

ZETA POTENTIALS OF CLAY MINERALS ESTIMATED BY AN ELECTROKINETIC SONIC AMPLITUDE METHOD AND RELATION TO THEIR DISPERSIBILITY

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ABSTRACT

Zeta (ζ) potential of clay minerals, which affects the dispersion and the flocculation in their water suspension, is generally determined by an electrophoresis method. This method is, however, required the diluted suspension system which is thoroughly dispersed, and needs considerably long times for the measurement. An electrokinetic sonic amplitude (ESA) method for the ζ -potentials was applied to four kinds of Na^+ -saturated clay minerals, kaolinite, halloysite, montmorillonite and allophane. The pH-dependence of ζ -potential was discussed comparing with the changes of their mean particle or aggregate sizes determined by a laser scattering method. The ζ -potential of kaolinite, halloysite, montmorillonite and allophane was -22 , -15 , -25 and -50 mV in the clay samples saturated with Na^+ at about pH 7.0, respectively. These approximated to the values reported in the previous studies. The ζ -potential of clay minerals estimated with the ESA method was clearly related with the dispersibility of their suspension at various pHs. The ESA method was effective for the estimation of ζ -potential of clay minerals, in conclusion.

Key words: Electrokinetic sonic amplitude, Dispersion and flocculation, Zeta potential of clays

INTRODUCTION

Zeta (ζ) potential, an electrokinetic phenomenon on the surface of clay minerals, affects the dispersion and the flocculation in their water suspension (Kida, 1962; Watanabe, 1966; Wada, 1981). The ζ -potentials of clay minerals have been generally determined by an electrophoresis method. This method is, however, required the diluted suspension system which is thoroughly dispersed, and needs considerably long times for the measurement (Furusawa, 1996). The features of dispersion and flocculation of clay particles in various pH are not directly observed by this method, in consequence. In addition to this electrophoresis method, the phenomena such as electroosmosis, streaming potential and sedimentation potential also have been applied for the estimation of ζ -potential in colloidal particles (Furusawa, 1996). Recently, Tone et al. (1997) and Tone et al. (1998) determined the ζ -potential of kaolin minerals by an ultrasonic vibration potential (UVP) method.

An electrokinetic sonic amplitude (ESA) method, which is similar to the UVP one, for the estimation of ζ -potentials was discussed by using four kinds of clay minerals, in this study. Moreover, their pH-dependence was also tested comparing with the changes of the

mean size of particles or aggregates determined by a laser scattering method, and their dispersibility were discussed.

The fundamentals of the ESA method are as follows (Furusawa, 1996): The ultrasonic waves are generated when the electromagnetic waves are radiated in the suspension of colloidal particles. The generated ultrasonic waves are measured with a detector by applying the piezoelectric effect, and the ζ -potential of the colloidal particles is determined. This ESA effect had been discovered by Oja et al. (1985). Ozaki (1995) pointed out that the ESA method need not observe the movement of individual particle, and is able to measure ζ -potential in the considerably high concentration systems, accordingly. The ζ -potential is obtained from a function of volume ratio of particle, angular frequency of applied electromagnetic wave, density of particle and dispersion medium, sound velocity in dispersion medium, permittivity of vacuum, specific permittivity of dispersion medium, viscosity of dispersion medium, and correction term.

MATERIALS AND EXPERIMENTAL METHODS

Four kinds of clay minerals were used in this study. Indonesia Kaolin, Longgan kaolin in China, Kunipia-F bentonite in Japan and Kanuma-tsuchi weathered pumice in Japan was used as the clay-mineral sample of kaolinite, halloysite, montmorillonite and allophane, respectively. The fraction less than 2 μm in diameter was prepared by a sedimentation method from each sample. Then, Na^+ -saturated clay samples were prepared by washing with NaCl solution and distilled water, and were provided for the following experiments. The purity of each sample was checked by a X-ray diffraction method, and very small amount and a small amount of mica minerals was confirmed in kaolinite and halloysite sample, respectively. Organic contaminants were not detected in all samples by thermal analyses.

The ζ -potential of clay mineral samples was estimated with an ESA apparatus, ESA-8000, developed by Matec Applied Science, USA. The frequency of electromagnetic wave is automatically adjusted to gain the maximum potential value in the range of 0.8–1.2 MHz inside this apparatus. The procedure was as follows: Clay mineral specimen of 0.3 g was suspended thoroughly in 300 ml of distilled water, then the pH of suspensions was adjusted by adding 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH, and the ζ -potential were measured. The potential was determined from the average value of five times measurements at each pH.

The mean size of clay particles or aggregates was estimated by a laser scattering method after Kurihara et al. (1999), using a Horiba, LA910-type laser scattering particle size distribution analyzer. The concentration of suspension was kept its absorbance to be about 70% in all measurements. The suspension was previously treated with an ultrasonic wave of 39 kHz and 40 W for five minute before the determination procedure of particle or aggregate size, and the measurement was repeated three times. The pH of suspensions was also adjusted in the same way as the measurement of ζ -potential.

The pH of suspensions was measured with a glass electrode. The content of aluminum and silicon, which were dissolved in the dispersion medium at extremely high or low pH, was determined by an atomic absorption spectrometry and a colorimetry with molyb-

denum blue, respectively.

RESULTS AND DISCUSSION

The ζ -potentials of Na^+ -saturated kaolinite, halloysite, montmorillonite and allophane with the pH changes estimated by the ESA method are present in Figure 1 to 4. For the calculation of these ζ -potentials, the value of 2.65, 2.55, 2.50 and 2.75 Mg m^{-3} was given as the density of kaolinite, halloysite, montmorillonite and allophane, respectively (Kitagawa, 1976; Egashira, 1987). Then the value of 2.56, 1.72, 1.30 and 13.7 μm was given as the mean particle size of kaolinite, halloysite, montmorillonite and allophane that was obtained by the laser scattering method. The ζ -potential obtained by using above parameters for kaolinite, halloysite, montmorillonite and allophane was 22 ± 2.1 , 15 ± 2.0 , 25 ± 2.0 and 50 ± 14 mV at pH 7.0, respectively.

The ζ -potential of kaolinite was +4, -2, -22 and -24 mV at pH 3.0, 4.0, 7.0 and 9.0, respectively. This value was -43 mV at pH 11.0, and decreased suddenly above pH 10. The potential of halloysite was 0, -15 and -28 mV at pH 3.0, 7.0 and 11.0, respectively, and the negative potential increased largely above pH 10. The ζ -potential of montmorillonite was constantly about -25 mV below pH 9, and increased negatively above pH 10. On the other hand, the ζ -potential of allophane was varied largely from positive to negative depended on pH of suspension, and was +490, +75, +32, -20, -50, -78, -67 and -83 mV at pH 2.0, 3.0, 5.0, 6.0, 7.0, 8.0, 10.0 and 11.0, respectively. The potential of allophane also increased negatively in high pH region, but the process of its increase was not smooth. The positive potential of allophane increased extremely below pH 3. This should be due to partial destruction of chemical structures in very low pH regions as mentioned below. Watanabe (1966) estimated the ζ -potential of clay minerals by the electrophoresis method, and showed that the potential of kaolinite at neutral pH is -52 mV which rises in the acid side as the decrease of pH but almost constant in the alkaline side, and that of allophane is -36 mV which rises largely to positive in acid side but declines gradually in alkaline side. Horikawa et al. (1988) reported -30 to -60 mV as the ζ -potential of Na^+ -saturated montmorillonite in various electrolyte concentration by the electrophoresis method. Tone et al. (1997) and Tone et al. (1998) determined the ζ -potential of kaolin minerals by the UVP method, and presented about -30 mV at neutral reaction, which varies toward positive as the decrease of pH but lowers a little in the alkaline side. According to Furusawa (1996), the ζ -potential of a kaolin mineral is -28 and -26 mV at pH 4.4, and -37 and -43 mV at pH 9.8 estimated by the ESA method and the electrophoresis method, respectively. Moreover, the negative value obtained by the ESA method is slightly lower than by the electrophoresis one, in general. This should be influenced by the difference of electrolyte concentration in suspension. The ζ -potentials of clay minerals obtained in this study approximated to the values reported in the previous studies, although they were a little small compared with the latter, especially in the electrophoresis of crystalline clay minerals except allophane.

In the crystalline minerals such as kaolinite, halloysite and montmorillonite, their ζ -potentials decreased suddenly above pH 10. This should be caused by the partial dissolution of silicon and aluminum from the structural lattice of clay minerals. In fact, the

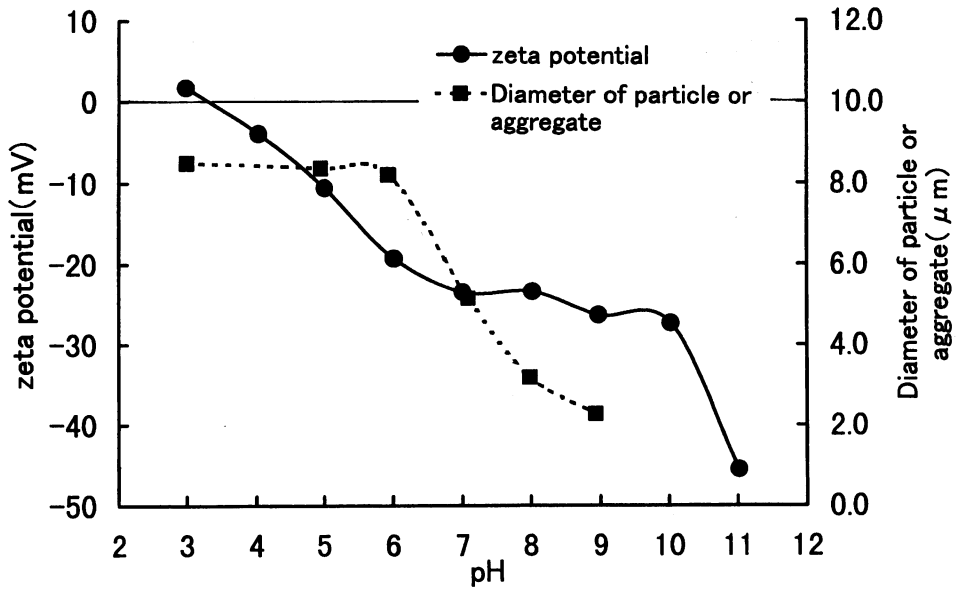


FIG. 1. Changes of ζ -potential and particle or aggregate size of Na⁺-saturated kaolinite with pH.

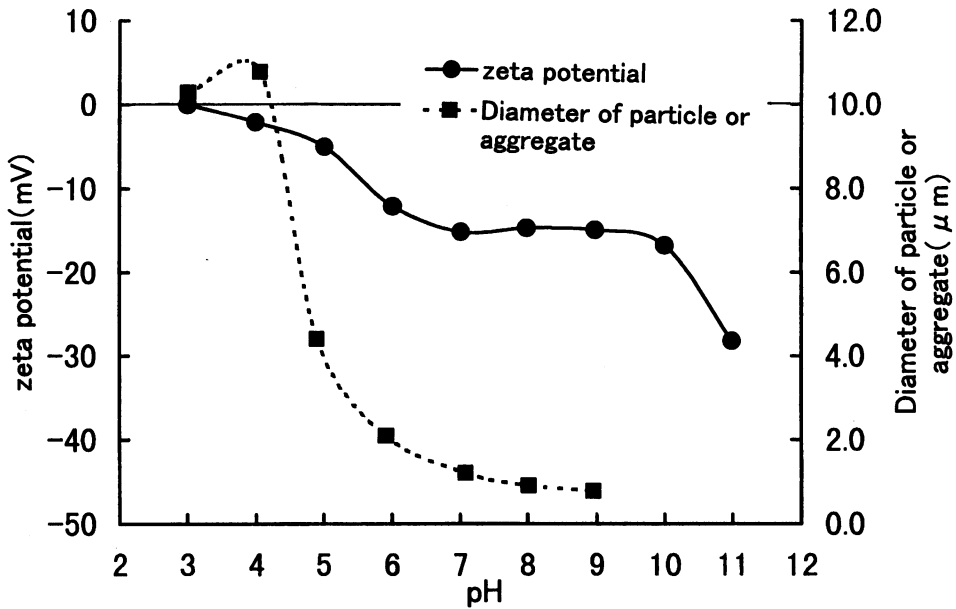


FIG. 2. Changes of ζ -potential and particle or aggregate size of Na⁺-saturated halloysite with pH.

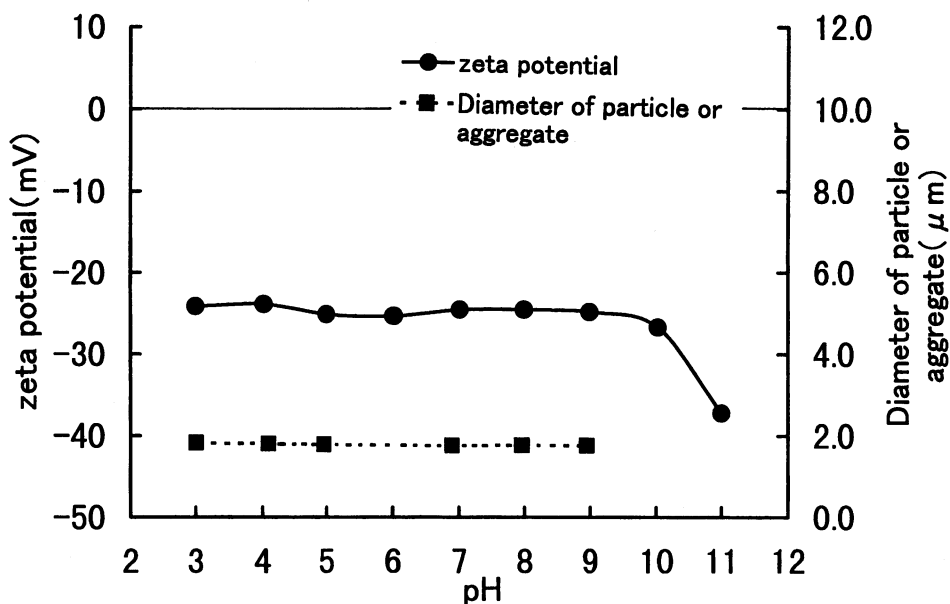


FIG. 3. Changes of ζ -potential and particle or aggregate size of Na⁺-saturated montmorillonite with pH.

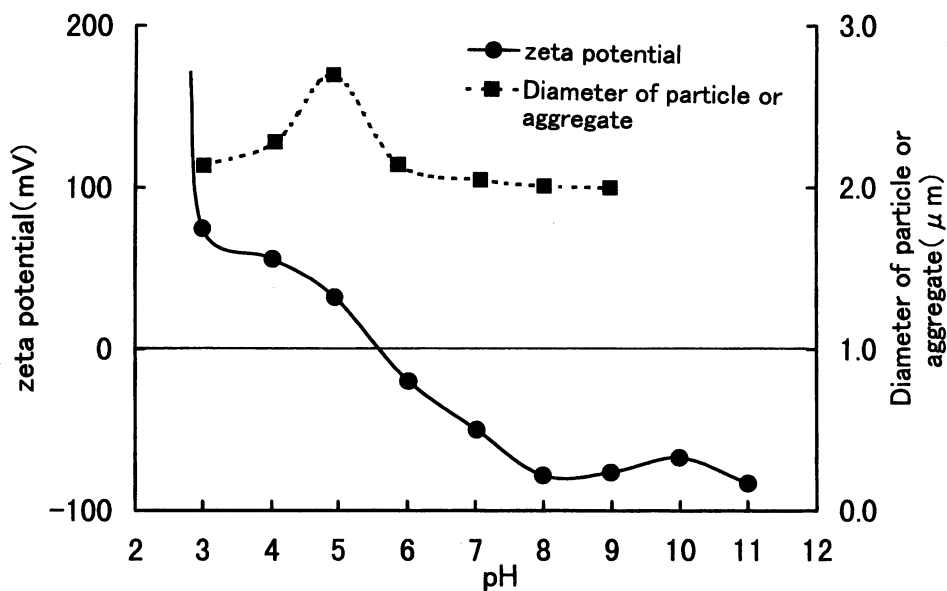


FIG. 4. Changes of ζ -potential and particle or aggregate size of Na⁺-saturated allophane with pH.

dissolved amounts of these elements increased in the regions under pH 3 and above pH 11 compared with near neutral pH as shown in Table 1, and were especially much in the high pH regions. The magnitude of ζ -potential of allophane, amorphous mineral, extremely increased, and silicon and aluminum also dissolved in the pH regions below 3 (Table 1), more seriously than crystalline minerals. These results suggested that the ζ -potentials of clay minerals were significant only between pH 3 and 10 owing to the stability of their chemical structures.

The mean diameters of particles or aggregates in the suspension of clay minerals estimated by the laser scattering method with the pH changes of dispersion medium are also shown in Figure 1 to 4. The mean particle or aggregate size of kaolinite and halloysite decreased with the increase of pH. This indicated that the dispersibility of kaolin minerals become higher in the alkaline medium than in acid one. In montmorillonite, its mean diameter was almost independent of the pH changes, and showed the high dispersibility in all pH regions. The particle or aggregate diameter of allophane was maximum near pH 5. The allophane particles not only dispersed in alkaline medium but also did in the acid regions below pH 4, because they have amphoteric charge.

In kaolinite and halloysite, both the ζ -potential and the particle or aggregate diameter decreased with the increase of pH as mentioned before, and their negative charge was a little and variable. The dispersibility of kaolin minerals was high in alkaline medium, because their charges originate in the dissociation of hydroxyl groups at the edge of crystal lattice. The ζ -potential and the particle size of montmorillonite were almost independent of the pH changes below pH 10 (Figure 3). The high dispersibility of montmorillonite in all pH regions indicated their abundant permanent charge resulting from the isomorphic substitution of magnesium or iron for aluminum in the structural lattice. This changes of ζ -potential and dispersibility with the pH also reflected the difference of particle shape or cation holding position between kaolin minerals and montmorillonite. Montmorillonite shows very thin paper-like particle and holds exchangeable cations mainly in their in-

TABLE 1. Dissolution of silicon and aluminum in suspensions of Na-saturated clay-mineral with pH change of dispersion medium

Clay minerals	pH	Dissolved, Si	mmol kg ⁻¹ Al
Kaolinite	2.7	1.4	1.7
	6.3	1.0	0.4
	10.9	8.6	17.1
Halloysite	2.7	2.6	17.4
	6.3	1.6	0.7
	11.1	13.2	46.7
Montmorillonite	2.6	13.1	37.7
	6.7	7.9	16.3
	11.1	18.2	62.8
Allophane	2.5	40.4	55.3
	6.9	10.4	3.7
	10.4	19.9	25.5

terlayer position. The ζ -potential of allophane varied largely from positive to negative depended on pH, and their diameter of particle or aggregate became maximum near pH 5 (Figure 4). The charge of allophane is mostly dependent on pH as well-known, and its positive charge originates by protonation of aluminol OH in acid side and negative charge by dissociation of both silanol and aluminol OH in alkaline side. Allophane showed an isoelectric point near pH 5.5 (Figure 4). This value coincided closely with the zero point of charge determined by an ion adsorption method (Itami et al., unpublished). The dispersibility of allophane decreased at an isoelectric point of about pH 5.5. It is indicated that the ζ -potential of each clay minerals was clearly related with their dispersibility in the suspension of various pHs.

CONCLUSION

The ζ -potentials of Na⁺-saturated kaolinite, halloysite, montmorillonite and allophane with the pH changes between 3 and 10 were estimated by the ESA method. Moreover, the changes of their mean particle or aggregate size from pH 3 to 9 also observed by the laser scattering method for the discussion of their dispersibility. The ζ -potential of kaolinite, halloysite, montmorillonite and allophane at neutral pH was -22, -15, -25 and -50 mV, respectively. The potentials of kaolin minerals decreased almost in the negative region, and their dispersibility increased, with the increase of pH. The ζ -potential and the dispersibility of montmorillonite were not varied with the pH changes. Allophane had the ζ -potential varied largely from positive to negative with the pH changes, and an isoelectric point at about pH 5.5. The dispersibility of allophane decreased especially between pH 4 and 6.

The ζ -potential of each clay minerals obtained in this study approximated to the values reported in the previous papers estimated by several methods. The change of ζ -potential was related to the dispersibility of each clay mineral in the suspensions of various pHs. This ESA method was effective for the estimation of ζ -potential of clay mineral, in conclusion. The discussion on clay minerals that are saturated with various cations except Na⁺, and on soil colloids should be remained as the future problems.

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