



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Charge Characteristics of Nano-Ball Allophane as Affected by Zinc Adsorption

¹Adel Ghoneim, ¹Naoto Matsue, ²Azza Ebid and ¹Teruo Henmi

¹Environmental Soil Science Laboratory, Faculty of Agriculture, Ehime University,
3-5-7 Tarumi, Matsuyama 790-8566, Japan

²Department of Bioresource Production, Faculty of Agriculture,
Ehime University, Hojo, 799-2424, Japan

Abstract: Effect of Zn adsorption on the change in charge characteristics of two nano-ball allophane samples with different Si/Al ratio at various pH values was studied. The Cation Exchange Capacity (CEC) values of the two nano-ball allophane samples were likely to decrease whereas Anion Exchange Capacity (AEC) increased after Zn adsorption at initial concentration of 0.18 mM. The change in charge characteristics of the allophane samples was controlled by equilibrium pH, amounts of Zn adsorption and Zn species in the solution. The decrease in CEC values after Zn adsorption was due to neutralization reactions between cationic Zn with Si-O⁻ functional groups. The decrease in CEC values was found to be higher in case of allophane sample with higher Si/Al ratio (KnP) than that with lower Si/Al ratio counterpart (KyP), due to its higher adsorptive capacity for Zn species. The slight increase in the AEC values after Zn adsorption was probably due to in part to the initial H⁺ ions released into the bulk solution. Molecular orbital calculation indicated that the adsorbed Zn species has a ability to accelerate the deprotonation of undissociated Si-OH groups near the adsorption sites by an inductive effect.

Key words: Zinc adsorption, allophane, surface charge, molecular orbital analysis, inductive effect

INTRODUCTION

Nano-ball allophane as a variable charge mineral has Cation Exchange Capacity (CEC) strongly dependent on electrolyte concentration, type of cation, solution pH and the method of determination. In addition, nano-ball allophane as a pH-dependent clay mineral has unique characteristics: it can have both negative and positive charges simultaneously. The main positive and negative charges are separated each other in the nano-ball allophane structure as shown in Fig. 1. The positive charges result from aluminol groups (Al-OH₂⁺) located at the pore region of the ball of allophane whereas the negative charges come from silanol groups (Si-O⁻) at inner side of the nano-ball allophane structure. These charge characteristics are different from those of the other pH-dependent clay minerals such as goethite and gibbsite (Parfitt, 1980).

The CEC and AEC values either decrease or increase depending upon materials adsorbed. The increase in CEC and declining AEC values have been reported after sulfate (Padilla *et al.*, 2002), molybdate (Elhadi *et al.*, 2001), citrate

(Hanudin *et al.*, 2000) and phosphate (Johan *et al.*, 1999) adsorption on the nano-ball allophane samples. The increase in the CEC values were attributed to charges brought into the nano-ball allophane by anionic forms of the compounds adsorbed. Recently, allophane in soils has been attracting considerable attention because of its significant contribution to the physical and chemical properties of tropical soils.

In our earlier study on Zn adsorption by the nano-ball allophane samples at various pH values (Ghoneim *et al.*, 2001; Ghoneim, 2002) indicated that the noticeable amounts of Zn were adsorbed by allophane samples under different pHs and the equilibrium solution pH decreased after the adsorption. Moreover, the adsorption was dependent on the difference in the chemical structure between nano-ball allophane samples and on Zn species. However, the effect of Zn adsorption on surface chemical characteristics of allophane, such as CEC and surface acidity, has not been investigated. Because Zn species adsorb strongly to oxygen atoms of functional groups of allophane (Ghoneim *et al.*, 2001), the Zn-adsorbed allophane as a newly formed compound

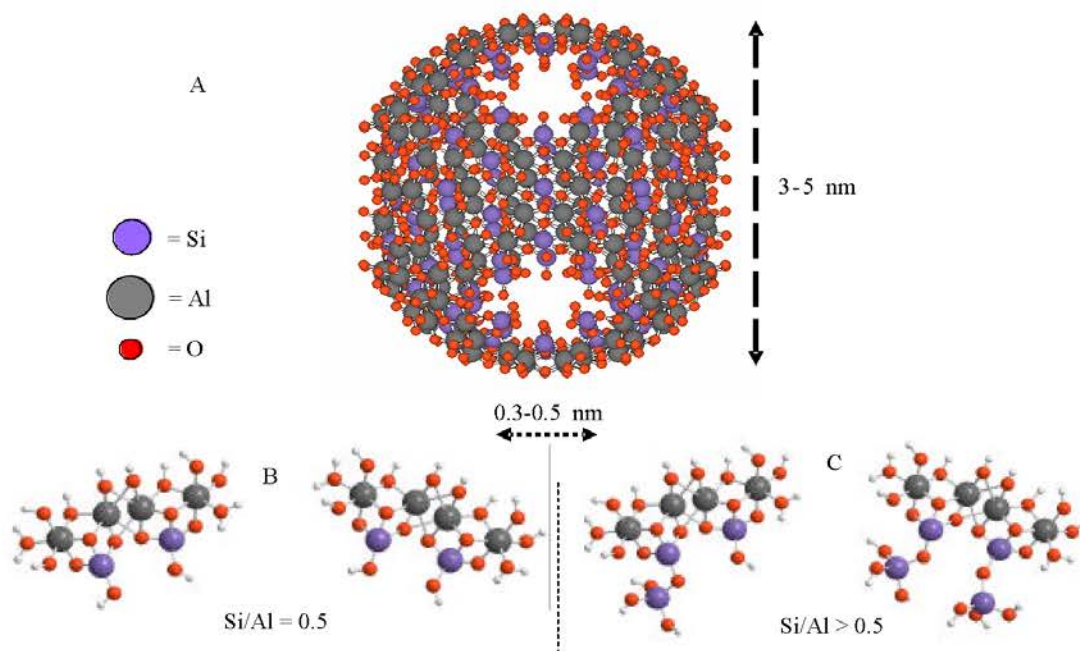


Fig. 1: Morphology and chemical structure of nano-ball allophane (A: morphology in section; B: atomic arrangement near the pore; C and D: atomic arrangement in cross section near the pore)

has different properties from the original allophane. The aim of this research was therefore to know the mechanism of change in charge characteristics of the nano-ball allophane as affected by Zn adsorption.

MATERIALS AND METHODS

Allophane samples: The study was conducted at Environmental Soil Science Laboratory, Ehime University, Japan, during 2001-2005. Two allophane samples were used in this study: one was designated as KyP with low Si/Al ratio (0.67) collected from Tottori prefecture near Mt. Daisen, Japan and KnP with high Si/Al ratio (0.99) collected from Kumamoto prefecture, near Mt. Aso, Japan. Fine clay fraction ($< 0.2 \mu\text{m}$) was separated from inner part of pumice grains after removing outer part to eliminate any possible contaminations such as volcanic glasses, opaline silica and imogolite. The separation was carried out by ultrasonification at 28 kHz followed by dispersion at pH 4 for KyP sample or pH 10 for KnP sample as described by Henmi and Wada (1976). The collected samples were flocculated by NaCl solution, washed with distilled water to remove excess salts and then freeze-dried. The freeze-dried samples were subjected to electron microscopy, IR, DTA and chemical analysis (data not shown) to ascertain the purity of the sample. The results indicate that the

sample were free from the impurities described above. Atomic arrangement near the defect (pore) of hollow spherical nano-ball allophane with low Si/Al ratio is shown in Fig. 1B. That of allophane with high Si/Al ratio is shown in Fig. 1C, wherein some accessory silicon is attached and dimeric or polymeric SiO_4 tetrahedra are formed.

Zinc adsorption, CEC and AEC measurements: Zinc adsorption was carried out by equilibrating 50.0 mg of the freeze-dried KyP and KnP allophane samples with 100 mL of mixed solutions of ZnCl_2 and NaCl in 250 mL pre-weighed centrifuge bottles. The pH levels of the solutions were adjusted between 3 and 10 (initial pH) by adding either HCl or NaOH solutions. The final Zn concentration varied from 0.0 to 0.18 mM and Na concentration as background media was kept at 10 mM. The suspensions were shaken for 24 h, centrifuged at 3500 rpm for 20 min after which equilibrium pH of the supernatant was measured. Further, the level of Zn and Na concentrations in the supernatant were determined by using Polarized Zeeman Atomic Absorption Spectrophotometer (Z-5000). The CEC and AEC values of the samples were determined according to the modified equilibrium method (Schofield, 1949). After the Zn adsorption experiment, the centrifuge bottle plus their content was weighed after decanting the

supernatant to calculate the volume of entrained solution. Then, 50 mL of 1M NH_4NO_3 solution was added to the contents of the centrifuge bottles, shaken for 5 h and then, centrifuged and the NH_4NO_3 supernatant decanted and kept. The last step was repeated one more time and the levels of Na and Cl concentration in the supernatant were determined. The Na was determined by atomic absorption spectroscopy and Cl by colorimetry according to the method of Huang and Johns (1967). The CEC and AEC values were calculated as the difference in Na and Cl between extracted and entrained. To find out the more possible reactions proposed, MOPAC 2002 program with AM1 basis set as a semi empirical molecular orbital method was employed. The cluster models for allophane were built up with Si tetrahedra and Al octahedra by using bond distances of Si-O = 0.1618 nm, Al-O = 0.1912 nm and O-H = 0.0944 nm.

RESULTS AND DISCUSSION

Change in charge characteristics: Charge characteristics of the two nano-ball allophane samples, KyP and KnP, with and without Zn adsorption in 10 mM NaCl background solution are shown in Fig. 2 and 3. The CEC values of the original allophane samples tended to increase while the AEC decreased with increasing equilibrium solution pH. Shape of the pH-CEC curves of the original samples was a representative of nano-ball allophane as reported by Padilla *et al.* (2002), Nartey *et al.* (2001), Hanudin *et al.* (2000) and Johan *et al.* (1999). The CEC value for the original KnP allophane sample was higher than for the KyP. This result is attributed to the difference in the chemical structure between the two nano-ball allophane samples as shown in Fig. 1. The higher amounts of the negative charges for the KnP sample prove the existence of more polymeric SiO_4 tetrahedra attached to the main frame of nano-ball allophane structure, which causes an increase in the K_a value of the Si-OH group in the nano-ball allophane structure. Fundamental structure of the nano-ball allophane as proved (Henmi *et al.*, 1997; Matsue and Henmi, 1993) has Si/Al ratio of 0.5, the imogolite structure and the additional polymeric SiO_4 tetrahedra increase the ratio. Therefore, the KnP allophane sample with a higher Si/Al ratio is considered as the SiO_4 adsorption product of the lower Si/Al ratio (KyP) and the adsorbed SiO_4 tetrahedra let to increase the amounts of negative charge.

Figure 2 and 3 also shows AEC plots, evaluates the positive charge sites on the allophane samples as a function of solution pH. As expected, the AEC values

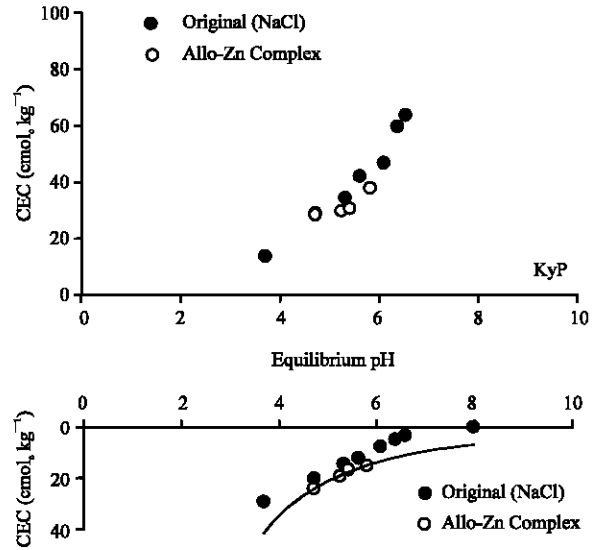


Fig. 2: Charge characteristics of the KyP sample before and after Zn adsorption. Initial concentration was: 0.18 mM

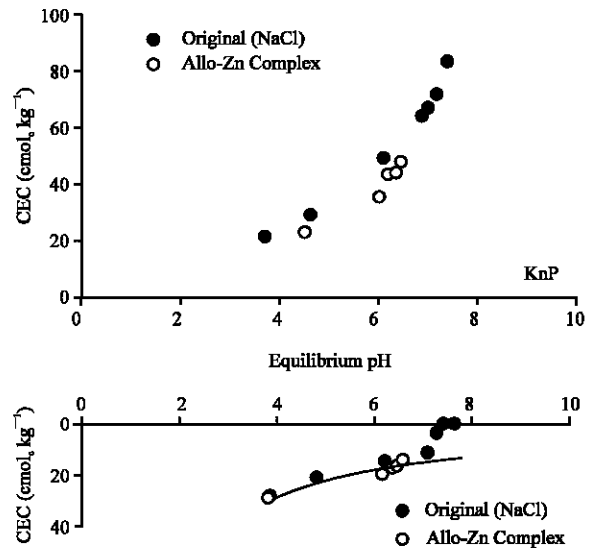


Fig. 3: Charge characteristics of the KnP sample before and after Zn adsorption. Initial concentration was: 0.18 mM

decreased as the equilibrium solution pH increased, reflecting the deprotonation of the surface hydroxyl groups and the consequently the reduction in the positive charge. The AEC values were found to be generally higher in KyP allophane sample with a lower Si/Al ratio than for KnP. This was attributed to the higher Al content per unit mass of the KyP sample. The aluminol group content per unit mass decreased with the rising of the

Si/Al ratio of the allophane sample (Son *et al.*, 1998). In addition, abundance of the attached polymeric SiO₄ tetrahedra, which cause a steric hindrance effect on the aluminol groups at the pore region of the nano-ball allophane, explain the lower AEC values for the KnP than for the KyP even at the same equilibrium pH values.

It was seen between equilibrium pH of 4 and 8, that the two original allophane samples have both negative and positive charges (Fig. 2 and 3). These strikingly unique characteristics of the nano-ball allophane unlike the other pH-dependent clay minerals such as gibbsite and goethite (Parfitt, 1980) are attributed to the difference in the location of the silanol and aluminol functional groups in the nano-ball allophane structure (Fig. 1).

Effect of zinc adsorption on CEC and AEC: The obtained CEC values of the two nano-ball allophane samples tended to decrease after Zn as shown in Fig. 2 and 3 for the KyP and KnP, respectively. The decrease in the CEC value from the original sample was found to be slightly higher in KnP than in KyP. The decrease in the CEC values after Zn adsorption on nano-ball allophane was accompanied by release of H⁺ into bulk solution (Ghoneim *et al.*, 2001; Ghoneim, 2002). The release of H⁺, which was found to be higher in case of KnP than for the KyP, could be an indication of its greater decrease in the CEC values than for KyP. The observed increase in CEC after anions adsorption was attributed to the charge carried by the anions and to the new negative charges created on Si–OH groups near the adsorption site due to an inductive effect (Padilla *et al.*, 2002; Nartey *et al.*, 2001). The decrease in the CEC value with Zn adsorption is attributed to neutralization reactions between the dissociated Si–O⁻ functional groups with the positive species of Zn.

Substantial decrease in AEC values has been reported after adsorption of anions on the nano-ball allophane samples (Padilla *et al.*, 2002; Nartey *et al.*, 2001; Elhadi *et al.*, 2001; Hanudin *et al.*, 2000). In these studies, the decreases in AEC values were thought to be due to neutralization of positive charges Al–OH₂⁺ by the anionic form of the compounds adsorbed. In the current work, a slight increase in the AEC values was found for the two nano-ball allophane samples after Zn adsorption (Fig. 2 and 3). This is probably due to in part to the initial H⁺ released into the bulk solution after Zn adsorption, which may have reacted with Al–OH functional group to form the new positive charge, Al–OH₂⁺ (Ghoneim, 2002).

The net change in the CEC (Δ CEC) was calculated as the difference between CEC values before and after Zn adsorption at a same equilibrium pH value. Figure 4 shows

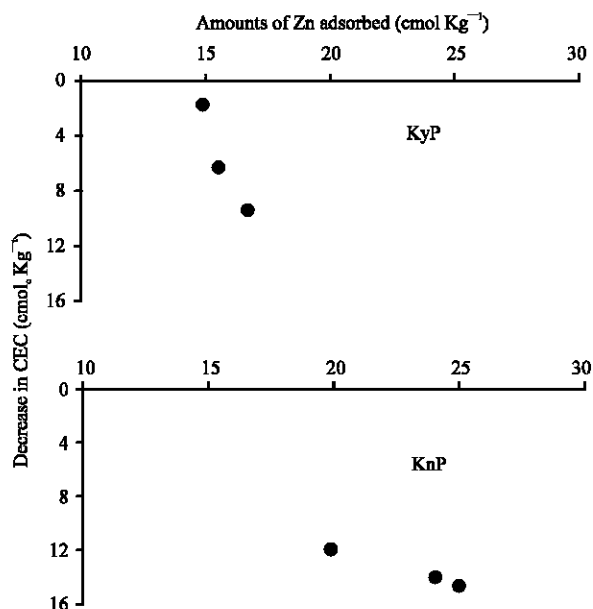


Fig. 4: Relationship between change in CEC and amounts of Zn adsorbed. Initial concentration was: 0.18 mM

relationship between amounts of Zn adsorbed and Δ CEC of the nano-ball allophane samples at initial Zn concentration of 0.18 mM. The amounts of Zn adsorbed on KyP were 14.9, 15.5 and 16.7 cmol kg⁻¹ at initial solution pHs of 4, 6 and 7, respectively and the consequent Δ CEC values were -1.9, -6.4 and -9.3 cmol_c kg⁻¹, respectively. For KnP sample, the amounts of Zn adsorbed was higher than that for KyP (19.9, 24.1 and 25.0 cmol kg⁻¹) at initial solution pHs of 4, 6 and 7, respectively and the equivalent Δ CEC values were also higher (-12.1, -14.1 and -14.4 cmol_c kg⁻¹, in that order). The calculated Δ CEC values for KnP was higher than for KyP and this was most likely due to the fact that the KnP, allophane sample with a higher Si/Al ratio, showed a higher adsorptive capacity for Zn species than for the KyP sample (Ghoneim *et al.*, 2001; Ghoneim, 2002).

In all cases, the amounts of Zn adsorbed were higher than Δ CEC of the two samples (Fig. 4). It is noticed here that the obtained CEC value in this study is the amount of Na adsorbed on allophane sample when the Zn adsorption is in equilibrium. The higher amount of Zn adsorption compared with decrease in CEC (decrease in adsorbed Na) indicates that Zn exchanged not only exchangeable Na but also H of Si–OH group on allophane.

The amount of Zn adsorption was higher in KnP than for KyP sample at a same initial Zn concentration (Ghoneim *et al.*, 2001). To compare the effect of Zn adsorption on CEC between the two allophane samples at

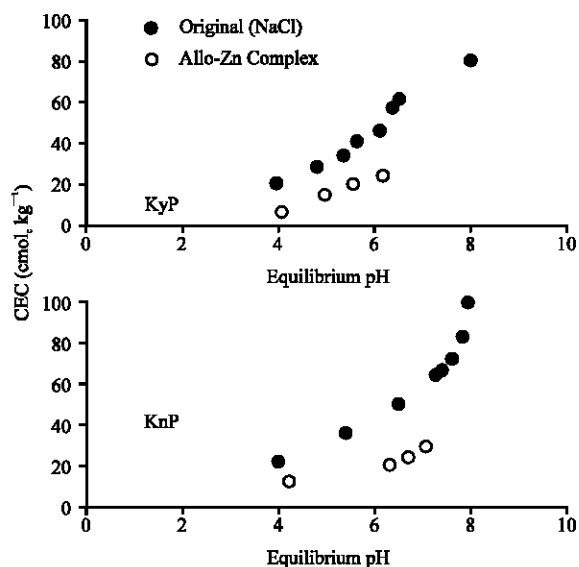
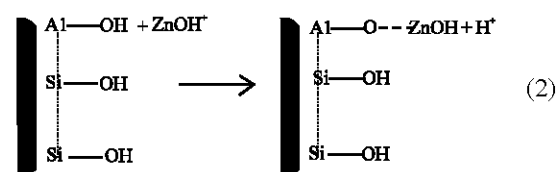
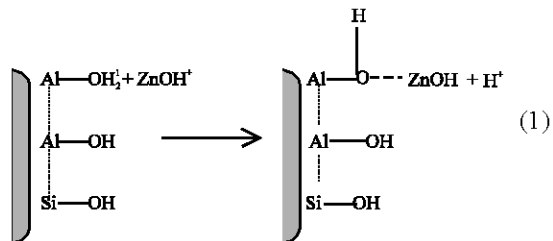


Fig. 5: Relationship between CEC before and after Zn adsorption. Constant adsorption of: 15.0 cmol kg⁻¹

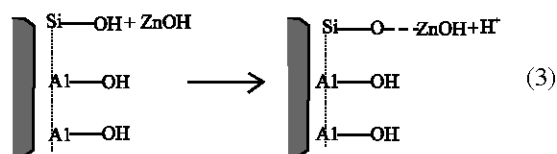
a same Zn adsorption level, constant adsorption experiments were carried out. Figure 5 shows the pH-CEC plots of KyP and KnP samples with a constant Zn adsorption of 15.0 cmol kg⁻¹, together with those of the original samples (Zn = 0). The higher the equilibrium pH, the greater the ΔCEC or Na adsorption, for the two samples. This means that at higher pH, the added Zn tended to preferentially exchange Na adsorbed on Si-O⁻ group on allophane as a cation exchange reaction. The results in Fig. 5 also indicate that the decrease in CEC (ΔCEC) was higher in case of KnP sample than for KyP, at a same equilibrium pH. A possible change in the form of Zn, from the polyvalent Zn²⁺ to monovalent ZnOH⁺ at higher pH, could be another factor controlling the adsorption. These results suggest that the equilibrium pH, amounts of adsorption and species of Zn are the main factors controlling adsorption of Zn by nano-ball allophane samples. The molecular orbital calculation confirmed that the bond length between Zn atom and O atom of the silanol group (Si-O⁻) was shorter for ZnOH⁺ than for Zn²⁺, indicating that the possibility of ZnOH⁺ adsorbed stronger than Zn²⁺ on the nano-ball allophane at higher pH.

Proposed mechanism of the change in charge characteristics: The adsorption sites of the nano-ball allophane for the positive forms of Zn are mainly Al-OH₂⁺, Al-OH and Si-OH functional groups. The adsorption

mechanisms might therefore be written as follows. Al-OH₂⁺ and Al-OH existed at the pore region of nano-ball allophane and the reactions are schemed as:

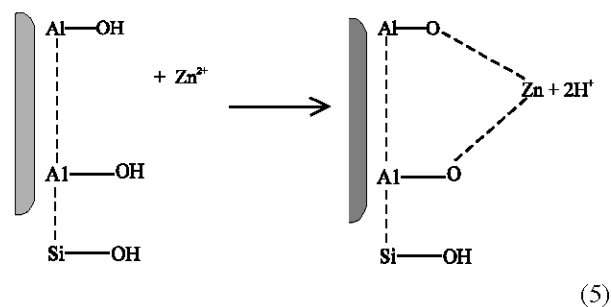
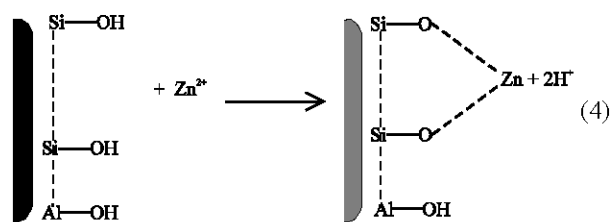


Reaction with Si-OH is illustrated as:



Equations 1 to 3 portray Zn adsorption as monodentate reactions, where one H⁺ was released into the bulk solution.

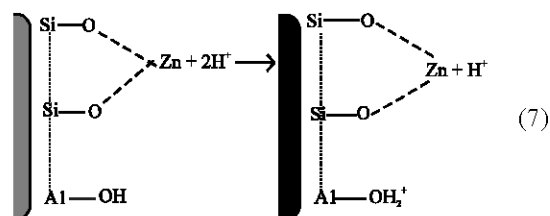
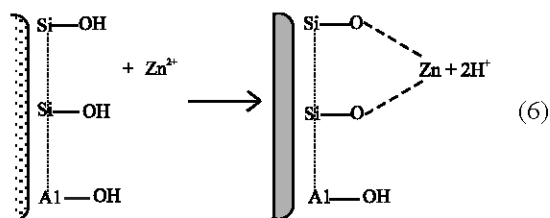
Zinc would react with two silanol or aluminol groups (reactions 4 and 5), by binuclear reaction in which two H⁺ are released into the solution.



The adsorption of Zn was represented as specific adsorption with release of two H⁺ for each mole of Zn²⁺ ions adsorbed and bring about decrease in solution pH as observed experimentally (Ghoneim, 2002).

Molecular orbital calculation indicated that, when the cluster model of allophane has one dissociated silanol group (Si-O⁻), the monmeric Zn²⁺ adsorbed strongly to the dissociated silanol group and also weakly to two undissociated silanol groups. The O-H bond length of silanol groups near the Zn adsorption site were longer than those of the other silanol groups. This means that the Zn²⁺ has a possibility to accelerate the deprotonation of undissociated silanol groups near the adsorption site. This induced increase in Brønsted acidity of the near silanol groups may interpret smaller ΔCEC as compared to Zn adsorbed (Fig. 4).

The following reactions explain the slight increase in the AEC values after Zn adsorption on the allophane samples.



In the reactions 6 and 7, part of the H⁺, which was initially released into the bulk solution after zinc adsorption (Ghoneim *et al.*, 2001) may have reacted with Al-OH group to form the new positive charges, Al-OH₂⁺ (Eq. 7) and the excess of the protons remain in the bulk solution and decrease the solution pH (final H⁺ release). This is in conformity with the results in the previous experiment (Ghoneim *et al.*, 2001) showing decrease in solution pH after Zn adsorption.

REFERENCES

Elhadi, E.A., N. Matsue and T. Henmi, 2001. Effect of molybdate on some surface properties of nano-ball allophane. *Clay Sci.*, 11: 405-416.

Ghoneim, A.M., N. Matsue and T. Henmi, 2001. Zinc adsorption on nano-ball allophanes with different Si/Al ratios. *Clay Sci.*, 11: 337-348.

Ghoneim, A.M., 2002. Reaction of nano-ball allophane with zinc and copper and its mechanism by molecular orbital method. The United Graduate School of Agricultural Sciences, for Doctoral Course, Ehime University, Japan. Ph.D Thesis, pp:148.

Hanudin, E., N. Matsue and T. Henmi, 2000. Change in charge characteristics of allophane with adsorption of low molecular weight organic acids. *Clay Sci.*, 11: 243-255.

Henmi, T. and K. Wada, 1976. Morphology and composition of allophane. *Am. Miner.*, 61: 379-390.

Henmi, T., N. Matsue and E. Johan, 1997. Change in surface acidity of allophane with low Si/Al ratio by reaction with orthosilicic acid. *Jpn. J. Soil Sci. Plant Nutr.*, 68: 514-520 (in Japanese with English abstract).

Huang, W.H. and W.D. Johns, 1967. Simultaneous determination of fluorine and chlorine in silicate rocks by a rapid spectrophotometric method. *Analytica Chimica Acta*, 37: 508-515.

Johan, E., N. Matsue and T. Henmi, 1999. New concepts for change in charge characteristics of allophane with phosphate adsorption. *Clay Sci.*, 10: 457-468.

Matsue, N. and T. Henmi, 1993. Molecular orbital study on the relationship between Si/Al ratio and surface acid strength of allophane. *J. Clay Sci. Soc. Jpn.*, 33: 102-106 (in Japanese with English abstract).

Nartey, E., N. Matsue and T. Henmi, 2001. Charge characteristics modification mechanisms of nano-ball allophane upon orthosilicic acid adsorption. *Clay Sci.*, 11: 465-477.

Padilla, G.N., N. Matsue and T. Henmi, 2002. Change in surface charge properties of nano-ball allophane as influenced by sulfate adsorption. *Clay Sci.*, 12: 33-39.

Parfitt, R.L., 1980. Chemical Properties of Variable Charge Soil. In: *Soil with Variable Charge*. THENG, B.K.G. (Ed.), New Zealand Soc. Soil Sci., Soil Bureau, DSIR, Lower Hutt, New Zealand, pp: 167-194.

Schofield, R.K., 1949. Effect of pH on electric charges carried by particles. *J. Soil Sci.*, 1: 1-8.

Son, L.T., N. Matsue and T. Henmi, 1998. Boron adsorption on allophane with nano-ball morphology. *Clay Sci.*, 10: 315-325.