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ELECTROPHORETIC BEHAVIOR OF IMOGOLITE UNDER ALKALINE CONDITIONS

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Abstract—Electrophoretic mobility of imogolite has been reported as positive (migration toward the negative electrode) below pH 9, and zero above pH 9. However, when mobility of dilute imogolite suspensions (5×10^{-3} kg/m^3) was measured, it was found to be negative above pH 9. The reason that imogolite does not behave as a negative colloid when the clay concentration is not very dilute is because the imogolite forms floccules large enough to prevent migration. Imogolite has a PZNC at about pH 6, and has a PZC at pH 8.5–9.0 showing a relatively low absolute mobility under alkaline conditions compared to that under acid conditions. The fact that imogolite behaves like this is understandable given the location of negative charge appearing on the inside surface of the thin fibrous tube, according to the structural model of imogolite.

Key Words—Electrophoresis, Imogolite, Mobility, PZC, PZNC, Viscosity.

INTRODUCTION

Horikawa (1975a) measured the electrophoretic mobility of imogolite and found that imogolite shows positive mobility (moves toward the negative electrode) below pH 9 and shows zero mobility above pH 9. Because this result was quite different from expected behavior based on charge characteristics of imogolite obtained by buffer curves (Inoue and Wada, 1971), he explained that the difference in the results could be reconciled if the positive charges were on the outside surface of the imogolite tube and the negative charges were on the inside surface, according to the structure model presented by Cradwick *et al.* (1972). Harsh and Xu (1990) also reported the same result.

In addition, Horikawa (1975b) reported a strange phenomenon that, when imogolite was mixed at a rate of 30% with allophane, the mixture behaved the same as imogolite, showing zero mobility above pH 9.

However, when we measured the electrophoretic mobility of very dilute imogolite suspension, we found that the imogolite moved clearly toward the positive electrode above pH 9, which means imogolite possesses electrophoretic negative charge above pH 9. Because this result is different from Wada's (1989), we believe that it is necessary to clarify the colloidal properties of imogolite at high pH.

CLAY SAMPLES

Imogolite samples were separated from fresh soil taken from the upper part of the Kanumatsuchi weathered pumice bed obtained at Kanuma City, Tochigi Prefecture, Japan. The following procedure was used for purification of the samples.

After washing the soil with water, a gel-like substance floated to the surface. This material was collected, oxidized with H_2O_2, treated with Na-citrate-$NaHCO_3$-$Na_2S_2O_3$ (Mehra and Jackson, 1960) and 2% Na_2CO_3 heating at 90°C for 15 minutes in a water bath (Jackson, 1956; modified by Wada and Greenland, 1970). The colloidal particles less than 50 nm in Stokes' diameter were obtained by the centrifugal sedimentation method after dispersion with HCl at pH 4–5. The imogolite colloid was flocculated by adding 100 ml of saturated NaCl solution to each 1 liter of clay suspension collected. The sample was then dialyzed to decrease the ionic concentration of the equilibrated external solution to less than 1 mS/m. In order to remove allophane from the imogolite sample, the sample was treated by diluting it to a very low concentration, adjusting the pH to between 8 and 10 with NaOH, stirring it with ultrasonic waves for about ten minutes, then removing the allophane which was dispersed and separated from the flocculated imogolite after allowing it to stand 3–6 hours. This procedure was repeated approximately 20 times. The basic idea of this treatment is same as that described by Horikawa (1975a). Although the treatment for allophane removal was performed carefully, imogolite samples still contained slight amounts of allophane.

Pure allophane samples were obtained from the fresh soil of the lower part of the weathered Kanumatsuchi pumice bed. After washing the gel-like substances out of the soil with water, allophane was then separated by dispersing the soil at pH 9–10 with NaOH. The other procedure for the preparation of the allophane was almost the same as that for imogolite except for

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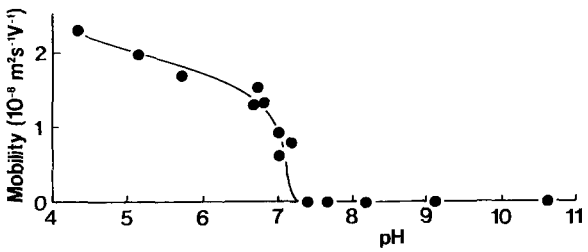


Figure 1. Electrophoretic mobility of imogolite with clay concentration of 1.0×10^{-1} kg/m^3.

the final process of the purification. It was much easier to get pure allophane samples than it was to get pure imogolite samples.

EXPERIMENT

Electrophoretic mobility was measured using a horizontal quartz Briggs-cell having a 0.74 mm inside thickness combined with a microscope and video system. Mobilities were measured after adjusting the pH of the samples with HCl or NaOH and after waiting overnight for the samples to equilibrate. The ionic strengths of the samples were adjusted to 0.004 mol/kg with NaCl, and measurements were performed under a constant electric current. The mobility of the imogolite was measured for two different concentrations (1×10^{-1} kg/m^3 and 5×10^{-3} kg/m^3). Temperature of the sample during the measurements was controlled at 20° ± 2°C.

RESULTS AND DISCUSSION

Mobilities of imogolite obtained from two different clay concentrations

Mobilities shown in Figure 1 are for samples having a clay concentration of 1×10^{-1} kg/m^3. This is a typical clay concentration for electrophoretic measurements.

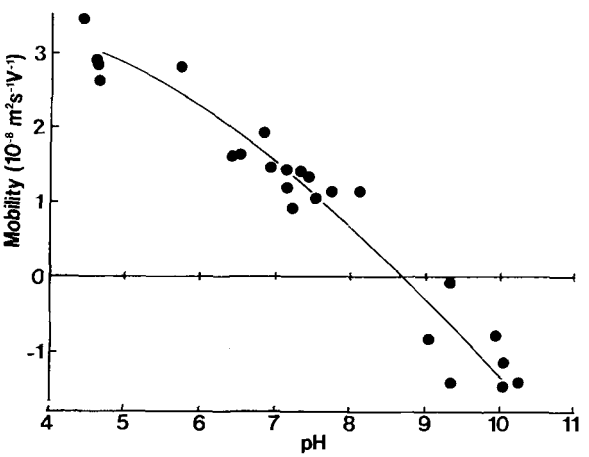


Figure 2. Electrophoretic mobility of imogolite with clay concentration of 5.0×10^{-3} kg/m^3.

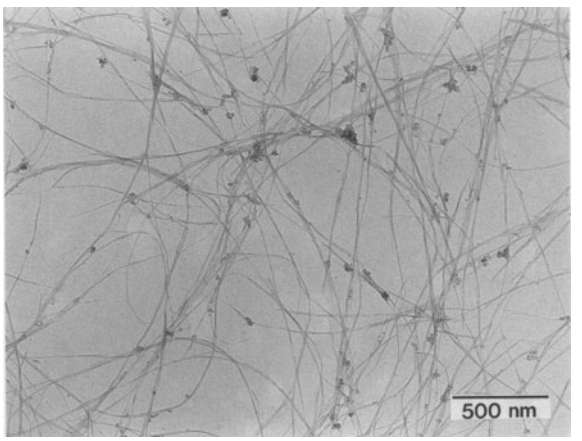


Figure 3. Transmission electron micrograph of imogolite prepared from Kanumatsuchi weathered pumice. Allophane content was estimated to be approximately 5%.

Mobilities showing zero above pH 7.4 are basically the same as those reported by Horikawa (1975a).

Mobilities of these same samples diluted to a concentration of 5×10^{-3} kg/m^3 were measured, and the results are shown in Figure 2. Imogolite showed negative values of mobility above pH 9.

Influence of allophane present in imogolite sample

Purified imogolite samples contained small amounts of allophane as shown in Figure 3. Figure 4 shows an imogolite sample containing 10% added allophane. From several photographs of imogolite samples containing known additions of allophane, it was estimated that the purified imogolite samples contained approximately 5% allophane.

When allophane exists in an imogolite sample, the allophane may affect the mobility of the sample since the allophane shows negative mobility under alkaline conditions as shown in Figure 5; therefore, we made

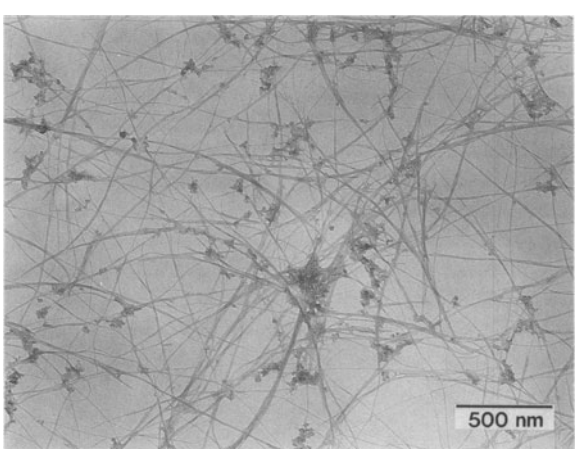


Figure 4. Transmission electron micrograph of a mixture of the imogolite sample used (90 wt.%) and allophane (10%).

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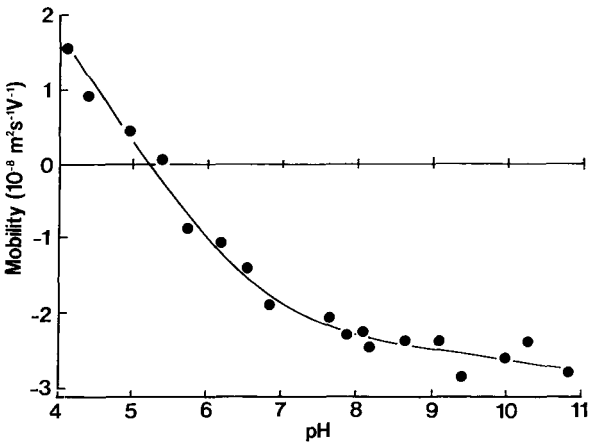


Figure 5. Electrophoretic mobility of allophane with clay concentration of 5.0×10^{-3} kg/m^3.

several samples containing various ratios of allophane and imogolite. Mobilities were then measured with constant clay concentrations of 5×10^{-3} kg/m^3. Figure 6 shows that a linear relationship was obtained between the mobilities and the mixing ratios of allophane and imogolite at pH 9.5. According to Figure 6, the mobility of pure imogolite will appear to have a negative value at pH 9.5, even though the mobility of the imogolite sample was influenced by the presence of allophane.

Peculiar structure of floccules and the viscosity of imogolite

Figure 7 shows the viscosity of imogolite measured by rotation viscometer. It was obtained with the clay

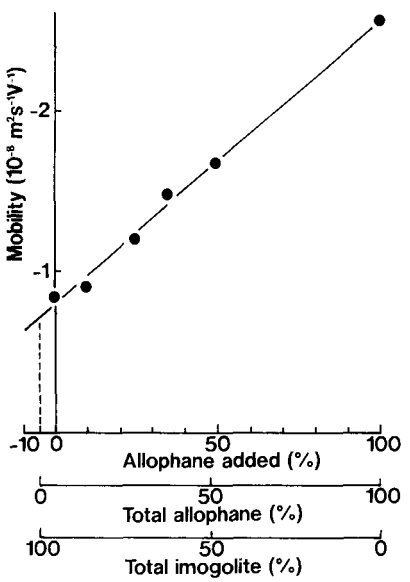


Figure 6. Electrophoretic mobility of imogolite and allophane mixtures with clay concentration of 5.0×10^{-3} kg/m^3, and pH 9.5. Allophane content in the imogolite sample was estimated to be approximately 5%.

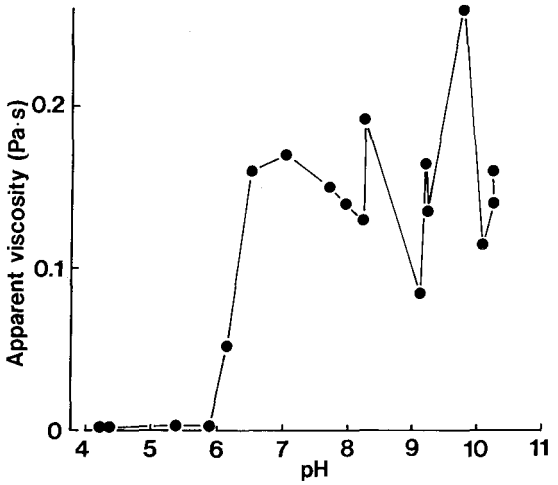


Figure 7. Relation between apparent viscosity and pH of imogolite with clay concentration of 1.0×10^{-1} kg/m^3, and shear rate of 0.6 s^{-1}.

concentration being 1×10^{-1} kg/m^3, which was the same concentration used in the more concentrated samples examined by electrophoretic measurements. The apparent viscosity of imogolite show two different values separated by a boundary point at about pH 6; above the boundary point the viscosities are several orders of magnitude higher than the values below the point. The apparent viscosity shown in Figure 7 is the viscosity measured under the shear rate of 0.6 s^{-1}.

Moreover, imogolite with this clay concentration shows remarkable non-Newtonian flow (thixotropy) above pH 6 as represented by the consistency curve in Figure 8, while it shows Newtonian flow below pH 6. Considering this flow curve at pH 9.15 and that the shear rate at which the mobility is calculated to be 1×10^{-8} $m^2s^{-1}V^{-1}$ is 0.007 s^{-1}, the viscosity of the imogolite under the condition that mobility has been measured must be tremendously high (rough estima-

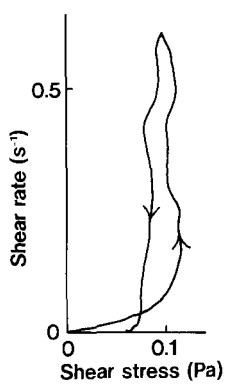


Figure 8. Consistency curve for imogolite suspension with clay concentration of 1.0×10^{-1} kg/m^3, pH 9.15, and ionic strength of 0.004 mol/kg by NaCl.

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tion tells that the viscosity at pH 9 would be about 900 times higher than that at pH 6). This is why the mobility of imogolite is so susceptible to the clay concentration especially under alkaline conditions.

It is easy to observe by an ordinary microscope or even with the naked eye the phenomenon that the fibrous imogolite particles form large floccules and/or become immobilized on the inside surface of a quartz cell.

Conclusions

According to ion exchange measurements (Karube *et al.,* 1990), the point of zero net charge, PZNC (Sposito, 1984) of imogolite is about pH 6 and negative charge predominates under alkaline conditions. On the other hand, according to electrophoretic measurements (Figure 2), the point of zero charge, or PZC, at which mobility of the imogolite shows zero value was found to be pH 8.5–9.0. Negative mobility, detected as migration toward the positive electrode, was confirmed above the PZC. However, as shown in Figure 2, the absolute value of the imogolite mobility is relatively low under alkaline conditions compared to that under acid conditions.

These results are understandable according to the structural model of imogolite (Cradwick *et al.,* 1972) that has the negative charge site on the inside surface of the tube, basically the same as reported by Horikawa (1975a). Since we found imogolite to have negative mobility above pH 9, the influence of the negative charge on the inside surface must extend to the outside of the tube. This effect would increase to a certain extent at high pH but never become high enough to disperse the imogolite itself. Imogolite is easy to flocculate under alkaline conditions due to the unique fibrous shape, thin fiber diameter, and the fact that negative charges arise on the inside surface of the tube structure.

REFERENCES

Cradwick, P. D. G., Farmer, V. C., Russell, J. D., Masson, C. R., Wada, K., and Yoshinaga, N. (1972) Imogolite, a hydrated aluminium silicate of tubular structure: *Nature Physical Sci.* **240,** 187–189.

Harsh, J. B. and Xu, Shihe. (1990) Microelectrophoresis applied to the surface chemistry of clay minerals: *Advances in Soil Sci.* **14,** 131–165.

Horikawa, Y. (1975a) Electrophoretic phenomena of aqueous suspensions of allophane and imogolite: *Clay Science* **4,** 255–263.

Horikawa, Y. (1975b) Electrokinetic behavior of allophane-imogolite mixtures in alkaline media: *Clay Science* **4,** 265–269.

Inoue, T. and Wada, K. (1971) Reactions between humified clover extract and imogolite as a model of humus-clay interaction: Part 1: *Clay Science* **4,** 61–70.

Jackson, M. L. (1956) *Soil Chemical Analysis—Advanced Course,* published by the author, Madison, Wisconsin, 71–76.

Karube, J., Sugimoto, H., and Nakaishi, K. (1990) Charge characteristics and electrophoretic mobility of allophane and imogolite: *Nogyodoboku Abstract of Annual Meeting* (in Japanese), 322–323.

Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate: in *Clays & Clay Minerals,* Proc. 7th Natl. Conf., Washington, D.C., 1958, Ada Swineford, ed., Pergamon Press, New York, 317–327.

Sposito, G. (1984) *The Surface Chemistry of Soils:* Oxford University Press, New York, 81.

Wada, K. and Greenland, D. J. (1970) Selective dissolution and differential infrared spectroscopy for characterization of "amorphous" constituents in soil clays: *Clay Miner.* **8,** 241–254.

Wada, K. (1989) Allophane and imogolite: in *Minerals in Soil Environments,* J. B. Dixon and S. B. Weed, eds., Soil Sci. Soc. Am., Madison, Wisconsin, 1051–1087.

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