

## CHARGE CHARACTERISTICS OF CLAYS EVALUATED WITH CAESIUM CHLORIDE IN SPECIAL REFERENCE TO DISPERSION BEHAVIOR

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### ABSTRACT

A method to determine negative and positive charge of clays applying  $\text{Cs}^+$  and  $\text{Cl}^-$  as an index cation and anion respectively was proposed. Special attention was paid for pH and electrolyte concentration in equilibrium solution so as to relate the charge characteristics with dispersion behavior of clays. In order to establish the proposed method as suitable charge determination, interlayer fixation of  $\text{Cs}^+$  was compared with that of  $\text{K}^+$  and  $\text{Na}^+$  by using some reference and soil clays including vermiculite and mica. As a result,  $\text{Cs}^+$  was not virtually fixed by any type of clays unless drying process was included. The flocculating effect of  $\text{Cs}^+$  enabled negative charge determination in the systems with high pH and low electrolyte concentration which was difficult to quantify with  $\text{Na}^+$  due to the dispersion of fine particles. The charge characteristics evaluated by the proposed method indicated that the montmorillonite was the typical clay mineral with permanent charge. In contrast, pH and electrolyte concentration dependence of the sericite suggested the characteristic property of variable charge rather than permanent. This observation was discussed from the aspect of the assumed heterogeneity of surface charge sites in the sericite.

Key words: Cation exchange capacity, Cs ion, Dispersibility, Interlayer fixation, Montmorillonite, Negative adsorption, Sericite, Vermiculite

### INTRODUCTION

Charge characteristics of soil clays is one of the most important factors to evaluate soil fertility. Retention capacity of nutrients is closely related to cation exchange capacity (CEC) of soils together with anion exchange capacity (AEC). In addition, physical properties of soils such as aggregate stability and dispersion/flocculation behavior are also affected by revealed charges (Itami et al., 1996). It is therefore essential needs for proper agricultural management to evaluate CEC of soils quantitatively.

In the previous paper (Itami and Tamamura, 1999), we proposed the modified version of the ion adsorption method introduced by Schofield (1949). In the proposed procedure,  $\text{Cs}^+$  was used as an index cation for the negative charge determination of montmorillonite, and the method was found to have following advantages: (1) the manipulation of the experiment was improved, leading to reduction in the experimental time, because the montmorillonite saturated with  $\text{Cs}^+$  exhibited little dispersion or swelling; (2) saturation with  $\text{Cs}^+$  made the negative adsorption of  $\text{Cl}^-$  negligible, so that  $\text{Cs}^+$  adsorption on the clay could directly estimate the negative charge of the clay without correction for the

negative adsorption of  $\text{Cl}^-$ ; (3) there was little risk of contamination from the ambient circumstances in determining  $\text{Cs}^+$ .

As a result of the combined effect of these merits, the higher reproducibility was obtained in the estimation of the negative charges using  $\text{Cs}^+$  as an index cation compared with the conventional method using  $\text{Na}^+$ . In addition, flocculation effect of  $\text{Cs}^+$  saturation enabled the measurement of the higher pH and lower electrolyte concentration systems, which had been difficult with  $\text{Na}^+$  due to clay dispersion.

In order to elucidate the adaptability of this method to any type of soil clay, one essential thing remains to be confirmed. Namely, it must be ascertained whether  $\text{Cs}^+$  is fixed or not in interlayer space of 2:1 clay minerals during the experimental procedure. It is well known that  $\text{Cs}^+$  has great affinity especially to 2:1 clay minerals (Francis and Brinkley, 1976; Cornell, 1993; Maes et al., 1998). Based on these characteristics,  $^{137}\text{Cs}$  which is a radioactive isotope of Cs released from nuclear tests has been used as a tracer to assess the extent of soil erosion in many countries (Lance et al., 1986; Wicherek and Bernard, 1995; Helmke and Sparks, 1996). If some clay minerals fix  $\text{Cs}^+$  irreversibly, the cation exchange capacity measured by  $\text{Cs}^+$  adsorption might be underestimated. Therefore, the purposes of this study were to examine whether  $\text{Cs}^+$  was fixed or not by 2:1 clay minerals in the same manner as  $\text{K}^+$  and  $\text{NH}_4^+$ , and to confirm the validity of the Cs ion adsorption method for evaluation of charge characteristics of clays.

## MATERIALS AND METHODS

### *Samples*

Vermiculite is the most likely clay mineral in regard to the  $\text{K}^+$  or  $\text{NH}_4^+$  fixation phenomenon. Because pure vermiculite was not easily available, soil samples of surface horizons in two forest soils (OD1, OD2) rich in vermiculite were used as the alternatives. These soils have continuously been supplied with organic matter which release organic and/or inorganic acids and exceptionally maintain vermiculite in the surface horizons without interlayering (Hirai et al., 1990). In addition, one upland soil (H8) containing mica clay mineral and hydroxy interlayered vermiculite (HIV), and three clays from mineral deposits (Mt, montmorillonite from Kunimine Industrial Corporation; St, sericite, a kind of dioctahedral mica minerals, from China; Kt, kaolinite from Indonesia) were used. The origin of the soil samples and the general properties of all samples are shown in Table 1 and 2, respectively.

For the soil samples, organic matter was decomposed with warmed hydrogen peroxide solution prior to the following experiments. Because of the limited amounts, the soil samples were directly analyzed without the fractionation of clay-sized particles. For the clay samples from deposits, the fraction less than 2  $\mu\text{m}$  in diameter was previously separated by a sedimentation method according to the Stokes' law after  $\text{Na}^+$  saturation and pH adjustment by NaOH. The clay mineralogy of all the samples was determined by X-ray diffraction (XRD) (RIGAKU Geigerflex) using the oriented specimen. Trace amounts of impurities were detected in the sericite and the kaolinite clay samples (Table 2).

### *Examination of cation fixation*

For each sample, the CEC values determined with three index cations ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ ) were compared in the systems of pH 7 and equilibrium concentration of 50 mmol

TABLE 1. Location of soil samples

	Area (Latitude, Longitude)	Soil type (Horizon)	Land use
OD1	Odaigahara, Nara Pref. (34° 09' 02"N, 136° 06' 47"E)	Dystric Cambisol (A <sub>1</sub> )	Beech Forest
OD2	Odaigahara, Nara Pref. (34° 08' 57"N, 136° 07' 04"E)	Dystric Cambisol (A <sub>1</sub> )	Beech Forest
H8	Hikigawa, Wakayama Pref. (33° 36' 30"N, 135° 28' 30"E)	Dystric Cambisol (A <sub>p</sub> )	Upland field

TABLE 2. General properties of clay and soil samples

Sample	CEC* (cmol (+) kg <sup>-1</sup> )	Total carbon (g kg <sup>-1</sup> )	Texture (Size)	Clay mineralogy**	
				Dominant	Accessory
Montmorillonite (Mt)	86.2	—	<2 μm	Mt	none
Sericite (St)	10.2	—	<2 μm	St	Kt
Kaolinite (Kt)	7.4	—	<2 μm	Kt	mica
OD1	54.4	200.5	LiC	Vt	kaolin, mica
OD2	39.5	107.9	LiC	Vt	HIV, kaolin
H8	10.2	2.8	CL	HIV, mica	kaolin

\* Determined by a procedure according to Schollenberger method. \*\* Mt, montmorillonite; St, sericite; Kt, kaolinite; Vt, vermiculite; HIV, hydroxyaluminum interlayered vermiculite; mica, micaceous minerals; kaolin, kaolin minerals.

L<sup>-1</sup>. The procedure was practically based on that of Itami and Tamamura (1999).

Soil and clay samples were placed in a preweighed 50 mL plastic centrifuge tube with 25 mL of 0.5 mol L<sup>-1</sup> NaCl, KCl or CsCl and the contents shaken for 30 minutes. After centrifugation, the supernatant was decanted. This saturation process was repeated three times. The contents were then washed five times with 25 mL of 50 mmol L<sup>-1</sup> NaCl, KCl or CsCl with pH 7. After the fifth washing solution was discarded, another 20 mL of the solution with the same concentration as the washings were added as the equilibrium solution. During the equilibration, pH was read occasionally, and if necessary, adjusted to the neutral by the addition of each hydroxide solution (NaOH, KOH or CsOH) or HCl. After equilibration was achieved, the contents were centrifuged and the final pH of the supernatant was recorded. The supernatant was retained for the analysis of each cation (Na<sup>+</sup>, K<sup>+</sup> or Cs<sup>+</sup>) and Cl<sup>-</sup>. The tubes containing the residues were weighed to determine the amount of entrained solution. The residual sample was then extracted five times with 25 mL of 0.5 mol L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub>. The contents of each cation and Cl<sup>-</sup> in the combined extractions were quantified. Finally, the amount of each ion adsorbed by the sample in the equilibrium solution was calculated by correction for the entrained solution.

After NH<sub>4</sub>NO<sub>3</sub> extraction, three more extractions with 0.5 mol L<sup>-1</sup> LiCl were carried out. For the third extraction, the equilibrating period was prolonged for two days, during which the samples were shaken reciprocally.

The concentrations of Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> were determined by atomic absorption

spectrometry (PERKIN ELMER 3110) and  $\text{Cl}^-$  was by  $\text{Hg}(\text{SCN})_2$  spectrophotometry (SHIMADZU UV-1200V) (Frankenberger, Jr. et al., 1996).

#### *Evaluation of charge characteristics using CsCl*

The procedure to evaluate charge characteristics of clays using CsCl (Cs adsorption method) was basically identical to that mentioned above except that the equilibrium solution with concentration of 5 or 50  $\text{mmol L}^{-1}$  CsCl solution was prepared in the pH range from 3 to 9. The same montmorillonite and sericite clay as in the fixation experiment was used after the purification mentioned previously.

## RESULTS AND DISCUSSION

#### *Cation fixation*

Among the samples used in this study, montmorillonite saturated with  $\text{Na}^+$  (abbreviated as  $\text{Na}^+$ -montmorillonite hereafter) is considered to be the most dispersive clay. In fact, during the washing process with 50  $\text{mmol L}^{-1}$  NaCl before equilibration,  $\text{Na}^+$ -montmorillonite was dispersed, so that ultracentrifugation (15000 rpm) was indispensable to avoid loss of the clay in decantation. This observation is attributable to the fact that the critical concentration for dispersion was found to be 250 to 100  $\text{mmol L}^{-1}$  in pH 7 for  $\text{Na}^+$ -montmorillonite (Itami and Tamamura, 1999). In contrast, ordinary centrifugation (3500 rpm) was enough to sink the suspended fine particles in the other  $\text{Na}^+$ -saturated clays and all the clays saturated with  $\text{K}^+$  and  $\text{Cs}^+$ . The concentration of the equilibrium solution (50  $\text{mmol L}^{-1}$ ) used in this study is thought to be sufficiently high for  $\text{K}^+$ -saturated system to prevent dispersion because montmorillonite saturated with  $\text{K}^+$  is dispersed in concentration lower than 25 to 5  $\text{mmol L}^{-1}$ . The montmorillonite saturated with  $\text{Cs}^+$  was still less dispersive than the  $\text{K}^+$ -saturated one.

In order to replace  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  on clays by  $\text{NH}_4^+$ , four replications of  $\text{NH}_4^+$  extraction would be sufficient because the amounts of three cations in the fifth extraction were found to be wholly insignificant. The amounts of the extracted ions with 0.5  $\text{mol L}^{-1}$   $\text{NH}_4\text{NO}_3$  for  $\text{Na}^+$ -,  $\text{K}^+$ - and  $\text{Cs}^+$ -saturated clays are summarized in Table 3 together with those of the secondarily extractable cations with 0.5  $\text{mol L}^{-1}$  LiCl. It should be noted that the negative adsorption of  $\text{Cl}^-$  in the  $\text{Na}^+$ -montmorillonite accounted for more than 10% of the amount of the extracted  $\text{Na}^+$ . Hence, it follows that the negative charge of  $\text{Na}^+$ -montmorillonite was in total the sum of the  $\text{Na}^+$  adsorption and the  $\text{Cl}^-$  negative adsorption. In contrast, the negative adsorption in the others was almost negligible. The amount of adsorbed  $\text{Cs}^+$  in montmorillonite was larger than that of  $\text{Na}^+$  as shown in Table 3, which had been observed in the previous study (Itami and Tamamura, 1999). This suggested that  $\text{Cs}^+$  was adsorbable at the interlayer position of montmorillonite because of its large ionic radius (El-Akkad et al., 1982) and small hydrated ionic radius (Israelachivili, 1995) as compared with  $\text{Na}^+$ .

Fixation of  $\text{K}^+$  or  $\text{Cs}^+$  seemed not to occur in all the samples because the amounts of net charge in Na systems were comparable to those in K or Cs systems (Table 3). According to Barshad (1948) and Sawhney (1972), when mica and  $\text{K}^+$ -vermiculite are exhaustively leached with solutions of cations with large hydration, interlayered  $\text{K}^+$  is gradually replaced by these cations. If  $\text{Cs}^+$  is fixed by some clays, the same phenomenon is expected to occur. Therefore, the secondary extraction of the residues with LiCl was

TABLE 3. Fixation of cation

Sample	Final pH	Amount of adsorption (cmol kg <sup>-1</sup> )			Residual cation* (cmol kg <sup>-1</sup> )
		Cation	Cl <sup>-1</sup>	Net charge	
<b>Na<sup>+</sup></b>					
Mt	6.9	80.0	-11.3**	91.3	0.8
St	6.9	7.0	-0.1	7.1	0.3
Kt	6.9	2.4	0.2	2.2	0.0
OD1	7.1	15.7	-0.4	16.1	0.1
OD2	7.1	16.0	-0.4	16.4	0.0
H8	6.9	6.3	-0.1	6.4	0.0
<b>K<sup>+</sup></b>					
Mt	7.1	92.1	-1.6	93.8	1.1
St	7.0	8.6	0.0	8.6	0.5
Kt	7.0	4.2	0.3	3.9	0.2
OD1	7.0	16.4	-0.4	16.8	0.2
OD2	7.0	16.9	-0.4	17.3	0.2
H8	7.1	7.8	-0.1	7.9	0.1
<b>Cs<sup>+</sup></b>					
Mt	6.9	103.7	-0.9	104.6	0.4
St	6.9	7.7	0.0	7.7	0.2
Kt	7.0	3.0	0.2	2.8	0.1
OD1	6.9	16.6	-0.3	16.8	0.1
OD2	7.0	17.3	-0.3	17.6	0.1
H8	7.0	8.9	0.0	8.9	0.0

\* Amount of secondarily extractable cation with LiCl. \*\* Negative value means negative adsorption of Cl<sup>-</sup>.

designed in order to examine whether the residual Cs<sup>+</sup>, if any, was extracted with Li<sup>+</sup> which possesses the largest hydration shell among monovalent cations.

Vermiculite is considered to fix K<sup>+</sup> in the interlayer sites, in general. Judging from the trivial amounts of the secondarily extractable cations (Table 3), it can be said that all the samples did not fix Cs<sup>+</sup> as well as K<sup>+</sup>. For this reason, the interlayer sites for fixation seem to be already saturated with some non- or hardly-exchangeable cation species as far as naturally occurring vermiculite is concerned. As a result, K<sup>+</sup> or Cs<sup>+</sup> fixation would not be observed in laboratory experiments even if some clays show the characteristic XRD pattern of vermiculite.

Apart from fixation of K<sup>+</sup> within the hexagonal cavities of basal oxygen planes of 2:1 clay minerals, many workers pointed out that mica minerals had stronger selectivity for K<sup>+</sup> or Cs<sup>+</sup> over other cations than vermiculite especially at low electrolyte concentrations (Francis and Brinkley, 1976; Komarneni, 1978). It is sometimes attributed to the stronger selectivity of frayed-edge sites in mica minerals rather than interlayer sites (Cremers et al., 1988; Staunton and Roubaud, 1997). The frayed edges are regarded to result from weathering in mica. Partially weathered mica should consist of a collapsed 1.0 nm central core and expanded frayed edges. Cations such as K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> which produce interlayer collapse would be selectively adsorbed at frayed edges to produce more stable collapsed structure similar to that of the central core (Sawhney, 1972).

In this context, the probable clay mineral fixing  $\text{Cs}^+$  is considered to be mica rather than vermiculite. As indicated by Sawhney (1972), however, cations fixed at frayed edges can be replaced by  $\text{NH}_4^+$  which resembles  $\text{K}^+$  and  $\text{Cs}^+$  in size. The use of  $\text{NH}_4\text{NO}_3$  to replace the adsorbed  $\text{Cs}^+$  in this experiment, therefore, appears to be reasonable. According to the data obtained in this study (Table 3), it is suggested that the  $\text{Cs}^+$  adsorption method presents little problem in respect of underestimation for the CEC measurement due to the fixation. In the previous reports which claimed  $\text{Cs}^+$  fixation in some clays, drying processes were often included to promote fixation (Barshad, 1948; Frantz and Carlson, 1987; Anderson and Sposito, 1991).

*Charge characteristics of montmorillonite and micaceous clay evaluated by the proposed method*

Figures 1 and 2 shows the pH and electrolyte concentration dependence of the montmorillonite and sericite evaluated by the  $\text{Cs}^+$  adsorption method in pH range from 3 to 9, respectively. The electrolyte concentration of 5 and 50  $\text{mmol L}^{-1}$  in the equilibrium solution was selected so as to interpolate the typical concentration of soil solution in the temperate region which is reported to be about 10  $\text{mmol L}^{-1}$  (Bolt and Bruggenwert, 1976). Positive and negative values in the ordinate correspond to amounts of  $\text{Cs}^+$  and  $\text{Cl}^-$  adsorption, which are equivalent to negative and positive charges of clays.

Figure 1-a and -b show that the charge characteristic of the montmorillonite is typical of permanent charge as recognized. Little dependence on pH and electrolyte concentration is observed. In contrast, the net charge of the sericite increases with increasing pH, indicating a characteristic of variable charge rather than permanent one (Fig. 2-a and -b). Moreover, the pH-charge curves appear to be irregular especially in the 5  $\text{mmol L}^{-1}$  system. This type of relationship was previously reported on a micaceous upland soil where the charge characteristics were evaluated by the conventional ion adsorption method using NaCl (Itami et al., 1996).

In connection with the pH and electrolyte concentration dependence of andic soils, Wada and Okamura (1980) proposed the following relationship:

$$\log \text{CEC} = a \text{ pH} + b \log C + c \quad (1)$$

where  $a$ ,  $b$  and  $c$  are coefficients derived by regression analysis. This empirical equation was reported to be able to also extend to 2:1 clay minerals (Okamura and Wada, 1983; Wada and Okamura, 1983). Based on the present data shown in Figs. 1 and 2, however, adaptability of the relationship is doubtful at least in case of montmorillonite and sericite. In particular, the net charge of the sericite in 5  $\text{mmol L}^{-1}$  increased irregularly with increasing pH instead of smooth increase expected from equation (1). Hendershot and Lavkulich (1983) also observed the similar trend of irregularity concerning the relationship between pH and charge using the mica and kaolin minerals. There seem to be no theoretical reasons why the CEC should increase, according to Okamura and Wada (1983), exponentially in high pH regions.

As the reason for the observed irregularity, it could be pointed out that some workers indicated the heterogeneity of the surface of mica minerals (Brouwer et al., 1983; Staunton and Roubaud, 1997). Sawhney (1972), from the cation selectivity data, distinguished the three different types of negative charge sites on mica surfaces: (1) the basal surface; (2) the frayed edge; and (3) the interlayer site. If so, there should be no reasons that the charge

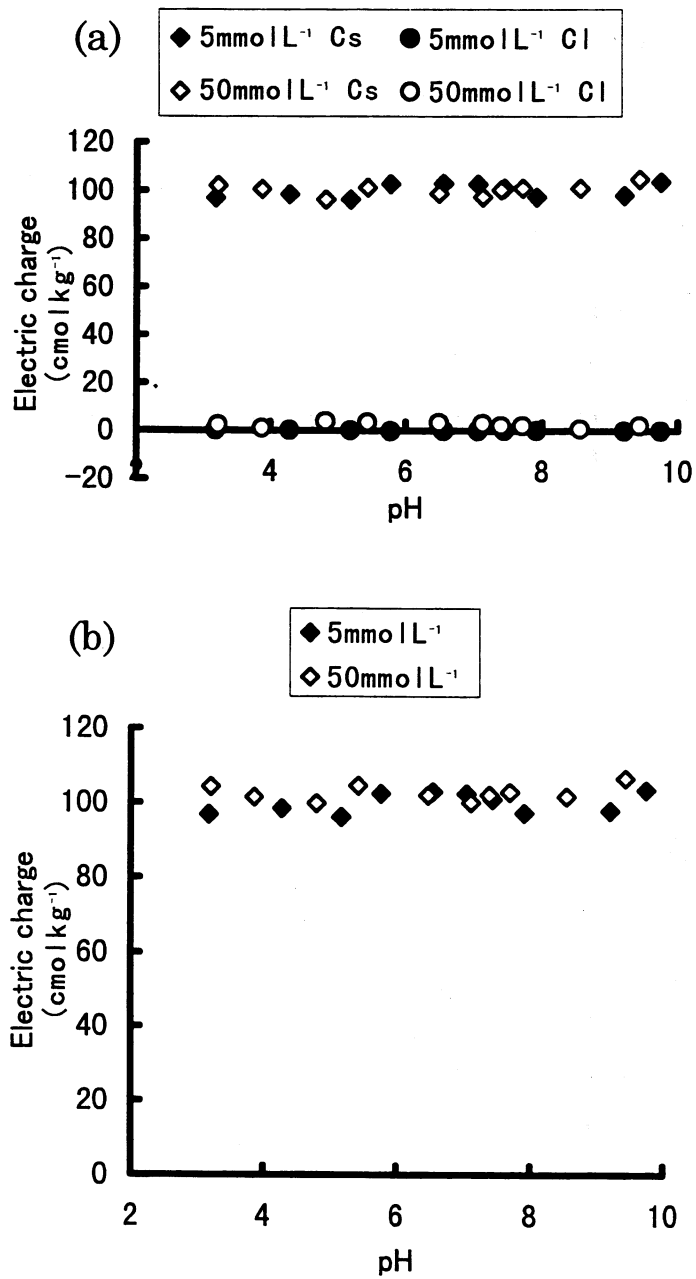


FIG. 1. Electrolyte and pH dependence of montmorillonite evaluated by Cs adsorption method: (a) negative and positive charge; (b) net charge.

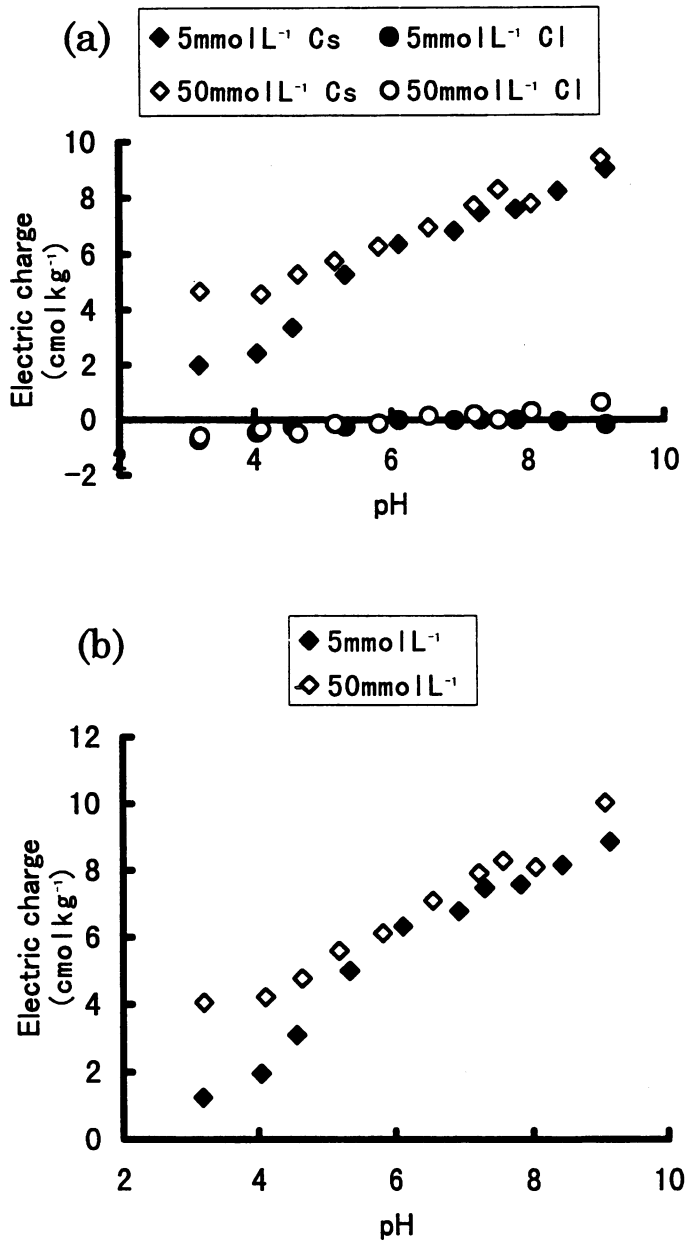


FIG. 2. Electrolyte and pH dependence of sericite evaluated by Cs adsorption method: (a) negative and positive charge; (b) net charge.



characteristics of these sites are all the same and explicable by the unitary interpretation. As far as the sericite is concerned, the charge characteristic seems not to be accountable by the distinct division of permanent and variable charge.

### CONCLUSION

In the procedure of this study, Cs<sup>+</sup> was not fixed by 2:1 clay minerals. The use of the Cs<sup>+</sup> adsorption method is considered to be effective to evaluate charge characteristics of clays. In particular, it is expected to relate charge characteristics with dispersion behavior of clays because this method can be adapted to high pH and low electrolyte concentration systems where major concern is paid in regard to dispersion behavior. The flocculation effect of Cs<sup>+</sup> enables the reproducible determination of negative charges in systems otherwise dispersed.

The effect of organic matter on Cs<sup>+</sup> adsorption is currently controversial. While Anderson and Sposito (1991) proposed the charge determination by use of Cs<sup>+</sup> for phyllosilicate alone, Cremers et al. (1988) and Staunton and Roubaud (1997) showed little contribution of organic matter on Cs<sup>+</sup> adsorption. Whether the Cs<sup>+</sup> adsorption method can be applied for extensive clays including natural soil clays is to be confirmed by accumulation of data. Considering the electrolyte concentration of the soil solution under forest vegetation are much lower than that of upland soils, the flocculating effect of Cs<sup>+</sup> should be effective to determine the charge characteristics of high pH regions in natural soil clays. At least, however, this method is so far believed to be worthwhile for evaluation of "physical charges" which must be closely related with dispersion behavior.

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### REFERENCES

- ANDERSON, S.J. and SPOSITO, G. (1991) *Soil Sci. Soc. Am. J.*, **55**, 1569–1576.
- BARASHD, I. (1948) *Am. Mineral.*, **33**, 655–678.
- BOLT, G.H. and BRUGGENWERT, M.G.M. (1976) *Soil Chemistry. A. Basic Elements*, Eds. G.H. Bolt and M.G.M. Bruggenwert, p. 1–12, Elsevier Sci. Publ. Co., Amsterdam.
- BROUWER, E., BAEYENS, B., MAES, A. and CREMERS, A. (1983) *J. Phys. Chem.*, **87**, 1213–1219.
- CORNELL, R.M. (1993) *J. Radioanal. Nucl. Chem.*, **171**, 483–500.
- CREMERS, A., ELSÉN, A., DE PRETER, P. and MAWS, A. (1988) *Nature*, London, **335**, 247–249.
- EL-AKKAD, T.M., FLEX, N.S., GUINDY, N.M., EL-MASSRY, S.R. and NASHED, S. (1982) *Thermochemica Acta*, **59**, 9–17.
- FRANCIS, C.W. and BRINKLEY, F.S. (1976) *Nature*, **260**, 511–513.
- FRANKENBERGER, JR., W.T., TABATABAI, M.A., ADRIANO, D.C. and DONER, H.E. (1996) *Methods of soil analysis*. Part 3. Chemical methods. Ed. D.L. Sparks et al. p. 833–867, SSSA Book Ser. 5. SSSA and ASA, Madison, WI.
- FRANTZ, G. and CARLSON, R.M. (1987) *Soil Sci. Soc. Am. J.*, **51**, 305–308.
- HELMKE, P.A. and SPARKS, D.L. (1996) *Methods of soil analysis*. Part 3. Chemical methods. Ed. D.L. Sparks et al. p. 551–574, SSSA Book Ser. 5. SSSA and ASA, Madison, WI.
- HENDERSHOT, W.H. and LAVKULICH, L.M. (1983) *Soil Sci. Soc. Am. J.*, **47**, 1252–1260.
- HIRAI, H., ARAKI, S. and KYUMA, K. (1990) *Soil Sci. Plant Nutr.*, **36**, 623–632.

- ISRAELACHVILI, J.N. (1995) *Intermolecular and surface forces* (trans. by Kondo, T. and Ohshima, H.) p. 35–50, Asakura, Tokyo.
- ITAMI, K., KOSAKI, T. and KYUMA, K. (1996) *Soil Sci. Plant Nutr.*, **42**, 521–530.
- ITAMI, K. and TAMAMURA, T. (1999) *Clay Sci.*, **10**, 469–476.
- KOMARNENI, S. (1978) *Soil Sci. Soc. Am. J.*, **42**, 531–532.
- LANCE, J.C., MCINTYRE, S.C., NANEY, J.W. and ROUSSEVA, S.S. (1986) *Soil Sci. Soc. Am. J.*, **50**, 1303–1309.
- MAES, E., DELVAUX, B. and THIRY, Y. (1998) *Euro. J. Soil Sci.*, **49**, 133–140.
- OKAMURA, Y. and WADA, K. (1983) *J. Soil Sci.*, **34**, 287–295.
- SAWHNEY, B.L. (1972) *Clays Clay Miner.*, **20**, 93–100.
- SCHOFIELD, R.K. (1949) *J. Soil Sci.*, **1**, 1–8.
- STAUNTON, S. and ROUBAUD, M. (1997) *Clays Clay Miner.*, **45**, 251–260.
- WADA, K. and OKAMIRA, Y. (1980) *J. Soil Sci.*, **31**, 307–314.
- WADA, K. and OKAMURA, Y. (1983) *Soil Sci. Soc. Am. J.*, **43**, 902–905.
- WICHEREK, S.P. and BERNARD, C. (1995) *CATENA*, **25**, 141–151.