

# Electrophoretic mobility of some tropical soil clays: effect of iron oxides and organic matter

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## Abstract

The effect of organic matter and iron oxides on the electrophoretic mobility (EM) behaviour of some colloidal clay fractions of some tropical soils was studied. The clays from the A-horizon of the soils were treated to remove organic matter (oxidation by Na hypochlorite treatment), ferrihydrite (by acid ammonium oxalate) and better crystalline iron oxides (reductive dissolution by dithionite–citrate–bicarbonate treatment). Organic matter and iron oxides particularly better crystalline ones contributed to the pH-dependent charge. The removal of organic matter resulted in an increase in the EM and isoelectric point (iep). Deferration decreased both the EM and iep of the soil clays. Increase in pH resulted in negative EM while salt concentration did not have consistent effect on the EM and iep values. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* electrophoretic mobility; isoelectric point and tropical soil clays

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## 1. Introduction

The net particle electrical potential at the plane of shear can be inferred from the rate and direction of colloidal particle movement in response to an applied potential gradient (Hunter, 1981). Measurement of electrophoretic mobility (EM) as a function of pH and ionic strength provides an indication of the charge properties of mineral surfaces. The EM of colloidal particles can be determined by direct observation of single particles moving in an applied field, which is

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tedious and time consuming (Anderson and Bertsch, 1993). A more recent method of EM measurement involves the use of the Doppler effect (Anderson and Bertsch, 1993). In this method two coherent laser beams are crossed at the stationary layer in the capillary cell, resulting in interference fringes. One of the beams is modulated with a given frequency, resulting in fluctuations in scattered light intensity with the same frequency. If the particles move due to an applied field, a shift in frequency is observed due to particle movement. This shift is used to determine the EM (Hunter, 1993).

The dominant clay mineral of strongly weathered tropical soils is kaolinite. It is well known that kaolinite and other components, such as iron oxides and organic matter, interact to influence the charge properties of the soils. Iron oxides in tropical soils may have large specific surface areas (Cavallaro and McBride, 1984), and hence their presence, even in small amounts, could have a great influence on variable charge reactions. The importance of organic matter derives from its large charge and large surface area (White and Zelazny, 1989).

The purpose of the study was to investigate the influence of selective removal of Fe oxides, organic matter and variation of pH on the EM of kaolinitic tropical soil clays.

## 2. Materials and methods

### 2.1. Soils

Seven soils samples from the A horizons, were used. Some selected properties of the soils from which the clay fractions ( $< 2 \mu\text{m}$ ) were extracted are presented in Tables 1–3. The clay fraction of Pugu kaolinite, a reference material with properties similar to kaolinite from tropical soils, a synthetic goethite and three organic fractions — viz. Humic acid, fulvic acid and humin extracted from a Kenyan soil (supplied by Dr. Declan Barraclogh, Soil Science

Table 1  
Description of the soils

Sample no.	Soil series	Country of origin	Soil taxonomy <sup>a</sup>	Depth (cm)
1	Barombi Kang	Cameroon	Typic Paleudult	20–40
2	Kumasi	Ghana	Plinthic Paleudult	0–20
3	Munchong	Malaysia	Tropeptic Haplorthox	20–35
4	Onne	Nigeria	Typic Paleudult	20–30
5	Red Yellow Latosol	Brazil	Typic Acrustox	20–40
6	Richelieu	Mauritius	Ultisol <sup>b</sup>	0–10
7	Segamat	Malaysia	Typic Acrorthox	0–20

<sup>a</sup>Soil Survey Staff (USDA-SCS, 1975).

<sup>b</sup>Full classification not available.

Table 2  
Some properties of the soils

Sample no	Clay (%)	pH (1:2.5 H <sub>2</sub> O)	O.C <sup>a</sup> (%)	Fed <sup>b</sup> (%)	Feo <sup>c</sup> (%)
1	25	5.6	0.5	5.41	0.14
2	10	4.8	1.2	0.78	0.05
3	17	4.6	3.2	6.67	0.07
4	27	4.4	0.6	0.84	0.13
5	57	4.8	2.3	2.17	0.07
6	9	6.3	2.3	6.69	0.31
7	21	4.5	1.3	4.70	0.06

<sup>a</sup>Organic carbon (Nelson and Sommers, 1975).

<sup>b</sup>Citrate–dithionite–bicarbonate–extractable Fe (Mehra and Jackson, 1960).

<sup>c</sup>Acid ammonium oxalate extractable Fe (Mckeague and Day, 1966).

Department, University of Reading) were used as reference materials for the EM measurement.

### 2.1.1. Pre-treatments

The clay fractions of the soils were separated after the pH of the slurry was adjusted to 9 by 0.1 M sodium hydroxide solution followed by ultrasonic dispersion.

The organic matter of the clay fractions was left intact and these samples were designated as untreated clay fractions. Some of these samples were successively treated as follows:

1. Sodium hypochlorite (5.25% NaOCl) solution adjusted to pH 9.5 with concentrated HCl (Cavallaro and McBride, 1984) to oxidize organic matter.

Table 3  
Mineralogical composition of the clay fractions of the soils.

Sample no.	Soil series	Kaolinite <sup>a</sup>	Goethite <sup>a</sup>	Hematite <sup>a</sup>	Gibbsite <sup>b</sup>	Quartz <sup>b</sup>	Illite <sup>b</sup>
1	Barombi Kang	+++ <sup>c</sup>	++	+	–	+	–
2	Kumasi	+++	++	–	–	+	+
3	Munchong	+++	++	+	–	+	–
4	Onne	+++	++	+	–	+	–
5	Red Yellow Latosol	+++	++	+	+	+	–
6	Richelieu	+++	++	–	–	+	–
7	Segamat	+++	++	–	–	–	–

<sup>a</sup>Determined by DTA/TG.

<sup>b</sup>Determined by XRD.

<sup>c</sup>+++ = abundant; ++ = scarce; + = present.

– not detected by XRD and DTA/TG techniques.

2. Ammonium oxalate to remove ferrihydrite (Fe<sub>o</sub>) (McKeague and Day, 1966; Schwertmann, 1964).
3. Sodium bicarbonate to remove the remaining well-crystalline free iron oxides (Fe<sub>d</sub>) (Mehra and Jackson, 1960). The Fe, Al and Si in the extracts were measured with an inductively coupled Plasma atomic emission spectroscopy (Perkin Elmer Optima 3000). The standards were made in matrices identical to the extracts except for Fe, Al and Si.

### 2.1.2. Electrophoretic mobility

EM measurements were made using a zetamaster instrument (Malvern with a rectangular) (5 mm × 2 mm) quartz cell at room temperature. Approximately 3 mg samples of clay were washed twice with 5 ml of 1 M NaClO<sub>4</sub> followed by three washings with 5 ml of 10 mM NaClO<sub>4</sub>. 20 ml of the suspension solution (1 mM or 10 mM NaClO<sub>4</sub>) adjusted to pH 3 to 9, using either 1.0 M HClO<sub>4</sub> or 1.0 M NaOH, were added; giving a concentration of approximately 0.15 g L<sup>-1</sup>. The suspension was dispersed for 3 min using an ultrasonic probe and then shaken overnight on an end over end shaker. The pH of the final supernatant was measured before the EM measurements were made.

The optical unit contained a 2 mW Helium Neon Laser. Triplicate EM was measured using a 30 count time, 150 mV voltage and 5 mA current. The EM was measured for three separate injections for each sample, and the final value was an average of nine measurements.

## 3. Results and discussion

### 3.1. Constituent dissolution

Table 4 shows amounts of Fe, Al and Si extracted by oxalate and DCB treatments. The ratio of Fe<sub>o</sub> to Fe<sub>d</sub> which forms an index of amount of

Table 4  
Iron, aluminium and silicon contents (g kg<sup>-1</sup>) following ammonium oxalate (o) and dithionite–citrate bicarbonate (d) treatments of the clay fractions of the soils

Sample No	Fe <sub>o</sub>	Al <sub>o</sub>	Si <sub>o</sub>	Fe <sub>d</sub>	Al <sub>d</sub>	Si <sub>d</sub>	Fe <sub>o</sub> /Fe <sub>d</sub>
1	0.8	0.8	0.4	93.5	26.2	5.7	0.01
2	0.6	0.7	0.3	40.3	13.1	4.5	0.02
3	0.7	0.9	0.5	86.3	27.1	6.4	0.01
4	0.3	1.7	0.4	28.4	10.6	8.9	0.01
5	0.4	1.2	0.1	45.0	23.9	3.3	0.01
6	2.5	1.8	1.3	69.7	17.7	6.2	0.04
7	3.1	0.8	0.2	77.8	26.8	7.5	0.04

ferrihydrite in the soils (Schwertman, 1964) was small ( $< 0.04$ ) indicating that the Fe oxides were essentially goethite and/or hematite as crystalline Fe oxides common in most strongly weathered tropical soils. The NaOCl treatment extracted no iron, implying that there was no organically bound Fe in the clay fractions. Aluminium and Si contents in this extract were  $< 0.3 \text{ g kg}^{-1}$ .

Aluminium substituted for Fe in goethite is most likely the source of  $\text{Al}_d$ . The DCB treatment extracted more Al than the oxalate treatment. The amounts of Si extracted by the DCB and oxalate treatments were relatively small. The silicon levels in the extracts were in the following decreasing order: DCB > oxalate.

### *3.1.1. Electrophoretic mobility (EM) and isoelectric point (iep) of untreated clays*

The EM of all the samples were similar and ranged between  $-3$  and  $+2$  ( $\mu\text{m/s}$ ) ( $\text{V/cm}$ ). Some typical examples of EM measurements for the clays after various treatments as a function of pH in 1 mM and 10 mM  $\text{NaClO}_4$  solutions are shown in Figs. 1 and 2.

The EM values of the untreated samples were influenced by their mineralogy. The sample which contained some 2:1 phyllosilicate in addition to kaolinite (Sample No 2) had significantly lower EM (Fig. 2) and its iep was  $< 3.0$ . This behaviour of soil clay 2 was probably due to the presence of illite and consequently a large contribution of permanent charge to the total charge of the clay. By contrast, samples that contained only kaolinite exhibited more positive EM values and therefore had larger iep values (Table 5). The proportion of Fe oxides in the untreated samples, especially those whose layer silicate was only kaolinite, influenced the EM and iep values. Clays with relatively large amounts of Fe oxides possessed more positive EM than those which contained less Fe oxides. There was a positive correlation between iep and  $\text{Fe}_d$  (Fig. 3).

This is in line with the large iep value ( $> 7.0$ ) recorded for the synthetic goethite (Table 5). Similar large iep values (7–9) have been reported by Madrid et al. (1983), Parks (1965), Greenland (1975) and Cabrera et al. (1977).

In a kaolinite–iron oxide complex system, Greenland (1975) observed that goethite present contributed independently to the total charge and appeared to have iep value close to 8.

The presence of Fe oxides made the iep values of the untreated soil clays larger than that of Pugu kaolinite (Table 6), a pure mineral.

### *3.1.2. Electrophoretic mobility and iep of NaOCl-treated clays*

The removal of organic fractions resulted in more positive EM values of the NaOCl-treated samples (Figs. 1 and 2). An increase in EM for clay extracted from an Ultisol after removing organic matter has been reported by Kretzchmar et al. (1993). Dixit (1982) also observed a strong negative correlation between EM and organic matter content in some soil clays.

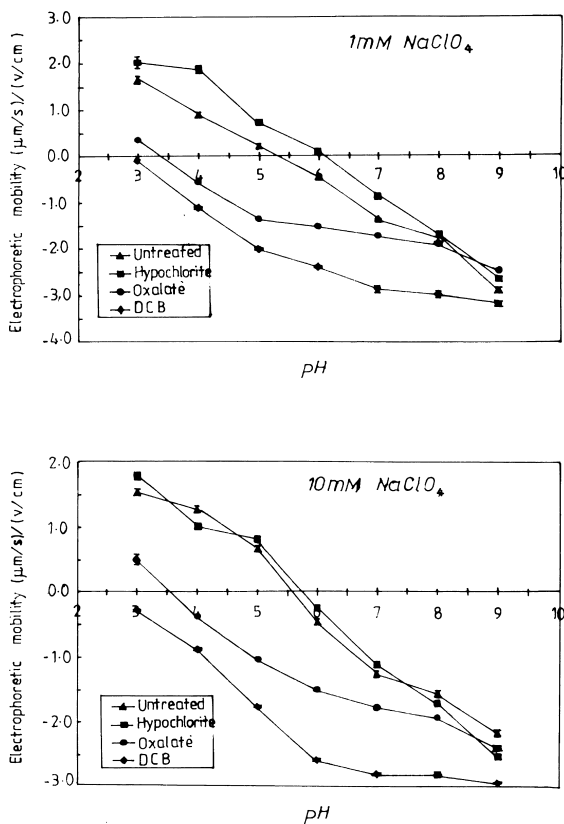


Fig. 1. Electrophoretic mobility as a function of pH in 1 mM and 10 mM  $\text{NaClO}_4$  for untreated and treated clay fractions of Barombi Kang soil, error bars indicate standard deviations.

A very small quantity of adsorbed humic substance is required to achieve a complete reversal in surface charge sign for goethite (Tipping and Cooke, 1982), hematite (Amirbahman and Olson, 1993), and kaolinite (Kretzschmar et al., 1993). The removal of organic fractions generally increased the iep values (Table 5), implying that organic matter adsorption by mineral surfaces lowered the iep values of the soil clays. A negative correlation was observed between iep and organic carbon contents of the untreated clays ( $r = 0.866$ ,  $P < 0.05$ ). It was possible that the carboxyl groups of the humic substances were complexed with Al or/and Fe, reducing the associated surface charge of humic substances and their effect on the EM of the soil clays (Kretzschmar et al., 1993).

### 3.1.3. Electrophoretic mobility and iep of oxalate and DCB-treated samples

The oxalate treatment for the removal of ferrihydrite decreased the EM values. Since this treatment extracted small amounts of Fe, it appeared adsorption of oxalate ions to the remaining positively charged surface might have reduced the EM and the iep values (Table 5).

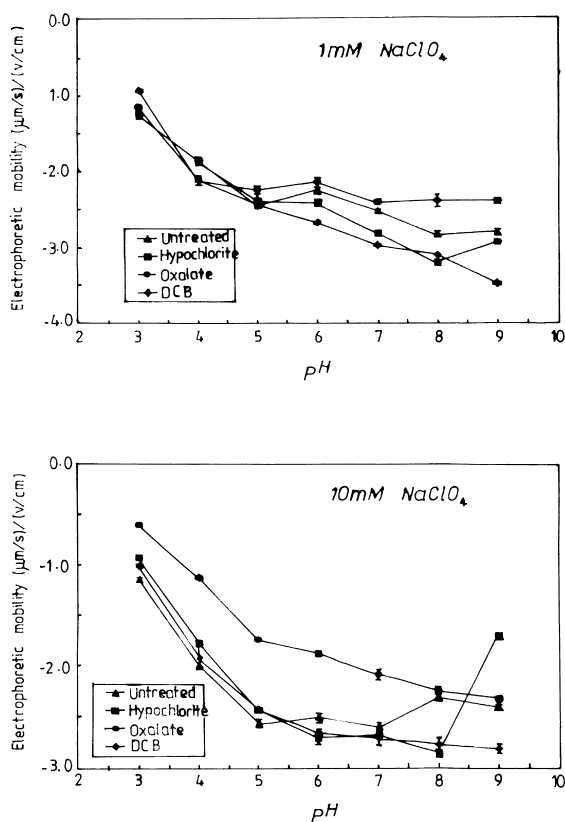


Fig. 2. Electrophoretic mobility as a function of pH in 1 mM and 10 mM  $\text{NaClO}_4$  for untreated and treated clay fractions of Kumasi soil, error bars indicate standard deviations.

The DCB treatment significantly reduced the EM and iep values of the samples. The reduction in EM could be partly due to the removal of Fe oxides

Table 5

Isoelectric point (iep) as determined from the electrophoretic mobility values for untreated and treated clay fractions measured in 1 mM and 10 mM  $\text{NaClO}_4$  solutions

Soil series	Untreated		NaOCl		Oxalate		DCB	
	1 mM	10 mM	1 mM	10 mM	1 mM	10 mM	1 mM	10 mM
Barombi Kang	5.6	5.6	6.1	5.7	3.4	3.6	3.0	3.0
Kumasi	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
Munchong	6.7	5.8	3.8	3.4	6.0	5.7	3.1	3.1
Onne	< 3.0	< 3.0	3.2	3.1	< 3.0	< 3.0	< 3.0	< 3.0
Red Yellow Latosol	3.6	3.6	4.9	4.5	4.4	4.1	3.5	4.1
Richelieu	4.3	< 3.0	6.0	5.7	4.8	4.4	3.1	3.1
Segamat	3.9	3.6	3.5	5.2	3.0	3.0	3.3	3.3

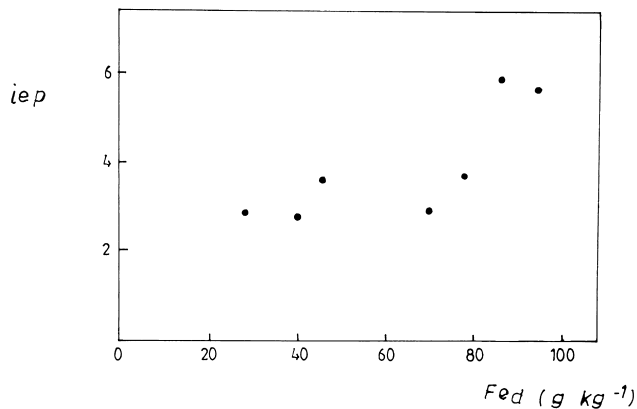


Fig. 3. Variation of isoelectric point (iep) measured in 10 mM  $NaClO_4$  with DCB-extracted Fe ( $Fe_d$ ) of the untreated soil clays.

and in part due to the adsorption of citrate, which lowered the surface charge of the clays (DCB-treated samples). The iep values as estimated from the EM data, were smaller than that reported for mineral kaolinite (iep = 4.2; Carroll-Webb and Walther, 1988; Anderson and Bertsch, 1993) and Pugu kaolinite (iep = 4.8; Table 6). The iep values for the soil clays studied, however, were comparable to that reported for some kaolinitic soil clays (iep = 2.8–4.8; Tschapek et al., 1974). It is worth noting that the iep values obtained were larger than those reported for siliceous Ultisol (iep  $\approx$  2, Elliott and Sparks, 1981) and some kaolinitic soil clays from Brazil (iep  $\approx$  2, Chorover and Sposito, 1995). Elliott and Sparks (1981) attributed their results to the presence of silica and fieldspars, while noting that organic matter could have the same (Chorover and Sposito, 1995).

### 3.1.4. The effect of salt concentration on EM and iep of soil clays

The EM behaviour of the untreated clays varied with salt concentration, with values being more positive as concentration of suspension solution ( $NaClO_4$ )

Table 6

Isoelectric point (iep) of a synthetic goethite, a disordered kaolinite (Pugu kaolinite) and organic fractions

Sample	iep <sup>a</sup>	
	1 mM $NaClO_4$	10 mM $NaClO_4$
Synthetic goethite	7.2	7.8
Pugu kaolinite	4.5	“–”
Humic acid	< 3.0	< 3.0
Fulvic acid	2.6	3.4
Humic	< 3.0	< 3.0

<sup>a</sup> Measured in suspension using 1 mM and 10 mM  $NaClO_4$  solutions.

“–” Data not available.



increased from 1 mM to 10 mM. However, the concentration of the suspension solution did not have consistent effect on the iep values of the untreated and treated soil clays, except some of the NaOCl-treated samples which recorded larger values as salt concentration decreased from 10 mM to 1 mM.

The effect of salt concentration on the EM of soil clays is, however, not clear in the literature. For example, Chan et al. (1984) reported that salt concentration had no effect on EM while Anderson and Bertsch (1993) observed a decrease in EM with increasing salt concentration.

#### 4. Conclusion

The EM and iep values of soil clays suspended in NaClO<sub>4</sub> solution were dominated by the type and content of phyllosilicates and iron oxides in the soil clays. Treatments for the removal of organic matter and Fe oxides markedly decreased the EM and iep values. The variation of EM with pH (3–9) for the soil clays was similar, becoming more negative with increasing pH. The effect of salt concentration on EM and iep values of the clays did not have a consistent trend.

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