

Distribution of the Surface Charges of the Peats in Different Ionic Strengths.

Sang Moon Chang and Jyung Choi

Department of Agricultural Chemistry, Kyung Pook National University, Taegu, Korea

(Received March 27, 1986)

이온 強度가 다른 溶液內에서 泥炭表面의 荷電特性

張 相 文 · 崔 炅

慶北大學校 農科大學 農化學科

抄 錄

電解質 溶液內에서 泥炭表面의 荷電量變化와 泥炭有機物の 化學的 性質에 關하여 調査하였다. 두 泥炭의 有機物 含量은 영양產 泥炭이 43.3%, 평택產 泥炭이 53.7%이었으며 粘土 鑛物은 大部分의 石英과 微量의 illite 長石類, kaolinite, hydrated-halloysite가 各各 混在되어 있었다. 試料中の 總酸基의 量은 평택產 泥炭이 1,257me/g로서, 영양產 泥炭보다 약간 많았으며, 有機物の pKa값은 영양產 泥炭이 13.1, 평택產 泥炭이 12.65이었다. 酸, 알칼리 滴定曲線은 영양產 泥炭은 pH 3.9와 4.4에서, 평택產 泥炭은 pH 3.8과 4.0에서 교차 되었다. 陰陽 ion 吸着量의 경우 영양產 泥炭에서는 pH 4.55~5.20(NaCl), pH 3.95~5.70(CaCl₂)에서, 평택產 泥炭의 경우에는 pH 4.15~5.40(NaCl), pH 3.80~4.15(CaCl₂)에서 各各 總荷電量이 陽에서 陰으로 바뀌었다. 그래서 本泥炭의 ZPC(zero point of charge)는 pH 4.0 부근에서 形成되는 것으로 나타났다.

Introduction

The roles of soil surface charges are greatly significant on many physico-chemical properties of soils such as water and plant nutrients holding abilities, soil colloidal stability, soil aggregate stability and subsequent resistance to soil erosion. It is well known that the retention of plant nutrients depends on the signs and magnitudes of surface charges associated with various soil constituents, that is organic and inorganic colloids.

There have been many studies on the surface charges of clay particles, sesquioxides¹⁻⁵⁾ of some oxisol and alfisol in the tropics⁶⁻⁹⁾ and of aridsol and inceptisol from Hawaii.¹⁰⁾ Choi and

his coworkers have investigated the application effects of clay minerals such as zeolite, montmorillonite on the purpose of increasing the water and plant nutrients holding capacities of soils.¹¹⁻¹⁴⁾ Voss and Park^{15,16)} suggested that clay minerals and organic matter contents in soils can play an important role in its surface charge characteristics.

As mentioned above, many studies for surface charge were carried out in the soil with a low level organic matter contents or clay minerals. However, little is known about surface charge characteristics of organic matter. Therefore, this investigation was undertaken to study the distribution of the surface charges in two peats and their physico-chemical properties.

Materials and Methods

1. Samples

The two peats which were originally located under the different depth conditions buried were used in this experiments. The general analytical methods of samples were carried out on the techniques described by Choi¹⁷⁾. Constituents of major minerals in the soils were identified by X-ray diffraction technique with JEOL X-ray diffractometer JDX-8E using the Cu K α radiation. Values of $\Delta \log K$, as the index of huminification degree, were evaluated with the humic acid powders which extracted from the peats and freeze-dried¹⁸⁾.

Table 1. Prescriptions of the peats used in the experiments

No	Buried depth (cm)	Location	Drainage	Layer height (cm)
P-A*	280	Yeongyang Kyung Pook	Kun Well drained	25~30
P-B*	0-10	Peongtack Kyung Gi	Kun Imperfectly drained	60~120

*P-A, P-B : Peat-A, Peat-B

2. Acid-base titrations

1) Titration procedures

0.5gr of peat samples was weighed into 100ml beakers added 20ml of three concentration of NaCl solution (1N, 0.1N, 0.01N). The pH was adjusted to 2.5-3.0 with 0.1N HCl. Then the suspension was titrated with 0.1N NaOH solution being stirring on a magnetic stirrer during titration. The titrants were delivered from microburette with the speed of 0.1ml every two minutes. Corning pH meter (Model 7) equipped with a glass-calomel reference electrode pairs was used to measure the pH. Blank titrations were carried out with the same volume of the NaCl solution and the amount 0.1N NaOH solution consumed at a given pH. The amount of NaOH consumed

by the sample, at any given pH value, was taken as equal to the amount of NaOH added to the suspension minus the amount of NaOH consumed to bring the same volume and the same concentration of NaCl solution to the same pH. The ZPC was considered to be the common intersection point of the titration curves carried out in the presence of three concentration of NaCl solution.

2) Determination of acidic group contents and pKa values

The contents of the acidic group of samples were determined by applying the linear titration plots derived by Mc-Callum and Midgley¹⁹⁾ in combination with Gran's plots²⁰⁾.

In order to obtain pKa values for the acidic functional groups, the Henderson-Hasselbalch plots were used.

$$\text{pH} = \text{pKa} + n \log \frac{\text{At} + [\text{H}^+]}{\text{At}(1-\theta) - [\text{H}^+]}$$

where, At: total contents of weakly acidic or very weakly acidic functional groups.

θ : degree of neutralization.

n: correction parameter of Henderson-Hasselbalch plot.

Ka: acid dissociation constant.

2. Ion adsorption measurements

For the determination of the distribution of positive and negative charges as a function of pH in 0.1N NaCl, the following procedures were carried out.

3g of oven-dried samples was added to 50ml polyethylene centrifuge tube. Varying quantities of dilute HCl and NaOH were added to the centrifuge tubes with 25ml of 0.2N NaCl. Distilled water was added to fill up 50ml such that the final concentration of NaCl was 0.1N. After 3 days with continuous stirring, the tubes were centrifuged. The supernatants were used for pH measurement and determination of the contents of Na⁺, and Cl⁻.

The charge distributions in the presence of 0.1N CaCl₂ were evaluated as the described

Table 2. Physico-chemical properties of the peats used in the experiment.

Sample	pH*		Ash (%)	O.M. (%)	T-N (%)	C/N	0.03N NH ₄ F soluble-P (ppm)	C.E.C (me/100g)
	H ₂ O	KCl						
P-A	6.4	5.6	57.66	43.3	0.927	27.04	16.3	74.5
P-B	4.3	4.0	46.25	53.7	0.759	40.31	12.6	78.6

Exch. cations (me/100g)				Texture(%)			Surface area (m ² /g)	Mineralogy**
K	Na	Ca	Mg	Sand	Silt	Clay		
1.07	0.68	17.86	8.76	9.66	16.75	31.2	218.36	Qz>> It=Fd
0.96	0.71	14.94	8.14	0.25	18.7	27.2	201.72	Qz>> It=Kt=H.H

*Solution : Sample = 2.5 : 1

**Qz : Quartz, H.H: Hydrated-Halloysite, It : Illite, Fd : Feldspars, Kt : Kaolinite

above. Sodium and calcium were determined with a atomic absorption spectrophotometer and Cl⁻ by titration method²¹⁾ with 0.05N AgNO₃ in the presence of K₂CrO₄ as the indicator. The amount of ions adsorbed by the soil sample at any given pH value was taken as equal to the amount of the ions added to the suspension and the exchangeable ions of the soil samples minus the amount of the ions of the supernatant of equilibrating suspension.

Results and Discussion

1. Physico-chemical properties of sample

The inorganic matter contents of samples were 45~60% and P-B sample contained more organic matter contents than P-A sample which located at subsoil layer (Table 2). P-B sample had less surface area than P-A sample, however the CEC of P-A sample was rather higher than P-B sample. Therefore, P-A sample contained high contents of inorganic matter which had low CEC value.

The clay fractions which extracted from the peats by the pipetting method¹⁷⁾ was saturated with Mg or K after removal of organic matter, Fe, soluble Al and Si (Fig. 1, 2). The X-ray diffractogram patterns of the two soils showed almost the same. On Fig. 1, 2, it is noted that

quartz were dominant in both soils, and showed only barely detectable quantities of 1 : 1 type or 2 : 1 type clay minerals, that is, illite, kaolinite, hydrated-halloysite and feldspars.

2. Acid dissociation constants (pKa)

The contents of the total titratable functional groups of organic matters was determined by applying the linear titration plots derived by Mc-Callum and Midgley¹⁹⁾.

At the beginning of titration(lower pH region), equation (1) was used as follows.

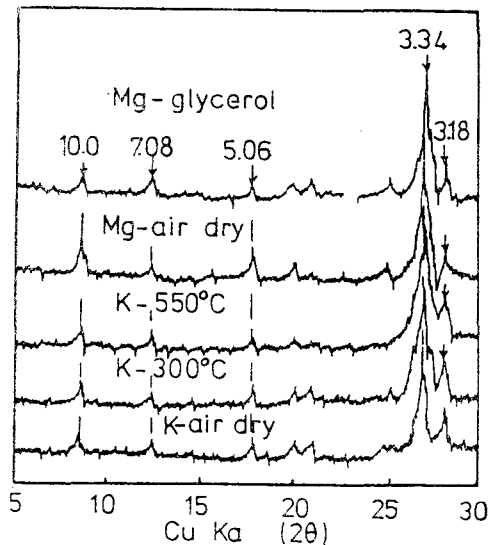


Fig. 1. X-ray diffractograms of the clay fractions of P-A sample

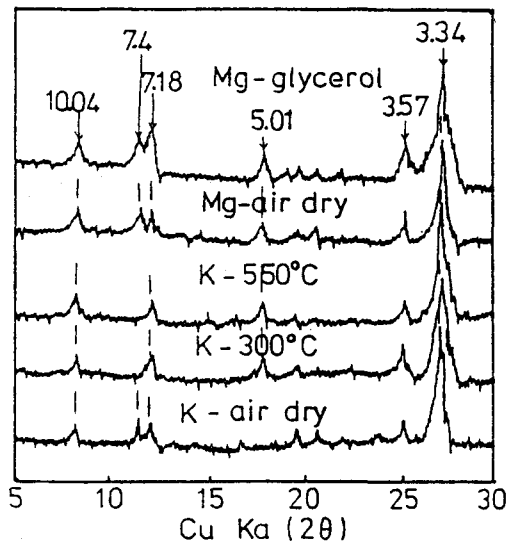


Fig. 2. X-ray diffractograms of the clay fractions of P-B sample

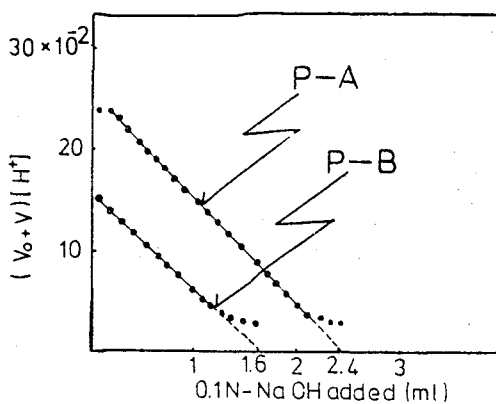


Fig. 3. $(V_0+V)[H^+]$ plotted against the amount of 0.1N NaOH in the initial stage of titration (0.1N NaCl)

$$(V_0+V)[H^+] = m(V_s - V) \quad (1)$$

where, V_0 : initial volume of a mixed acid solution.

V : volume of titrant base added.

V_s : volume of titrant base equivalent to the strong acid.

m : concentration of titrant base.

As shown in Fig. 3, volumes of titrant base added equivalent to the strong acid were 2.4ml (P-A) and 1.6ml (P-B). On the other hand, at

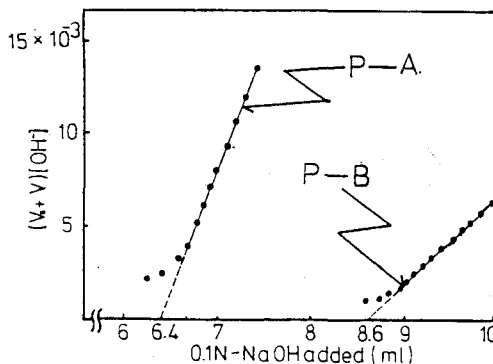


Fig. 4. $(V_0+V)[OH^-]$ plotted against the amount of 0.1N NaOH in the final stage of titration (0.1N NaCl)

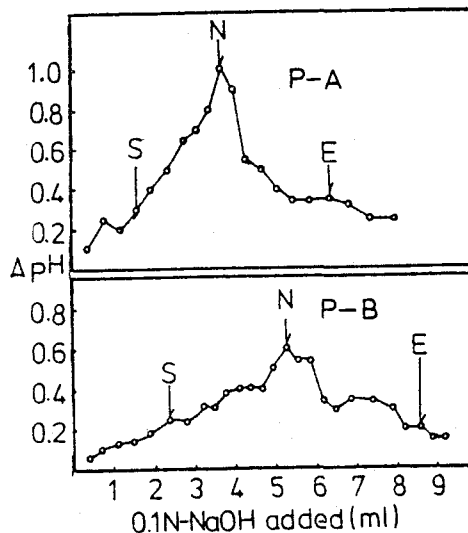


Fig. 5. ΔpH variations plotted against the amount of 0.1N NaOH added in the titrations of titrates mixtures (0.1N NaCl)

final stage of titration (higher pH region), the following simplified equation (2) was used.

$$(V_0+V)[OH^-] = m(V - V_e) \quad (2)$$

where, V_0 : initial volume of a mixed acid solution.

V : volume of titrant base added.

V_e : volume of titrant base equivalent to the total acidity.

m : concentration of titrant base.

Table 3. Chemical properties of the peats and their $\Delta \log k$

Sample	Total acidity (me/g)	Weakly acidic group (me/g)	pKa ₁	Very weakly acidic group (me/g)	pKa ₂	Ka ₁ · Ka ₂	$\Delta \log k^*$
P-A	0.973	0.426	3.95	0.547	9.15	8.035×10^{-14}	0.825
P-B	1.257	0.588	4.05	0.699	8.60	1.995×10^{-13}	0.968

* $\Delta \log k$: Humification degree of humic acids extracted from peats.

6.4ml(P-A) and 8.6ml(P-B) of the base added consumed by the total acidic groups of organic matter of peats.

The curves of pH plotted against each portion of the titrant strong base added was shown in Fig. 5. With the addition of bases and the consequent rise in alkalinity, first the hydrogen from the carboxyl groups and then the hydrogen from the phenolic groups ionizes and is replaced by other cations²². The amount of titrant base that corresponded to the range from the initial point, S in Fig. 5, up to the point where the variation of pH reached a maximum on the titration curves (pH max.) was considered to be a contents of the weakly acidic functional groups, that is, carboxyl groups. The titrant base that corresponded to the range from pH max. to the final end point was considered to be a contents of the very weakly acidic functional groups which are phenolic, alcholic hydroxyl groups.

A Henderson-Hasselbalch plot was shown in Fig. 6; it indicated that pKa values of the acidic functional groups were 13.1(P-A) and 12.65(P-B), and the acid dissociation degree of P-B sample was stronger than P-A sample. As shown in Table 3, $\Delta \log K$ value of P-B sample was

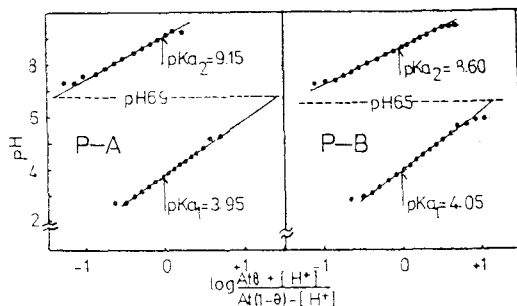


Fig. 6. Henderson-Hasselbalch plots of peats.

largers than P-A sample. Therefore, humification degree of organic matter in P-B sample was higher than P-A sample.

3. Surface charges determined by potentiometric titration

Titration curves of these peats measured on the methods described by De Bryun and Park²³ were as follows.

As the Fig. 7, 8, the titration curves at different concentration of NaCl solutions crossed at pH 4.15 and 4.4 in P-A sample, pH 3.8 and 4.0 in P-B sample. De Bryun and Park suggested that at the pH of intersection point of titration curves the amounts of the adsorbed H⁺ or OH⁻ on the surface would be equal, and then the total net charge may be showed the zero.²³ Despite of consuming of only a small fraction of titrant, pH value of suspensions increase significantly in the range of pH 6.3~7.4. These results suggest that the pH value of the suspension may increase by the adding of titrant, while there is the little

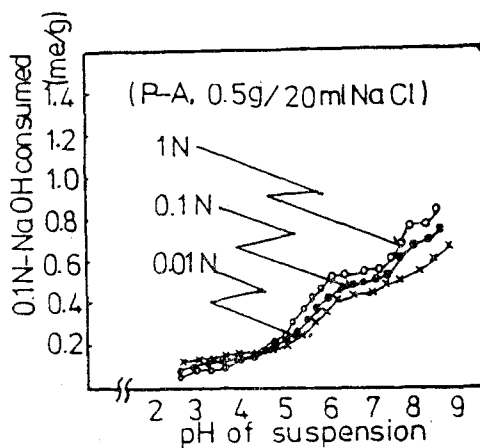


Fig. 7. Acid-base titration curves for the P-A sample.

Table 4. The amount of surface net charge of peats in 0.1N NaCl and CaCl₂ solution

Sample	pH	Na ⁺ (me/g)	Cl ⁻ (me/g)	Net charge (me/g)	pH	Ca ⁺⁺ (me/g)	Cl ⁻ (me/g)	Net charge (me/g)
P-A	3.40	0.017	0.073	+0.057	3.25	0.025	0.079	+0.054
	4.15	0.034	0.069	+0.039	3.50	0.033	0.069	+0.036
	4.55	0.04	0.045	+0.005	3.95	0.055	0.057	+0.002
	5.20	0.051	0.049	-0.002	5.70	0.183	0.038	-0.145
P-B	3.60	0.063	0.134	+0.071	3.35	0.083	0.156	+0.073
	3.80	0.08	0.116	+0.036	3.80	0.108	0.151	+0.043
	4.15	0.121	0.120	+0.001	4.15	0.117	0.114	-0.003
	5.40	0.126	0.10	-0.026	4.40	0.133	0.069	-0.064

H⁺ dissociated from the sample. This phenomenon have coincide with Choi's report²³⁾.

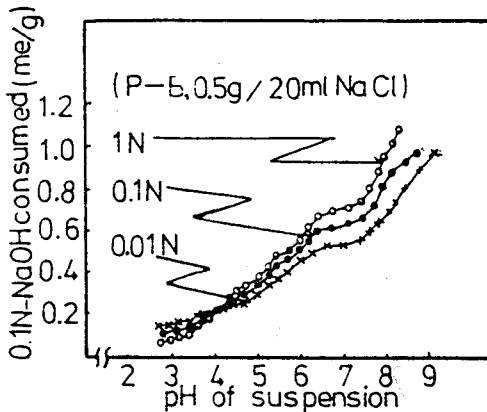


Fig. 8. Acid-base titration curves for the P-B sample.

4. Surface charges determined by measurement of ion adsorptions

The results of the direct measurement of positive and negative charges by measurement of the adsorption of cation and anion in 0.1N CaCl₂ solutions were as follows (Table 4).

As the above, net charges of the surface were changed from positive to negative between pH 4.55 and 5.20(P-A), pH 4.15 and 5.40(P-B) in 0.1N NaCl solution. These results showed that the ZPC obtained by the ion adsorption measurement was higher than that by the potentiometric titration(Fig. 7, 8). In the case of 0.1N CaCl₂

solution, the sign of the net charge of two peats was changed at the pH 3.95~5.70 and pH 3.80~4.15 each other. For the ZPC of predictive value, it ought to be fairly constant. However, depending on the nature of the supporting electrolyte, considerable shifts in ZPC have been reported.²⁴⁻²⁶⁾

With Na₂SO₄, it moved to higher and with CaCl₂ to lower values in comparison with NaCl. The results of this study showed that ZPC of in 0.1N CaCl₂ was lower values than that of 0.1N NaCl. It can be supposed that this phenomenon may results from the specific adsorption of Ca⁺⁺. Therefore, ZPC value which positive and negative net charges of the surface lead to equal may be pH 4~5. Park, Posner and Breeuma found that ZPC values of kaolinite, crystalline Fe oxides and Al oxides were pH 3.3~5.0, pH 6.6~6.7 and the above of pH 7.7, respectively.^{3, 4, 24)}

In general, it was reported that the presence of iron and aluminum oxides will tend to increase the ZPC towards the higher pH values³⁾ while the presence of clay minerals and organic matter with permanent or pH-dependent charge will tend to shift the ZPC of the soil to lower pH values¹⁶⁾. For these samples, at low pH values, the positive charges may result from protonation of hydrous oxides. At higher pH values, desorption of protons from uncomplexed phenolic and carboxylic functional groups of organic matter may be the major contributor of negative charges. Thus, the ZPC

results from the overall mineralogical composition and organic matter contents of the soil⁶⁾.

Mineralogical composition of these samples was found that quartz was dominant in both peats, and illite, kaolinite, hydrated-halloysite and feldspars were contained in a trace. Therefore, authors suppose that the magnitude of the surface charge of these samples may not be influenced strikingly by the clay minerals, and then the change of these net surface charges primarily depends on the dissociation constant of the functional acidic groups of the organic matter in samples. ZPC of these samples was found to be near pH 4.0.

Abstract

The distribution of the surface charges in two kinds of peats and their physico-chemical properties have been studied by means of the potentiometric titration and by ion adsorption in different strength of electrolytes.

The organic matter contents were 43.3% and 53.7% in Yeong Yang peat and Peong Tack peat, respectively. Their X-ray diffractograms showed that quartz was dominant in both peats, and illite, kaolinite, hydrated-halloysite and feldspars were contained in a trace. Total acidic group contents was 1.257me/g in Poeng Tack peat that was a little more than of Yeong Yang peat. The pKa values of Yeong Yang and Poeng Tack peat were 13.1 and 12.65, respectively. The titration curves at different ionic strength of electrolytes crossed at pH 3.9 and 4.4 in Yeong Yang peat, and pH 3.8 and 4.0 in Peong Tack peat. The pH ranges of suspensions when the net surfacecharge of the peats varied from positive to negative value were pH 4.55~5.20 (NaCl) and pH 3.95~5.70 (CaCl₂) in Yeong Yang peat, and pH 4.15~5.40 (NaCl) and pH 3.80~4.15(CaCl₂) in Peong Tack peat. Therefore, it is apparent that the zero point of charge of these peats was about pH 4.0.

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