

## NEGATIVE SURFACE CHARGE DISTRIBUTION AMONG CONSTITUENTS OF THE SOIL CLAY FRACTION AS INFLUENCED BY pH CHANGES

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**A b s t r a c t.** An examination of negative charge distribution among solid soil phase components and its relations to pH of the equilibrium solution was conducted by model experiments on clays separated from selected acidic soils. It was noted that negative charge blocking by iron and aluminium oxides occurs, with the most pronounced effect in brown and podzol clays. On the basis of measured values of sample charges before and after removal of organic matter the organic matter charges were calculated to have a more linear pH dependence than that seen for natural clays. This effect is attributed to the presence of positive charges in the clays investigated.

### INTRODUCTION

Negative charges occur in soils as permanent and variable (pH dependent) charges. Their magnitude and character depend on the presence of particular soil components such as organic matter, iron and aluminium compounds and clay minerals. The main physicochemical parameter governing the quantity of surface charge is pH of the soil equilibrium solution.

Permanent negative charge is present in crystalline clay minerals and it is due to lattice defects and impurities. The quantity of permanent charge is not equal to the sum of lattice defects since part of them may be compensated by specifically adsorbed interlamellar cations as e.g., potassium in the case of

illite and hydrobiotite [4]. Permanent charge is pH independent until the destruction of the mineral lattice occurs.

Soil organic matter contains numerous functional groups able to undergo acidic dissociation. A soil solution pH increase leads to the neutralization of organic protons causing negative charging of organic surfaces. Due to the broad range of dissociation constants, the negative charge of organic matter depends almost linearly on pH [5]. A somewhat artificial division of organic functional groups can be made, such as strongly, moderately, and weakly dissociated [1].

Charging of organic matter may also be caused by the neutralization of aluminum ions complexed by organic functional groups [9].

Variable negative charge in soils can be also due to the neutralization of Al and/or Fe polymeric ions adsorbed on the internal or external surfaces of clay minerals [6,7,12].

Negative surface charge occurs also on soil constant potential components (e.g., sesquioxides) above the point of zero charge [3].

The purpose of the present work was the examination of negative charge distribution among solid soil phase components and its relations to pH of the equilibrium solution.

## MATERIALS AND METHODS

Materials under investigation consisted of six sodium forms of soil clay fractions separated from Polish acidic soils of different origin. The characteristics of the soils and their clay separates is presented in a previous publication [8].

Natural clay fractions were pretreated for subsequent removal of organic matter, iron oxides and aluminium oxides. This was followed by the adjustment of samples to different pH values according to the scheme given in the previous publication [8].

From the samples adjusted to different pH values exchangeable cations were extracted by double equilibration with a N barium chloride solution. After washing with distilled water, samples were equilibrated five times with 0.01 N BaCl<sub>2</sub> solutions which were at the same pH as the given sample. The 0.01N barium chloride solution was adjusted to the pH of the sample with either 0.01 N HCl or saturated Ba(OH)<sub>2</sub> solutions. For these samples the quantity of

exchangeable barium (BaJW) was determined by extraction with a N lanthanum chloride solution and AAS measurement.

## RESULTS AND DISCUSSION

The quantity of BaJW measured was taken as the value of the negative surface charge ( $q^-$ ). It was assumed that the exchangeable hydrogen could be neglected [3,14] and that 'mobile' aluminium was removed during the pH 3 cleaning step (see [8]).

The value of the negative charge of the natural clay fractions as well as the clay fractions after consecutive removal of organic matter, iron and aluminium oxides are given in Table 1.

The negative charge of those fractions investigated increased with a pH increase. The highest increments were observed for samples containing organic matter (natural clays), and particularly above pH 5. This effect has been interpreted by many authors as the strong increase of organic matter exchange capacity at high pH's [10,13].

Table 1. Negative surface charge values (cmol n<sup>-1</sup> kg<sup>-1</sup>) of clays investigated as it depends on pH

pH	1A	1B	1C	1D	2A	2B	2C	2D	3A	3B	3C	3D
3.0	24.7	24.3	24.9	26.2	22.9	21.0	22.6	25.1	50.9	45.0	49.2	62.5
3.5	26.4	25.2	26.7	28.3	23.5	20.4	22.9	25.5	53.6	47.5	51.0	64.1
4.0	31.2	27.9	29.1	30.0	24.2	21.0	23.2	25.8	58.9	48.9	53.5	67.0
4.5	37.6	29.1	38.0	37.0	26.9	21.8	23.5	26.1	64.5	49.6	54.2	68.9
5.0	41.6	33.0	31.6	32.4	30.2	22.3	23.7	26.4	71.1	51.8	56.7	70.6
6.0	49.3	31.4	32.3	32.9	38.1	22.5	23.9	27.0	82.7	54.1	60.3	70.9
7.0	62.4	33.1	32.9	33.5	44.8	23.6	24.3	27.4	93.2	59.2	63.5	70.9
8.0	75.3	34.7	33.8	34.0	50.6	25.8	25.2	27.9	102	62.4	65.9	72.0
8.5	81.3	35.6	34.2	34.6	54.3	27.7	26.1	28.2	108	63.7	66.8	72.6
pH	4A	4B	4C	4D	5A	5B	5C	5D	6A	6B	6C	6D
3.0	24.3	21.9	22.8	24.3	40.4	40.3	44.4	50.0	18.0	15.4	17.8	21.8
3.5	26.1	22.2	23.3	24.4	41.5	41.8	45.0	50.7	18.7	15.6	18.0	22.0
4.0	31.2	22.7	24.2	25.0	43.5	42.4	45.8	51.2	19.2	15.9	18.4	22.8
4.5	36.1	23.6	24.9	25.6	46.0	42.9	46.1	52.4	20.3	16.0	18.8	23.4
5.0	39.4	24.8	25.8	26.4	51.0	43.6	46.2	52.8	22.6	16.4	19.0	23.9
6.0	46.2	25.2	26.5	27.0	58.5	44.5	47.3	52.6	28.9	17.0	20.2	24.5
7.0	59.9	27.1	27.2	27.8	63.7	46.8	48.9	53.2	32.4	17.6	21.3	24.5
8.0	73.0	28.5	28.6	28.9	70.1	47.7	50.9	54.0	35.0	20.5	22.7	24.9
8.5	82.0	29.2	29.0	29.2	73.2	49.1	51.5	54.5	36.9	21.3	23.3	24.9

Explanations: 1-Mollic Gleysol; 2-Eutric Cambisol; 3-Eutric Cambisol; 4-Stagnogleyic Phaeozem; 5-Orthic Luvisol; 6-Podzoluvisol. A-natural clays; B-after organic matter removal; C-after removal of iron; D-after removal of aluminium.

It appears that, by knowing the value of the negative charge for samples containing organic matter and for the same samples after organic matter removal, together with the amount of positive charge, the amount of negative charge of only the organic matter present in these samples can be evaluated. It is necessary to assume that, at a given pH, the charge of organic matter ( $q_{OM}$ ) is equal to the negative charge of the whole sample containing organic matter ( $q_{NAT}$ ), minus the negative charge of mineral constituents present in this sample ( $q_{MIN}$ ) plus the amount of negative charge of the organic matter which is neutralized by the blocking of positively charged surfaces ( $q_{OMB}$ ):

$$q_{OM} = q_{NAT} - q_{MIN} + q_{OMB} \quad (1)$$

If it is assumed that positive and negative charges of mineral constituents are the same for natural clays and clays after removal of organic matter (per mass unit) then

$$q_{MIN} = q_{OMR} (1 - \%OM/100) \quad (2)$$

where  $q_{OMR}$  is the sample negative charge after organic matter removal and  $\%OM$  is the percentage of organic matter in the sample and

$$q_{OMB} = q_{+OMR}(1-\%OM/100) - q_{+NAT} \quad (3)$$

where  $q_{+OMR}$  and  $q_{+NAT}$  are positive charge values for the sample after organic matter removal and for the natural sample, respectively.

Values of organic matter charge calculated according to formulas (1), (2), and (3), using values for positive charge from a previous publication [8], are presented in Fig. 1.

In Fig. 1, it can be seen that increments of negative charge of organic matter for e.g., one unit of pH are far more uniform than the increments of negative charge of the whole clay fractions containing organic matter. This agrees with the results of many

authors, that the charge of organic matter lineary increases with pH [2,11].

In Fig. 1 one can also observe significant differences between charge characteristics of organic matter from different soil materials. This is probably related to the presence of different functional groups and their relative amounts. For brown soils (samples 2, 3, and 5), organic matter charge dependence on pH is similar. At pH 3, the negative charge ranges between 1.3 to 1.8  $\text{cmol n}^{-1}\text{g}^{-1}$  increasing lineary with a slope of 0.7 per one pH unit. For black earth soils (samples 1, 4), the charge at pH 3 is about 0.5, and at low pH values it increases slowly (about 0.25 per pH unit). However, above pH 6, the slope increases to 0.8. The highest value of charge at pH 3 is noted for a podzol (sample 6). For this sample the charge increase with pH is the greatest. It can be concluded that there exist a strong dependence on organic matter characteristics and the dominant soil forming processes.

In low pH range the negative charge of natural clays increases more slowly than in high pH range (see Table 1). It appears that this phenomenon may be attributed to electrostatic neutralization of positive charge, which magnitude is particularly high at low pH range, by negative charge of organic matter. This confirms the role of positive charges in blocking soil organic matter charge.

The negative charge of samples containing no organic matter is the highest for samples after iron and aluminium removal. It is strongly manifested at low pH values. This can be attributed to the blocking of clay minerals negative charge by iron and aluminium oxide coatings. The influence of Al and Fe compounds on charge blocking is the most pronounced in brown and podzol soil (samples 2, 3, 5, 6). In the case of iron compounds, the charge blocking may be caused by amorphous forms of iron oxides because the surface area per unit mass of iron compounds is the highest in these samples. In the case of aluminium compounds,

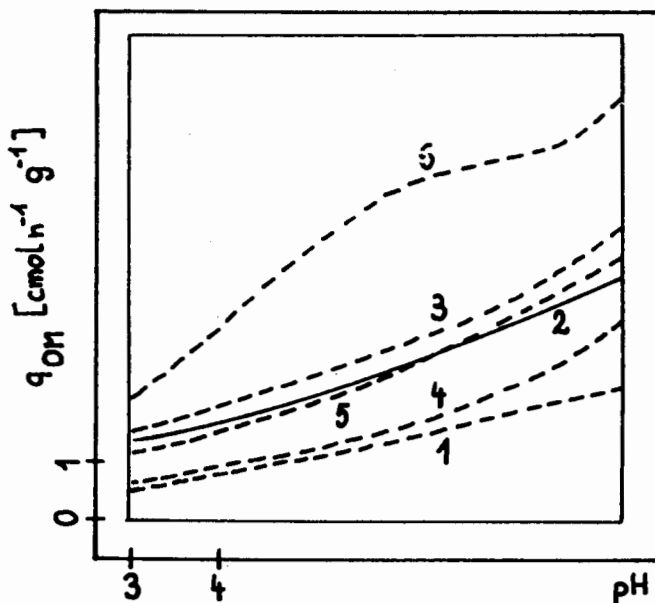


Fig. 1. Negative charge of organic matter in the clays investigated as it depends on pH. Curve numbers equal the numbers of the soils and clays investigated (see Table 1).

one additional mechanism of charge blocking can be taken into account for samples 3 and 5. Since these samples contain high amounts of montmorillonite (smectites), the interlamellar spaces can contain Al polycations neutralizing part of the permanent negative lattice charge.

#### CONCLUSIONS

1. Negative charges of the clays investigated are mainly due to the charges on both organic matter and clay minerals.

2. The phenomena of negative charge blocking by iron and aluminium oxides were observed, having the most pronounced effect in brown and podzol clays.

3. On the basis of values of negative and positive charges for samples before and after removal of organic matter, the organic matter charge was calculated as having a more linear pH dependence than was seen for natural clays. This effect is attributed to the presence of positive charges in the clays investigated.

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#### DYSTRYBUCJA UJEMNEGO ŁADUNKU POWIERZCHNIOWEGO WE FRAKCJI KOLOIDALNEJ GLEB NA TLE ZMIAN pH

Badano zależność od pH oraz rozkład ładunku ujemnego pomiędzy poszczególne komponenty fazy stałej dla frakcji koloidalnych wydzielonych z wybranych gleb kwaśnych Polski. Stwierdzono, że w badanych próbkach tlenki i wodorotlenki żelaza i glinu blokują powierzchniowy ładunek ujemny, co jest najbardziej wyraźne w glebie brunatnej i płowej. Na podstawie uzyskanych wielkości ładunku powierzchniowego przed i po usunięciu z próbek materii organicznej obliczono wielkości ładunków powierzchniowych dla samej materii organicznej. Zależność ładunku samej materii organicznej od pH miała bardziej liniowy charakter niż w obecności składników mineralnych, co wskazuje na rolę ładunku dodatniego składników mineralnych.