very low ratio, experimental results may be inaccurate because imogolite is a peculiar clay mineral with a thin fibrous shape. When allophane particles are separated under acidic conditions, imogolite might be present within the sample, but if separated under alkaline conditions, the sample might be pure because imogolite coagulates under alkaline conditions. When iron oxide removal treatment is used under alkaline conditions and allophane is separated successively, imogolite might be removed from the sample.

After carefully preparing pure allophane, we measured the relative viscosities of allophane suspensions in relation to pH to clarify the phenomenal characteristics of colloidal allophane. The particle weight and particle size of dilute allophane dispersed systems were then studied by the light scattering method. The size was cross-checked by ultrafiltration. The structure of allophane within dispersed systems is discussed.

EXPERIMENTAL

Allophane Sample

Allophane samples were separated from fresh soil taken from the lower part of the Kanumatsuchi weathered pumice bed at Kanuma City, Tochigi Prefecture,

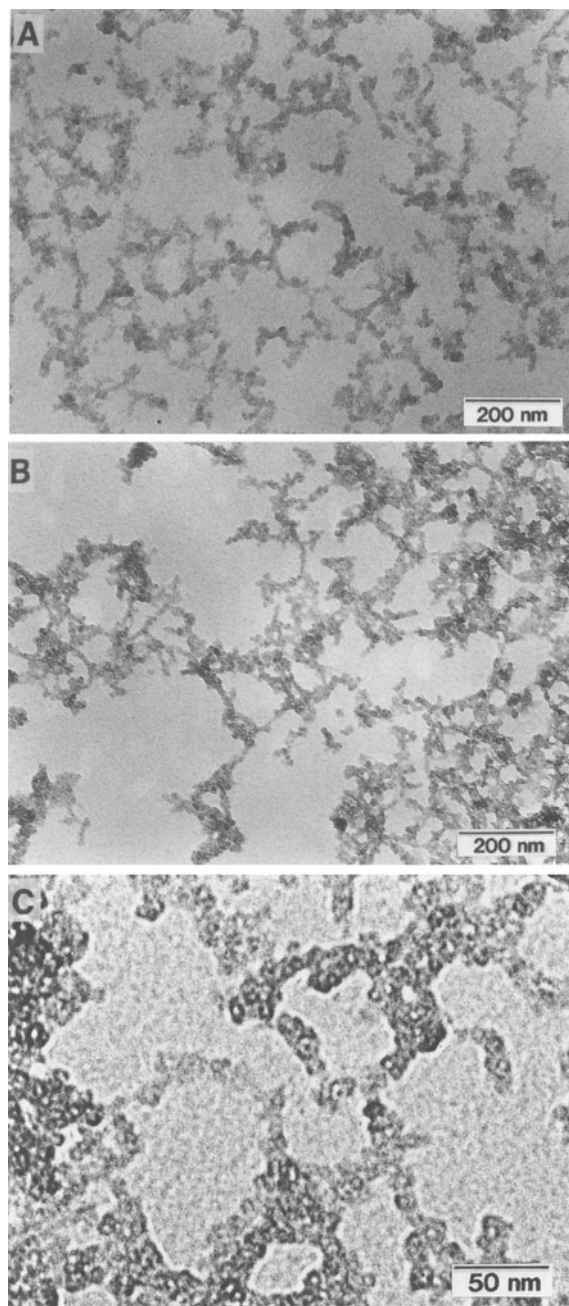


Figure 1. Transmission electron micrograph of apparently well dispersed allophane. Key = A) Deferrated, pH 9; B) Non-deferrated, pH 9; and C) Deferrated, pH 4.

Japan. The following procedure was used for sample purification.

DEFERRATED SAMPLE. After removing the gel-like substance, imogolite, by washing the soil with water, the soil was treated with H_2O_2 . Aggregates were squashed and passed through a sieve with an opening of about 0.5 mm to exclude coarse substances. The fine portion

was treated again with H_2O_2 and iron oxide was removed with $Na_2S_2O_4$ - $NaHCO_3$ -Na citrate (DCB) (Mehra and Jackson 1960). A single extraction with 2% Na_2CO_3 at 90 °C for 15 min during a waterbath (Jackson 1956; modified by Wada and Greenland 1970) was used to successively remove soluble allophanic material, as discussed by Wada (1989). The material was then dispersed at pH 9–9.5, adjusted with NaOH, and particles with a Stokes' diameter smaller than 50 nm were collected by centrifugation. The allophane colloid was coagulated by adding about 100 ml of saturated NaCl solution to each liter of the suspension. The sample was dialyzed against distilled water until the electric conductivity of the external solution was less than 1 mS/m.

NON-DEFERRATED SAMPLE. An allophane sample, which was not treated with DCB was prepared for comparison with the deferrated allophane. The preparation procedure was the same, except for the omission of iron oxide removal and the 2% Na_2CO_3 treatment.

Both samples were treated carefully so that they would not become dry during the preparation. The absence of imogolite fibers was confirmed by electron microscopy (Figure 1). The Al/Si molar ratio was 1.5 of the deferrated allophane separated from the Kanumatsuchi soil, a medium value among allophanes.

Measurement of Relative Viscosity

The relative viscosities of allophane suspensions at different pHs and clay concentrations were measured with an Ostwald viscometer at 22 °C. The pHs of the suspensions were adjusted with HCl or NaOH 1 d before measurement.

Measurement of Particle Weight and Particle Size by Light Scattering

Light scattering was used to determine the particle weight, the relative mass of a particle defined the same as molecular weight, and particle size of a colloid by measuring the scattered intensity of incident light (Tanford 1961).

Measurements of the clay concentrations, the derivative of the refractive index with respect to the clay concentration and the intensities of scattered light at different scattering angles were made. A Zimm plot was made, the abscissa being $\sin^2(\theta/2) + kc$, where θ = the angle of scattering, k = a constant, c = the clay concentration, and the ordinate Kc/R_{90} , which is a function that includes the wavelength of incident light, a derivative of the refractive index with respect to the clay concentration, the intensity of the scattered light, scattering angle, clay concentration and the constant of the apparatus. In this plot, by extrapolating θ and c to 0, the particle weight and the radius of gyration were obtained.

Heller et al. (1959) discussed theoretical errors in the light scattering method, incorporating the refrac-

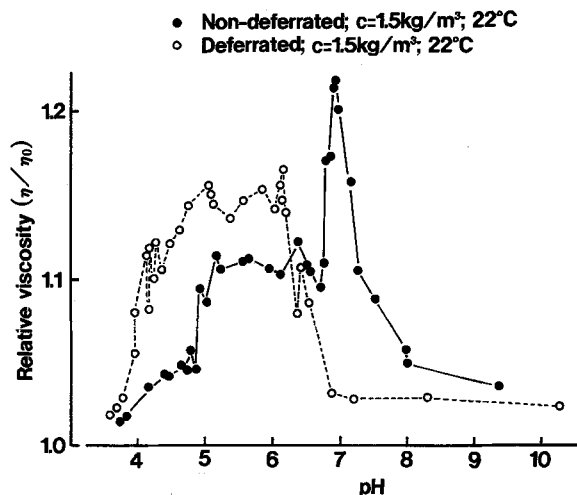


Figure 2. Relative viscosity of allophane suspensions in relation to pH.

tive index ratio of the particles to the medium and the ratio of the particle size to the wavelength as parameters. Accordingly, the maximum applicable size of clay is about 2 μm , with an error allowance of up to 50%.

An He-Ne laser light scattering apparatus was used for the measurements. The preparation of dust free samples was the most important point of this experiment. A portion of allophane from just under the surface of a sample, which had been standing for several months, was pipetted into a separate vial. A portion of the separated sample was used to measure the clay concentration by the weighing method, then the sample was diluted to various concentrations between $c = 2 \times 10^{-3} \text{ kg/m}^3$ and $1 \times 10^{-2} \text{ kg/m}^3$ for measurement. Each light scattering measurement was obtained for several samples of different clay concentrations as well as for pure water at scattering angle intervals of 15° within the range of 30° to 150° . The constant of the apparatus was determined from the intensity of benzene. The refractive index derivative with respect to the clay concentration was determined with a differential refractometer. Measurements were made at 22°C to prevent temperature fluctuations from affecting the refractive index.

Before measuring the allophane sample, use of the light scattering measurement method was confirmed with a standard sample of polyethylene oxide, and its applicability to clay minerals was checked using kaolinite and dehydrated halloysite. The results obtained for these two clay minerals agreed with the values estimated from an electron micrograph. However, errors within the range of one-half to twice the measured value were observed. These errors are attributable to particle size distribution, variance in the refractive index, impurities in the samples or all these, which are

inevitable when measuring natural clay minerals. As these are intrinsic properties of clay minerals, it is difficult to prevent this kind of error. Such errors could be acceptable depending upon the purpose of the measurement, but the shape of the particles was difficult to determine from the interference factor.

Particle Size Analysis by Ultrafiltration Through Membrane Filters

Particle size analysis of dispersed allophane was made by ultrafiltration through membrane filters. Two problems must be solved concerning the sieving of colloidal particles: 1) the uniformity of the filter pore size; and 2) clogging. The filter pore size problem was solved by the use of a Nuclepore membrane filter, which has uniform cylindrical pores. As a countermeasure to avoid the clogging problem, the samples were diluted as much as possible, and changes in the concentration before and after filtration were checked by turbidity measurement using a light scattering apparatus. In this way, changes in concentration were detectable even when a sample was diluted to as low as $0.5 \times 10^{-2} \text{ kg/m}^3$.

Nevertheless, as clogging might occur with an increase of the filtrate volume, the relation between this volume and passage through the filter was measured. This was also effective for checking and overcoming the effect of the residual water used to wash the implement, which was not dried after washing in order to keep it dust free. For this purpose, a glass filter holder 47 mm in diameter was connected to a water-jet pump capable of exerting a maximum suction of 95 kPa. If the particles could pass through the filter quickly, filtration would be over before this maximum was reached, but if filtration was slow, suction would be increased to the maximum. The effect of suction was therefore sufficiently small for this analysis, although it was not always constant.

Ten ml of the filtrate was collected at a time and examined by light scattering. Filtered air was introduced to break the vacuum, and the filtrate was pipetted, never decanted, to a sample cell to prevent dust contamination. The percentage of particle passage through the filter was estimated from the light scattering intensity ratio of the filtrate to the unfiltered sample.

RESULTS AND DISCUSSION

Characteristic Behavior of an Allophane Suspension Based on Relative Viscosity

The relative viscosity of allophane suspensions is high within the pH range at which the suspensions coagulate (Figure 2). The coagulation range, as judged from the viscosity, is pH 4–6.5 for deferrated samples and pH 5–7.2 for non-deferrated ones. This is related to the point of zero charge (PZC) of electrophoretic

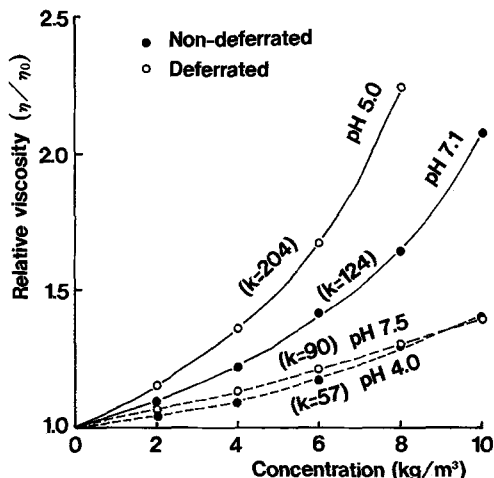


Figure 3. Changes in the viscosity of allophane suspensions under 22 °C in relation to the clay concentration. Key: Symbol κ = the constant of equation $\eta/\eta_0 - 1 = \kappa\phi$, at dilute suspension; and ϕ = the volume fraction of the solids.

behavior, that is, the viscosity of deferrated allophane shows a broad maximum centered at the PZC, pH 5.2 (Karube et al. 1992). Deferrated allophane has a higher viscosity than non-deferrated allophane at approximately the PZC for the same clay concentration. Wells and Theng (1985) reported that a deferrated allophane suspension showed greatly reduced shear stress, but this might have been due to imogolite which was present in their non-deferrated sample.

The relative viscosity of the non-DCB treated samples in Figure 2 has an obvious peak at approximately pH 7, the boundary pH of dispersion and coagulation. As a quantitative description of coagulation based on relative viscosity is unpredictable, these phenomena will be addressed.

Figure 3 shows the relative viscosities of allophane suspensions in relation to the clay concentrations. The relationship between relative viscosity (η/η_0) and particle concentration is expressed by Einstein's viscosity formula, $\eta/\eta_0 - 1 = \kappa\phi$, where: ϕ = the volume fraction of the solids, and κ = a constant, which becomes 2.5 providing that the particles are spherical and do not interact. For suspensions of deferrated allophane at pH 7.5 and non-deferrated allophane at pH 4.0, the κ values are at least twenty times larger than 2.5, even though the systems look well dispersed and the unit particles are spherical. Egashira (1977), who discussed the reasons for these phenomena, thought that allophane was present as disk-shaped particles with an axial ratio of 16.0–13.2, whereas Nitawaki et al. (1981) considered the allophane unit particles were covered by a hydration layer 2.5 nm thick. Although viscosity is affected by the colloidal structure, structure cannot be predicted on the basis of relative viscosity only.

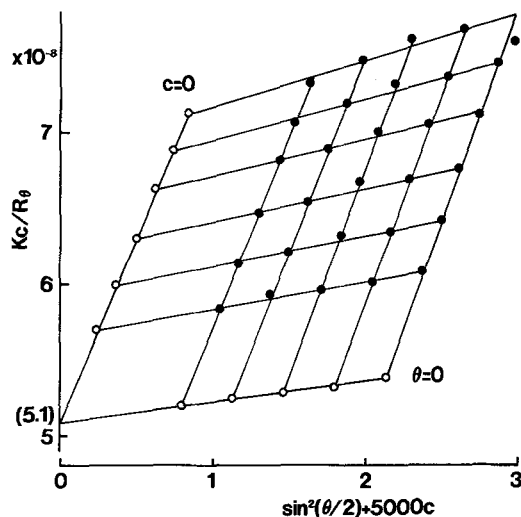


Figure 4. Zimm plot of deferrated allophane at pH 7.2.

Particle Weight and Particle Size Measured by the Light Scattering Method

Figure 4 shows a Zimm plot of deferrated allophane at pH 7.2. The average particle weight is 2.0×10^7 , the mean square radius of gyration is $1.98 \times 10^3 \text{ nm}^2$, the end-to-end distance of the assumed random coil is 110 nm and the diameter of the assumed spherule is 115 nm. Results are summarized in Table 1. On the whole, the measured particle weight was $2 \times 10^7 - 2.5 \times 10^8$, and the particle size, assumed to be a random coil, was 110–360 nm.

In contrast, the particle size of the prepared allophane sample was less than 50 nm Stokes' diameter, which means that the average size is smaller and closer to the size of the allophane unit particle. The particle weight of the unit allophane was calculated to be $3.5 \times 10^4 - 1.2 \times 10^5$, assuming that the diameter is 3.5–5.5 nm, the wall thickness 0.7–1.0 nm and the internal pores are filled with water. These values do not agree with those obtained by the light scattering method.

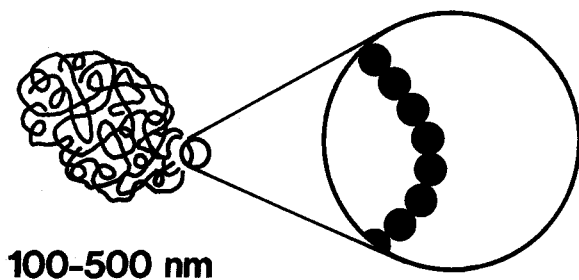
However, these values are acceptable without contradiction if the 200–7000 unit particles of allophane flocculate like a chain, forming a floccule 110–360 nm in diameter. According to the free-draining model (Hiemenz 1986), Stokes' diameter is a measure of a

Table 1. Experimental values obtained by the light scattering method.

	pH	Stokes' diameter	Particle weight [‡]	Size (random coil)	Number of unit particles
	4.9	<50 nm	1.7×10^8	240 nm	1400–4800
	6.9	<50 nm	2.5×10^8	360 nm	2100–7100
(D) [†]	7.2	<50 nm	2.0×10^7	110 nm	160–560
(D)	7.4	<50 nm	2.7×10^7	130 nm	220–760

[†] (D): deferrated.

[‡] Particle weight of unit allophane: $3.5 \times 10^4 - 1.2 \times 10^5$.



100-500 nm

Figure 5. Schematic representation of a domain (micro-floccule) of allophane and the primary flocculation of unit allophane particles.

chain-element rather than of the entire floccule because the drag force relates to the circumference of the particle. However, the light scattering method measures the size of the entire floccule. Taking these findings into consideration, we conclude that for deferrated allophane at pH 7.2, several hundred unit particles were assembled forming a domain 110 nm in size and were still dispersed in water.

As the shape of such domains is flexible, generally it will be rounded due to the micro-Brownian motion of the elements in the chains, providing there is no external force. Using the particle weight measured, the density of the domain is therefore 48 kg/m^3 , and the porosity 98%, assuming that the domain spherules have a diameter equal to the end-to-end distance. Figure 5 shows a representation of this conceptual schema based on idealized primary flocculation of unit allophane particles. Although these domains are not directly observable by electron microscopy because the sample must be dried out for observation, a transmission electron micrograph (Figure 1) shows traces of the chain network structure.

Particle Size Analysis by Ultrafiltration

For this discussion it is necessary to begin by examining the method of analysis. Kaolinite prepared to uniform size by centrifugal sedimentation was used. The particle diameter of the kaolinite was found to be 100–300 nm by electron microscopy. The findings obtained by this analysis show that approximately 10% of this kaolinite passed through a 200 nm pore diameter membrane filter, 50% through a 400 nm one, 70% through a 600 nm one and 85% passed through an 800 nm one. These results show that the kaolinite, the diameter of which corresponds to about one half the filter pore size could pass through the filter.

The reason for this is related to the thickness of the filter. The pore shape of this membrane filter is cylindrical, and the length of the cylinder is 10–50 times the pore diameter. In the cylindrical tube, if a particle passing through is delayed and caught up with by the next particle, clogging might occur in the pore. As the pore size and pore density for each filter are known,

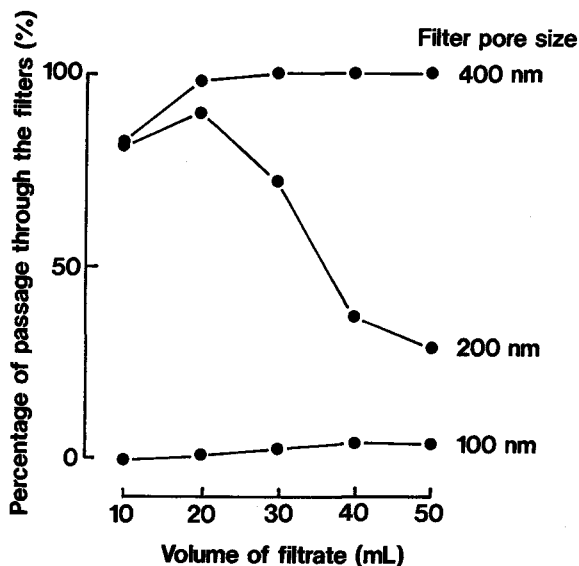


Figure 6. Particle size analysis by ultrafiltration. Deferrated allophane pH 7.7.

the number of particles that pass through each tubular pore can be estimated for any volume and any concentration of a sample using the particle weight measured by the light scattering method. Several tens to several hundreds of particles are estimated to pass through each pore for each 10 ml of sample filtered. Thus, a high ratio of passage occurs only when most of the particles pass through the pore tubes.

In regard to this problem, Elford (1931), who used collodion filters to measure the size of colloidal particles, reported that the smaller the pore size, the

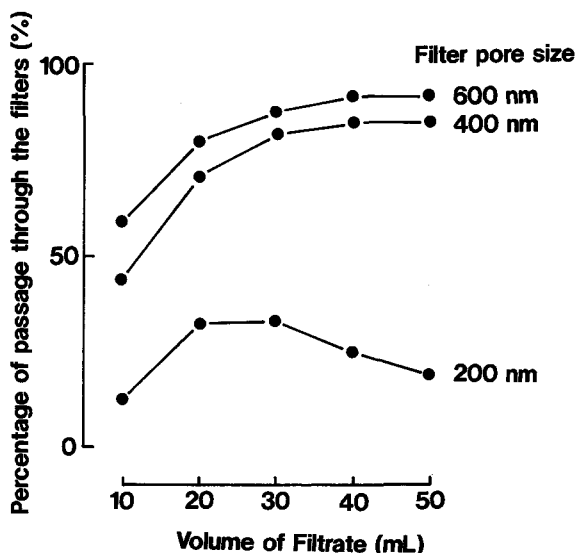


Figure 7. Particle size analysis by ultrafiltration. Non-deferrated allophane pH 3.9.

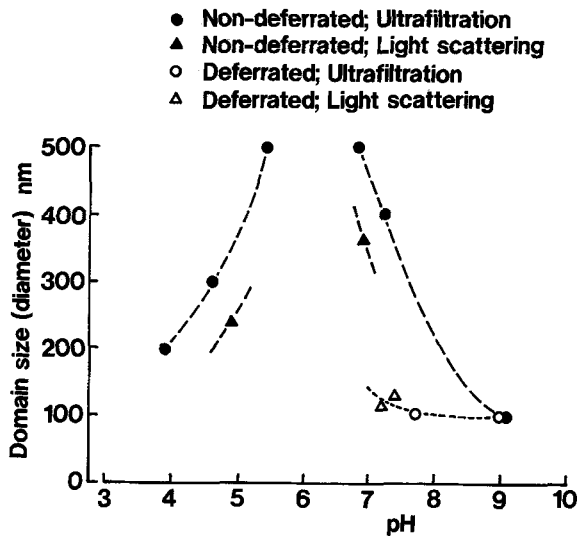


Figure 8. Domain sizes of allophane at dilute suspension in relation to pH.

smaller the ratio of the permeable particle size (p) to the filter pore diameter (d), and that the ratio p/d is 0.5–0.75 for the 100–500 nm pore size filter (Elford 1931; Jirgensons and Straumanis 1962). The results for kaolinite agree. Therefore, this result that particles with less than one half of the filter pore diameter can pass through the filter, applied to the allophane samples tested.

Figures 6 and 7 show the percentage of allophane particles that passed through the filters. In these figures, particle passage is low at the beginning of filtration due to the dilution with the residual water from washing. For deferrated allophane at pH 7.7, 100% of the particles passed through the 400 nm pore size filter, whereas about 5% passed through the 100 nm filter, and clogging occurred in the 200 nm pore size filter. Particle size was therefore estimated to be about 100 nm based on one-half of the 200 nm pore size. For non-deferrated allophane at pH 3.9, most of the sample passed through the 600 nm pore size filter, most but less of the sample through the 400 nm filter and relatively heavy clogging occurred in the 200 nm pore size filter. The particle size was therefore estimated to be about 200 nm.

The relationship between particle size and pH as determined by this method is shown in Figure 8 together with the light scattering results. Both sets of results are in good agreement. Particle size is small for the pH at which allophane is well dispersed and large for pH values at which allophane coagulates. The important finding is that the particles of allophane do not exist as individual units, but as domains about 100 nm in size within an apparently dispersed system. This result supports the model shown in Figure 5.

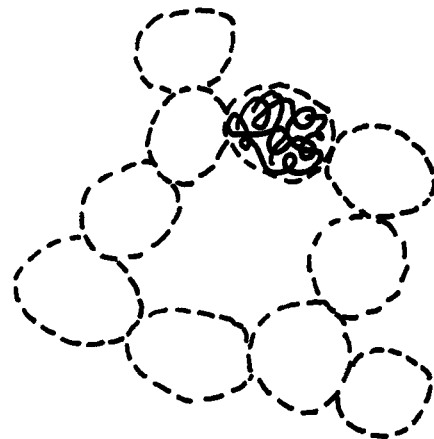


Figure 9. Schematic representation of a cluster (secondary floccule) formed by allophane domains within a dilute suspension.

On the Peak of Relative Viscosity in Figure 2

The viscosity of a colloidal solution usually increases when particles flocculate or coagulate. However, for a dilute solution as low as 1.5 kg/m³, the viscosity does not proportionally reflect the degree of flocculation. In Figure 2, the peak of viscosity is within the border range of dispersion and coagulation, but not within the medium range of coagulation. Such phenomena will arise when domains assemble and form secondary floccules or clusters of loose extended structure, as represented schematically in Figure 9. Hydrous iron oxide and allophane-like constituents may promote a loose structure because the peak is obvious for non-deferrated allophane.

CONCLUSIONS

Allophane disperses within water forming domains of about 100 nm in diameter even for dilute and apparently well-dispersed aqueous systems. A domain consists of unit particles forming like a chain due to primary flocculation. The size and number of constituent elements of these domains change with the pH of the system. A viscosity peak, present at the pH boundary of dispersion and coagulation, was assigned to loose secondary floccules or clusters that formed with the domains, rather than to the analogous extension of the domains.

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REFERENCES

- Egashira K. 1977. Viscosities of allophane and imogolite clay suspensions. *Clay Sci* 5:87–95.

- Elford WJ. 1931. A new series of graded collodion membranes suitable for general bacteriological use, especially in filterable virus studies. *J Pathol Bacteriol* 34:505–521.
- Hall PL, Churchman GJ, Theng BKG. 1985. Size distribution of allophane unit particles in aqueous suspensions. *Clays & Clay Miner* 33:345–349.
- Heller W, Nakagaki M, Wallach ML. 1959. Theoretical investigations on the light scattering of colloidal spheres. *J Chem Phys* 30:444–450.
- Hiemenz PC. 1986. Principles of colloid and surface chemistry. New York: Marcel Dekker, Inc. p 207–213.
- Jackson ML. 1956. Soil chemical analysis—Advanced course. Madison, WI: Published by the author. p 71–76.
- Jirgensons B, Straumanis ME. 1962. A short textbook of colloid chemistry. Chemistry. Pergamon Press. Japanese language edition (1967). Tokyo: Baifukan. p 21–24.
- Karube J. 1982a. Microstructure of allophane in disperse system by light scattering method. *Trans Jap Soc Irrig Drain Reclam Eng* 98:7–14 (in Japanese with English abstract).
- Karube J. 1982b. Domain size measurement of dispersed allophane with a membrane filter and a discussion on the allophane disperse system. *Trans Jap Soc Irrig Drain Reclam Eng* 99:17–23 (in Japanese with English abstract).
- Karube J, Nakaishi K, Sugimoto H, Fujihira M. 1992. Electrophoretic behavior of imogolite under alkaline conditions. *Clays & Clay Miner* 40:625–628.
- Kitagawa Y. 1971. The “unit particle” of allophane. *Am Mineral* 56:465–475.
- Maeda T, Takenaka H, Warkentin BP. 1977. Physical properties of allophane soils. *Adv in Agron* 29:229–264.
- Mehl JW, Oncley JL, Simha R. 1940. Viscosity and the shape of protein molecules. *Science* 92:132–133.
- Mehra OP, Jackson ML. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. In: Swineford A, editor. *Proc 7th Natl Conf Washington, DC, 1958*, New York: Pergamon Press. *Clays & Clay Miner* p 317–327.
- Nitawaki Y, Wada K, Egashira K. 1981. Particle-particle and particle-water interactions in aqueous clay suspensions. Part II. Viscosity data and interpretation. *Clay Sci* 5:319–331.
- Tanford C. 1961. Physical chemistry of macromolecules. New York: John Wiley & Sons Inc. p 275–316.
- Wada K. 1989. Allophane and imogolite. In: Dixon JB, Weed SB, editors. *Minerals in Soil Environments*. Madison, WI: Soil Sci Soc Am p 1051–1087.
- Wada K, Greenland DJ. 1970. Selective dissolution and differential infrared spectroscopy for characterization of “amorphous” constituents in soil clays. *Clay Miner* 8:241–254.
- Wada K, Nitawaki Y, Egashira K. 1981. Particle-particle and particle-water interactions in aqueous clay suspensions. Part I. Application of a modified Robinson equation to viscosity data. *Clay Sci* 5:313–318.
- Wada S, Wada K. 1977. Density and structure of allophane. *Clay Miner* 12:289–298.
- Wells N, Theng BKG. 1985. Factors affecting the flow behavior of soil allophane suspensions under low shear rates. *J Coll Interface Sci* 104:398–408.

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