

## Electrophoretic Mobility of Illite and Micaceous Soil Clays

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### ABSTRACT

Examination of the colloid chemistry of clays may provide an increased understanding of the structural stability of soil clays under field conditions. Electrophoretic mobility (EM) gives specific information about the net charge of a particle at the shear plane. An evaluation was made of the effect of the important water quality variables, electrolyte concentration, sodium adsorption ratio (SAR), and pH on the EM of Silver Hill illite and three micaceous soil clays. Increases in electrolyte concentration generally increased the mobility of the colloidal particles, contrary to double-layer prediction. The EM behavior is thus not explained by the commonly used double-layer theory of infinite plates; however, results can be explained if this double-layer theory is extended to consider charge spillover into clay particle edges and changes in variable edge charge. The EM increased faster when the SAR increased from 5 to 20 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> than at higher values of this parameter. These results are in agreement with tactoid formation and demixing theory previously developed by others for smectites. The EM for micaceous soil clays and specimen Silver Hill illite was more sensitive to changes in pH as the electrolyte concentration increased. These results are consistent with observations on variable-charge minerals where variable charge increases with increasing ionic strength. Removal of organic matter increased the EM in the pH 4 to 10 range studied.

**R**ECOMMENDATIONS regarding the dispersion hazard of a soil have typically included salt concentration and sodicity (Quirk and Schofield, 1955; Rhoades, 1982; Shainberg and Letey, 1984; Ayers and Westcot, 1985). Recent studies have indicated that such recommendations may not be sufficient; for example, Suarez et al. (1984) showed that high pH has an adverse effect on the hydraulic conductivity and dispersion of soils. Variable-charge components are considered important parameters in soil stability studies (Goldberg et al., 1988). More recently Pratt and Suarez (1989) showed that, for arid-land soils, a single stability line is not possible due to the high variability among soil types. Likewise it has been reported that, even for samples from the same soil type and mineralogy, large differences in CCC exist (Lebron and Suarez, 1989).

An increased understanding of the dispersion behavior of soils may be provided by examination of the colloid chemistry of the clays. The zeta potential ( $\zeta$ ), defined as the electrical potential in the double layer at the interface between a particle that moves in an electric field and the surrounding liquid (van Olphen, 1977), can be considered a fundamental property that is influenced by the salt concentration, exchangeable Na and pH. With numerous assumptions, the EM can be used to derive  $\zeta$  (Harsh and Xu, 1990). However, even if these calculations are not accurate enough for proper quantitative prediction, the EM results still give useful qualitative information.

The EM data have been used by numerous authors

to explain specific aspects of the colloid chemistry of soil particles. Bar-On et al. (1970) used EM measurements to determine the relative distribution of Ca and Na ions in external vs. internal positions in Wyoming bentonite. Studies related to monovalent cation selectively based on  $\zeta$  were reported by Xu (1988). Harsh et al. (1988) used microelectrophoresis and potentiometric titration for development of a structural model for allophane and imogolite. Gu and Doner (1990) determined the adsorption properties of hydroxy-Al polycations and their relation to the destabilization of clay suspensions.

In addition to these applications, determination of  $\zeta$  has also been considered a very good index of the magnitude of the repulsive interaction between colloidal particles (Hunter, 1981). This has been quantified using the following expressions. The total potential ( $V_t$ ) interaction between two particles is determined by the balance between the attractive ( $V_a$ ) and repulsive ( $V_r$ ) forces:

$$V_t = V_a + V_r \quad [1]$$

When the particles are separated by a distance  $x$  such that the attractive forces (London-van der Waals) equal the forces of repulsion (electrostatic), then  $d(V_a + V_r)/dx = 0$  and  $(V_a + V_r) = 0$ . Under these conditions, the potential-energy barrier disappears and flocculation occurs; this transition point also is the CCC and can be expressed as (Hunter, 1981):

$$\text{CCC} = (4\pi\epsilon_0)^3 0.107D^3 (kT)^5 \gamma^4 / N_A A^2 (ze)^6 \quad [2]$$

where CCC is expressed in moles per liter,  $\gamma$  is a function of the electric potential of the particle surface ( $\psi_0$ ),  $N_A$  is Avogadro's number,  $\epsilon_0$  is the permittivity of free space,  $D$  is the dielectric constant,  $k$  is the Boltzmann constant,  $T$  is temperature in Kelvin,  $A$  is the Hamaker constant (in joules),  $z$  is the valency of the ion, and  $e$  is the ion charge unit. Alternatively, the following expression was developed by (Hunter, 1981).

$$V(H) = 2\pi\epsilon_0 Da \zeta^2 \ln[1 + \exp(-\kappa H)] - (Aa/12H) \quad [3]$$

where  $H$  is defined as the distance of closest approach of spheres whose radius is  $a$ , and  $1/\kappa$  is the thickness of the double layer. This and many other expressions have been used to describe the coagulation process.

When OM is present, however, the maximum level of coagulation does not always occur at the minimum in  $\zeta$ ; this feature may be due to other effects such as steric stabilization (Napper and Hunter, 1972). Even for most semiarid dryland soils where the OM content is  $<10 \text{ g kg}^{-1}$ , OM is a major factor facilitating soil aggregation and structural stability. Colloids of amorphous organic material can bind soil particles, plant

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**Abbreviations:** EM, electrophoretic mobility; SAR, sodium adsorption ratio; CCC, critical coagulation concentration; OM, organic matter; IAP, ion activity product; ZPC, zero point charge; PZNPC, point of zero net proton charge; ICP, inductively coupled plasma.

residues, and living organisms together to create discrete structure-forming aggregates (Smith and Elliot, 1990). Results from different studies, however, show that OM may also act to increase dispersion (Gupta et al., 1984; Goldberg et al., 1988). The OM also affects other soil properties, such as the cation-exchange capacity and the specific surface area; thus, it is necessary to consider OM in colloidal studies of soil clays.

Our objectives were to examine the EM of several micaceous clays under different conditions of SAR, pH, and electrolyte concentration; compare changes in EM as a function of pH with and without OM, and relate the EM results with CCC data of the same micaceous clays.

## MATERIALS AND METHODS

Three clay micaceous soils and one reference clay mineral, Silver Hill illite, were studied. Table I shows the mineralogy and textural composition of the soil materials. Ebro Basin soil is an alkaline, fine, illitic, xeric soil collected in the northeast of Spain. Ramona, is a fine-loamy, mixed, thermic Typic Haploxeralf soil from southern California, and Clarence is a fine, illitic, mesic Aquic Argiudoll from Illinois. The reference clay was obtained from the Source Clay Minerals Repository of the Clay Minerals Society, Columbia, MO. Granulometric determinations were made in a Sedigraph 5000 ET (Micromeritics, Norcross, GA<sup>1</sup>) Iron and Al oxides were extracted by the method of Jackson et al. (1986), and cation concentrations were determined by ICP. Inorganic and organic C were analyzed by a CO<sub>2</sub> coulometer (UIC Corp., Joliet, IL). Mineralogical identification was carried out by x-ray powder diffraction. The electrophoretic mobility was determined using a Zeta-Meter System 3.0 microelectrophoresis apparatus, with a cylindrical cell, a Zeiss DR microscope and an Automatic Sample Transfer System (Zeta-Meter, Long Island City, NY). At least 20 particles were timed in each experiment. The procedure was repeated three times and the means calculated. The standard errors of these means were in all cases between  $0.01 \times 10^8$  and  $0.2 \times 10^8$  m<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>. The temperature was maintained at  $22 \pm 1^\circ\text{C}$ .

Sample preparation for the EM study was as follows: Micaceous clays were washed three times with distilled water and the clay fraction was extracted after 4 h of sedimentation. This fraction was equilibrated with solutions of different SAR, pH, and salt concentration. Each centrifuge tube containing 0.050 g of clay and 40 mL of the solution was shaken for 30 min and centrifuged. The procedure was repeated three times. After removal of the last supernatant the samples were weighed. Changes in electrical conductivity of the final supernatants were  $<0.05$  dS m<sup>-1</sup> relative to the original solution and pH changes  $<0.1$  unit. We next calculated the volume necessary to obtain a suspension density of 0.1 g soil L<sup>-1</sup>. The EM was measured in triplicate in 0.1 g L<sup>-1</sup> suspensions 1 h after their preparation. Readings at 48 and 72 h showed no changes in this parameter. The solutions used involved three levels of SAR [5, 20, and 80 (mmol L<sup>-1</sup>)<sup>0.5</sup>], three levels of electrolytic concentration (2, 5, and 10 mmol<sub>c</sub> L<sup>-1</sup>), and two levels of pH (7.5 and 9). A computer program with the equilibrium constants of Suarez (1977) was used to calculate the (Ca<sup>2+</sup>)(CO<sub>3</sub><sup>2-</sup>) IAP and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) of solutions with input of solution composition and pH. By adjustment of the input HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> and examination of the output IAP and pCO<sub>2</sub>, we determined which combination of pH, SAR, and salt concentration could be prepared to within 0.5 log units of calcite saturation (by bubbling

with CO<sub>2</sub> or replacing Cl<sup>-</sup> for HCO<sub>3</sub><sup>-</sup>). Solutions were initially prepared with CO<sub>2</sub>-free deionized water and CO<sub>2</sub> was bubbled into the solution until the desired pH was achieved. Calcite undersaturation  $>0.5$  log units occurred for some solutions that we indicate below. Only experiments with Ebro Basin soil are potentially affected by undersaturation with respect to calcite. The CCC of our micaceous soil clays was calculated using the method described by Goldberg and Glaubig (1987).

The effect of OM was studied by comparison of two clay fractions, one without any treatment and the other after removal of the OM by the method of Kunze and Dixon (1986). The materials studied were Silver Hill illite, Ramona soil, and Clarence soil. This experiment was conducted at five levels of pH (4, 6, 7.5, 9, and 10), an electrolyte concentration of 2 mmol<sub>c</sub> L<sup>-1</sup>, and SAR values of 5 and 80 (mmol L<sup>-1</sup>)<sup>0.5</sup>. In this case Cl<sup>-</sup> salts were used and the pH was adjusted by addition of small amounts of HCl or NaOH.

## RESULTS AND DISCUSSION

### Effect of Electrolyte Concentration on Electrophoretic Mobility

Increasing concentration resulted in increased clay particle mobility for all materials studied when the SAR [SAR = Na/(Ca + Mg)<sup>0.5</sup>, where concentrations are expressed in mmol L<sup>-1</sup>.] was greater than 5 (mmol L<sup>-1</sup>)<sup>0.5</sup>, as shown in Fig. 1 and 2 for Silver Hill illite and the Clarence soil clay, respectively. Similar trends were found for Ebro Basin and Ramona soils (Fig. 3 and 4)<sup>2</sup>. Decreases and increases in mobility are given here in terms of the absolute value in mobility. Ebro Basin soil clay was the most affected by salt concentration changes, with increases in mobility of up to 85% within the salt concentration range studied (Fig. 3a-3c). That the Ebro Basin soil was the most affected is not surprising if we consider that this soil is calcareous and, especially at low concentration, calcite dissolution may occur, and consequently reduce the SAR, for the solutions indicated in Table 2. Ramona soil clay experienced similar changes in EM as that observed for Ebro Basin soil, with increasing salt concentration, for all three SAR values examined (Fig. 4a-4c). For both of these clays, the electrolytic concentration effect on EM depended on SAR and pH. At SAR = 80 (mmol L<sup>-1</sup>)<sup>0.5</sup> the percentage increase in mobility for these clays was double that for SAR = 20 (mmol L<sup>-1</sup>)<sup>0.5</sup> when the salt concentration increased from 2 to 10 mmol<sub>c</sub> L<sup>-1</sup>.

Similarly, the change in EM with salt concentration at pH 9.0 was approximately double that at pH 7.5 for the Silver Hill illite and Ramona soil clay at SAR  $>5$  (mmol L<sup>-1</sup>)<sup>0.5</sup>. For Silver Hill illite, the salt concentration effect on EM was almost independent of the SAR when SAR was  $>5$  (mmol L<sup>-1</sup>)<sup>0.5</sup> (Fig. 1a and 1b). The EM of Clarence soil clay was the least affected by changes in salt concentration and was independent of SAR and pH for SAR  $>5$  (mmol L<sup>-1</sup>)<sup>0.5</sup>. In contrast to these data, increasing the salt concentration at pH 7.5 and SAR 5 decreased the mobility

<sup>2</sup> We chose two different formats for Fig. 1 and 2 and for Fig. 3 and 4 in order to more clearly show the EM relationship with salt concentration (Fig. 1 and 2) and SAR (Fig. 3 and 4). The relationships for the three soil clays and the mineral clay are similar, thus no additional information is given by presenting all the data in the same format.

<sup>1</sup> Trade names are provided for the benefit of the reader and do not imply any endorsement by the USDA.

Table 1. Mineralogy and composition of soils.

Soil	Particle-size distribution			Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Organic matter	CaCO <sub>3</sub>	Mineralogy
	Clay <2 μm	Silt 50-2 μm	Sand >50 μm					
Ebro Basin	257	692	51	19	4	1	400	Mica dioctahedral
Ramona	231	222	547	8	1	4	none	Mica di- and trioctahedral
Clarence	680	265	55	18	3	3	none	Mica dioctahedral

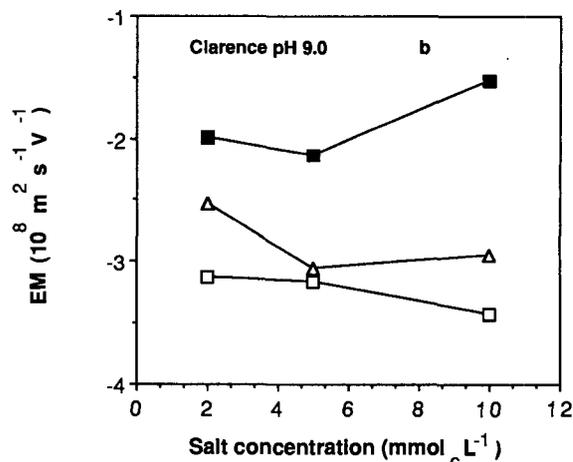
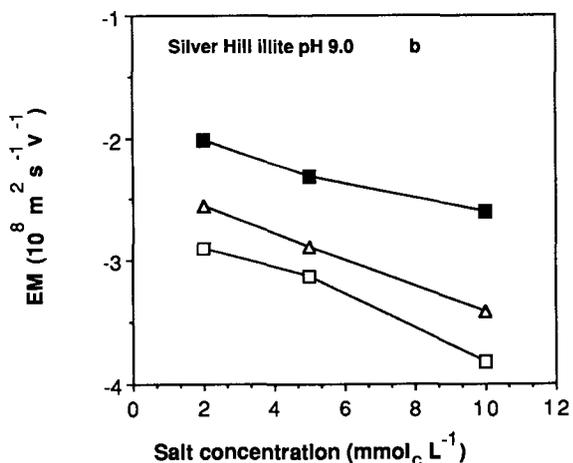
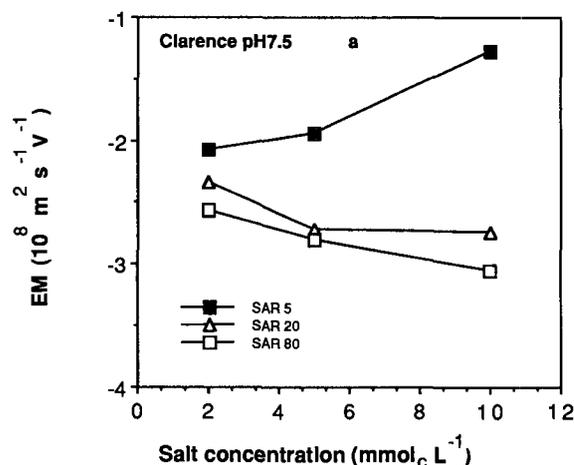
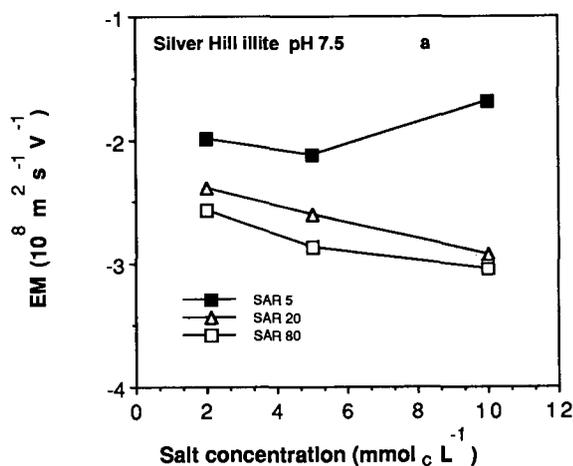


Fig. 1. Electrophoretic mobility (EM) as related to salt concentration and sodium adsorption ratio (SAR) for Silver Hill illite at (a) pH 7.5 and (b) pH 9.0.

Fig. 2. Electrophoretic mobility (EM) as related to salt concentration and sodium adsorption ratio (SAR) for Clarence clay soil at (a) pH 7.5 and (b) pH 9.0.

of Silver Hill and Clarence, particularly when the solution was  $>5 \text{ mmol}_c \text{ L}^{-1}$ . As explained below, these differences in EM response to salt concentration result from a variety of processes.

Double-layer theory for infinitely large flat plates of fixed charge predicts that the double-layer thickness decreases as the electrolytic concentration increases. Consequently, the negative charge outside the shear plane would be expected to decrease as the salt concentration is increased. For  $\text{SAR} > 5 \text{ (mmol}_c \text{ L}^{-1})^{0.5}$  and salt concentration  $> 5 \text{ mmol}_c \text{ L}^{-1}$ , however, our experimental results and those published by others for other clays are not in agreement with predictions using

this theory. Although our data are expressed in terms of solution SAR and not directly in terms of ESP, the EM trends with concentration are not explainable by changes in Na-Ca selectivity. For Silver Hill illite, Amrhein and Suarez (1991) found no significant differences in the Gapon constant for the same SAR when the salt concentration was varied from 25 to 500  $\text{mmol}_c \text{ L}^{-1}$ . This constancy in SAR-ESP relations with concentration was established for the SAR range of 5 to 50  $(\text{mmol}_c \text{ L}^{-1})^{0.5}$  (Amrhein and Suarez, 1991). As a result, the EM changes observed in our study occurred at constant ESP as the SAR was held constant and the salt concentration was increased.

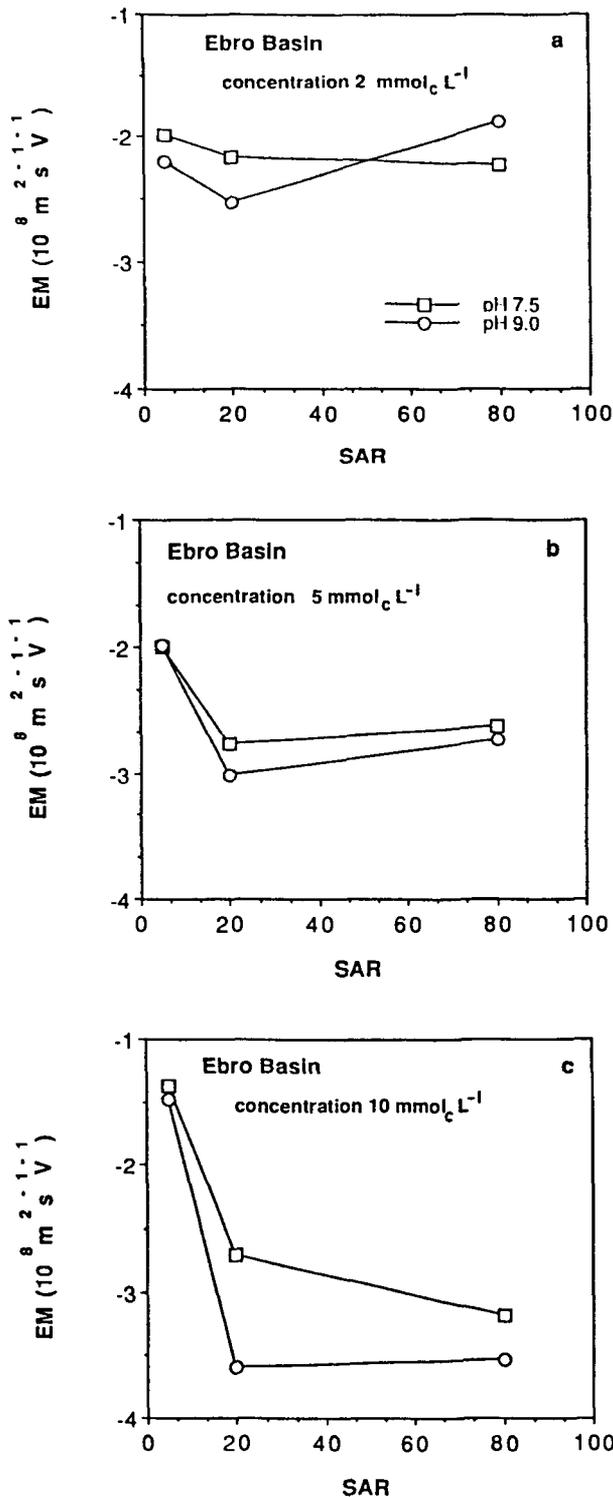


Fig. 3. Electrophoretic mobility as related to sodium adsorption ratio (SAR) and pH for Ebro Basin clay soil at salt concentration (a)  $2 \text{ mmol}_c \text{L}^{-1}$ , (b)  $5 \text{ mmol}_c \text{L}^{-1}$ , and (c)  $10 \text{ mmol}_c \text{L}^{-1}$ .

The effect of concentration on EM or on  $\zeta$  in different clay minerals has been studied by several authors. Anomalous behavior, meaning no changes or increased mobility with increased concentration, was found by Kemper and Quirk (1972) for bentonite, illite, and kaolinite clays saturated with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and

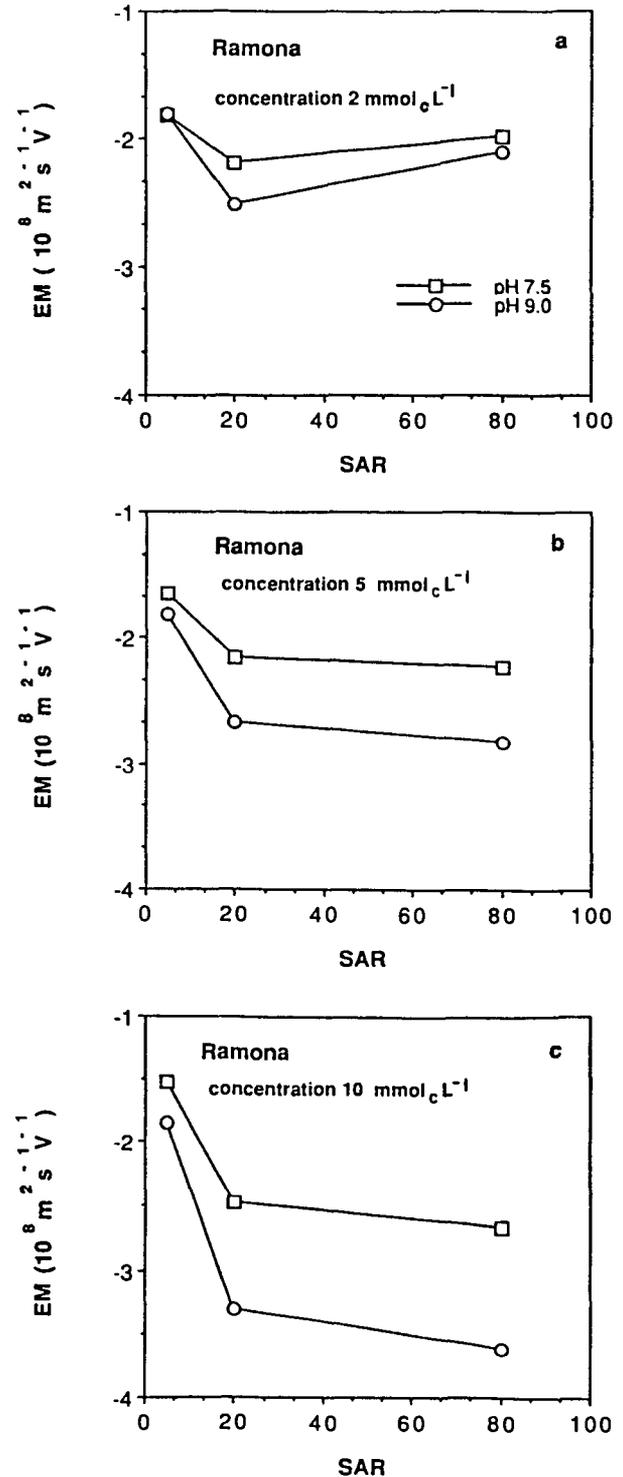


Fig. 4. Electrophoretic mobility as related to sodium adsorption ratio (SAR) and pH for Ramona clay soil at salt concentration (a)  $2 \text{ mmol}_c \text{L}^{-1}$ , (b)  $5 \text{ mmol}_c \text{L}^{-1}$ , and (c)  $10 \text{ mmol}_c \text{L}^{-1}$ .

$\text{La}^{3+}$  and by Callaghan and Ottewill (1974) for Na-saturated montmorillonite. Chan et al. (1984) found that the constant surface potential in montmorillonite and illite clays, in the range of electrolyte concentration of  $10^{-3}$  to  $0.05 \text{ M}$  and for the lyotropic series, was not explained by double-layer theory. Horikawa et al. (1988) discussed the same phenomena between

Table 2. Dispersed clay ( $\text{kg kg}^{-1}$ ) at salt concentrations of 2.0, 5.0, and 10  $\text{mmol}_c \text{L}^{-1}$ , sodium adsorption ratio (SAR) and pH for the three micaceous soils Ramona, Ebro Basin, and Clarence.

SAR	Clay dispersed					
	pH 7.5			pH 9.0		
	2.0 $\text{mmol}_c \text{L}^{-1}$	5.0 $\text{mmol}_c \text{L}^{-1}$	10 $\text{mmol}_c \text{L}^{-1}$	2.0 $\text{mmol}_c \text{L}^{-1}$	5.0 $\text{mmol}_c \text{L}^{-1}$	10 $\text{mmol}_c \text{L}^{-1}$
	$\text{kg kg}^{-1}$					
	<u>Ramona</u>					
5	0.89	0.78	0.80	0.84	0.84	0.70
20	0.89	0.84	0.82	0.82	0.78	0.82
80	0.89	0.84	0.89	0.85	0.63	0.85
	<u>Ebro Basin</u>					
5	†	0.08	0.08	1.00	1.00	0.08
20	†	†	0.48	†	1.00	0.78
80	†	†	0.49	†	†	0.78
	<u>Clarence</u>					
5	0.93	0.85	0.09	0.87	0.97	0.07
20	0.95	0.87	0.87	0.83	0.78	0.83
80	0.95	0.85	0.93	0.85	0.69	0.82

† Ebro Basin is a calcareous soil. Solutions with these SAR, pH, and salt-concentration conditions are undersaturated with respect to calcite and probably result in decreased SAR and increased salt concentration when equilibrated with this soil. Calculated dispersion values for these experiments may be underestimated by this procedure.

$10^{-4}$  and  $10^{-1}$  M for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $\text{Ca}^{2+}$  chloride solutions in relation to double-layer theory and concluded that the surfaces of montmorillonite and illite act like surfaces of constant potential instead of constant charge. The same conclusion was obtained by Miller and Low (1990) for several homoionic montmorillonites and illites. As these authors noted, these conclusions are not compatible with the consideration that the source of the face surface charge is generated by isomorphic substitution of ions within the crystal lattice. Harsh et al. (1988) found increases in EM with increases in concentration for hydroxy-Al and Na hectorite; their results are in agreement with ours.

The reduction (less negative values) in EM as the salt concentration decreases, as found in our experimental data, indicates that the colloid is approaching a flocculated state. These data are contrary to the observed adverse effects on the structural stability of arid-land soils when the salt content of irrigation water is decreased. This salt effect has been clearly demonstrated in studies of hydraulic conductivity, flocculation, and aggregate stability. A reduction in the electrolytic concentration increases the double-layer thickness, thus promoting repulsion and dispersion of particles. When the number of cations countering the negative surface charge in the shear plane is reduced, double-layer theory would be consistent with an increase in EM. The fact that the experimental measurements of EM were contrary to that expected requires a reevaluation of the double-layer model and its underlying assumptions.

Double-layer theory as commonly utilized considers only the faces of the particles, not the edges. This simplification has been sufficient to explain the gross effects of salt concentration and SAR on such parameters as hydraulic conductivity, flocculation, and aggregate stability. It is evident that this simplification is not sufficient if, at the shear plane, the net negative charge of the whole particle decreases with decreasing

concentration, as observed for EM measurements. The potential importance of the mica edges is, in part, the result of having variable charge in contrast to the permanent charge of the faces. It is, therefore, reasonable to consider the relative importance of the variable edge charge with respect to the face charge.

In addition to the net charge, the location, distribution, and availability of positive and negative charges is also important for linkage of soil clay particles. Secor and Radke (1985) calculated the diffuse double layer around a sharp corner. Their results predict that, for low electrolyte concentrations, the negative electrostatic field emanating from the particle face spills over into the edge region. Consequently, when spillover occurs, and the overall particle exhibits a negative charge, part of the negative charge of the face either neutralizes the positive edge charge or combines with the negative edge charge. When the salt concentration increases, the diffuse double layer compresses and the spillover effect decreases. As the concentration increases, this spillover effect on the shear plane can act opposite to the effect caused by compression of the double layer. Whereas higher salt concentrations compress the double layer, tending to reduce the net negative charge and thus the electrical potential outside the shear plane, the corresponding reduced cover of the edges increases the net negative charge and potential at the shear plane.

At a pH below the ZPC of the edges, also called PZNPC, the behavior of a particle will be the result of the sum of the concentration effect, spillover, and changes in edge charge. Using the concepts described above, the behavior of the micaceous samples can be explained in the range of concentration studied. In order to interpret the results in Fig. 1 for Silver Hill illite at SAR 20 or 80 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> it is necessary to distinguish between pH values at and below, and pH values above the PZNPC. When the pH is below the PZNPC the edges are positively charged. As the salt concentration is increased the double layer is com-

pressed, causing a decrease in the  $\zeta$  at the shear plane. This decrease in  $\zeta$  is compensated by rearrangement of the electrical field around the edges. Reduction of the spillover effect with increasing salt concentration apparently results in increased charge associated with the faces. Negative charges that were neutralizing the positive charges of the edges are now associated with the faces. Although positive edge charge is no longer shielded by spillover of negative charges, anion adsorption minimizes the quantity of positive charge outside the shear plane. It is important to note that, when the SAR = 5 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> and pH = 7.5, the clay particles actually experienced a reduction in  $\zeta$  as salt concentration increased. This distinct behavior is related to changes in particle size and formation of illite domains (Lebron and Suarez, 1991). Data in Fig. 2, 3, and 4 show similar results for the effect of salt concentration on EM for the three soil clays.

At pH values above the PZNPC, the edges are negatively charged. In this case spillover is relatively unimportant, as the edges and faces are negatively charged. Increasing the salt concentration leads to compression of the double layer, but also leads to increases in the net negative charge due to an increase in negative edge charge (Schulthess and Sparks, 1986).

There are discrepancies among data of PZNPC reported in the literature for clay minerals and variable-charge materials. Motta and Miranda (1989) calculated PZNPC values for kaolinite, montmorillonite, and illite from potentiometric titration curves and application of the Stumm et al. (1980) equation. The calculated PZNPC values at 25 °C, given by Motta and Miranda (1989) are pH 4.5 for kaolinite, 3.8 for montmorillonite, and 9.6 for illite. These values are uncertain, however, because the potentiometric titration curves vs. pH of minerals with significant permanent surface charge will not accurately describe the pH-dependent surface charge. Also, under acidic conditions mineral dissolution increases the titration value (Parker et al., 1979).

The variable charge at the edges of clay minerals originates from broken bonds from Si and Al groups, thus the surface of the illite edges can be considered similar to that of a mixture of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces. The ZPC of SiO<sub>2</sub> lies between pH = 2.8 and 3.0 and that of Al<sub>2</sub>O<sub>3</sub> at pH = 7.8 (Tschapek et al., 1974). The ZPC of a combination of these two groups is dominated by the ZPC of the Al<sub>2</sub>O<sub>3</sub> groups because Al<sub>2</sub>O<sub>3</sub> is more sensitive to pH changes (Tschapek et al., 1974). Also, the ZPC of mixtures of different percentages of silica and alumina were calculated by Schwarz et al. (1984). These pH values range from 4.85 for a system with 75% silica plus 25% alumina to 6.28 for 25% silica plus 75% alumina. Schwarz et al. (1984) used values of 4.1 for 100% silica and 7.18 for 100% alumina, in rough agreement with the value of Tschapek et al. (1974).

If we consider that kaolinite has one silanol, one aluminol, and one OH<sub>2</sub> per 0.379 nm<sup>2</sup> on the edge surface (Sposito, 1984, p. 40) and we interpolate from the Schwarz et al. (1984) data, we can expect that the PZNPC of kaolinite would be around 5.6. However, rheological measurements give values for PZNPC of kaolinite of 7.8 (Michaels and Bolger, 1964) and 7.3

(Rand and Melton, 1975). These data are in disagreement with the value of 4.5 given by Motta and Miranda (1989) based on potentiometric titrations.

A similar interpolation for illite, using the Schwarz et al. (1984) data, and based on the Srodon and Eberl (1984) unit cell formula for micas, gives a PZNPC of 5.3 for 60% silica and 40% of alumina groups in the ab plane. No rheological data are available for this mineral; consequently, it is not possible to make a decision at this point about the PZNPC of micas. Nevertheless, by analogy to the kaolinite system, the data indicate a value above 5.3 with an estimate of 7.5 as the likely value.

#### Effect of Sodium Adsorption Ratio on Electrophoretic Mobility

As predicted by double-layer theory, EM values became more negative when SAR increased (Fig. 1–4). The clays, however, did not respond uniformly in their EM behavior to changes in SAR at different salt concentrations. Clarence was the least sensitive of the soils to changes in concentration but was greatly affected by SAR and, together with Ebro Basin soil clay, produced the highest increase in mobility, especially at 10  $\text{mmol}_c \text{L}^{-1}$ . Ramona was almost unaffected by changes in SAR when the concentration was 2  $\text{mmol}_c \text{L}^{-1}$  (Fig. 4a). The increases in mobility for this soil clay were similar to those found for Silver Hill illite (Fig. 1).

We observed different behavior between SAR 5 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> and the other two SAR levels [20 and 80 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup>] for all micaceous materials. While clays with SAR = 5 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> showed a tendency toward less negative EM as concentrations increased above 5  $\text{mmol}_c \text{L}^{-1}$ , this situation did not happen consistently when SAR reached 20 or 80 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> (Fig. 1a and 2a). Theoretical values of the variation of the  $\zeta$  with SAR are not available in the literature because of the complexity of double-layer calculations in the presence of cations with different valences. When Ca is the main cation in the shear plane, however, its smaller dehydrated ionic radii (if present as inner-sphere complex) or double charge neutralizes more negative charges at the shear plane than when the more hydrated monovalent Na is on the exchange complex. For a given concentration, the net negative charge of the particle, and thus its electrophoretic mobility, has to be more negative as the SAR increases, as was observed by Horikawa et al. (1988). Also, the magnitude of the spillover has to be different depending on the predominant cation. We consider that the spillover effect is more important at higher SAR levels since, at low SAR, the face charge is neutralized close to the surface by Ca cations.

Additional evidence for the influence of the cation in the spillover effect, and a more complete interpretation of the concentration effect at low SAR on EM, is provided by the EM data for Ca-saturated clay (SAR = 0 and pH 6.9). The EM determinations were made for suspensions at different solute concentration. The results shown in Fig. 5 are for a range of salt concentrations that are lower than those used for the other experiments. Lower salt concentrations were selected because the CCC for Ca-saturated illite is 1.3  $\text{mmol}_c$

$L^{-1}$  at pH 7 (Goldberg and Forster, 1990); it is necessary to remain below this value in order to measure particle mobility. In a system containing Ca as the only cation, the thickness of the diffuse double layer is much smaller than for mixed Ca-Na systems. We can therefore consider that this compactness restricts the degree of overlap of the negative field onto the edges. Based on the data in Fig. 5, we consider that the compression of the double layer is the dominant effect and consequently the  $\zeta$  decreases even at salt concentrations of  $0.1 \text{ mmol}_c L^{-1}$ . As soon as we increase the Na content, the effect of the spillover is greater, as expected, since the double layer is not as compact. An additional factor associated with the SAR is the domain formation. In deionized water, and with  $<2\text{-}\mu\text{m}$  particles of Silver Hill illite, measurements of pure Ca-illite showed a particle-size distribution from 4 to  $10 \mu\text{m}$  vs. 0.7 to  $2.0 \mu\text{m}$  for pure Na-illite (Lebron and Suarez, 1991). These data support the formation of illite domains similar to the tactoids formed by smectites. Apparently in the presence of domains, the relative importance of the edges is less than in the platelets. We are presently investigating the manner in which particle size affects the mobility.

Greater increases in EM were found when SAR increased from 5 to 20 ( $\text{mmol } L^{-1}$ ) $^{0.5}$  than from 20 to 80 ( $\text{mmol } L^{-1}$ ) $^{0.5}$  (Fig. 3 and 4). This effect appears similar to that observed by Bar-On et al. (1970) for montmorillonite. Sodium-clay particles exist as single platelets, whereas Ca-montmorillonite exists in packets or tactoids. A small fraction of Na in the exchange complex of Ca tactoids is not sufficient to break the tactoid and most of the adsorbed Na will concentrate on the external surfaces. Consequently the EM will increase very rapidly at low exchangeable Na (or low SAR) because the external surface is being saturated mainly with Na. Results by Bar-On et al. (1970) suggest that, for montmorillonite, the ESP must be  $>20$  before Na penetrates into the tactoids and breaks the packet apart. Evidence for formation of domains with Ca-illite is not as well documented as for smectites, but is shown by the electron microscopy study of Greene

et al. (1978). These authors considered that Ca-illite domains are weaker than montmorillonite tactoids. The fast increase in the mobility of all micaceous materials as SAR was increased from 5 to 20 ( $\text{mmol } L^{-1}$ ) $^{0.5}$  provides EM data that supports the theory of domain formation with illite and micaceous clays. The results indicate the importance of ion demixing in describing the colloidal behavior of illite, and document the occurrence of demixing for soil micaceous clays despite likely oxide and OM coatings on these clays.

### Effect of pH on Electrophoretic Mobility

Changes in pH affect the variable charge of a colloidal system. The effect of pH on EM depends on the electrolyte concentration and SAR conditions in the suspensions of the micaceous clays. The data in Fig. 3 and 4 show that EM measurements are not very dependent on pH when SAR = 5 ( $\text{mmol } L^{-1}$ ) $^{0.5}$  and salt concentrations are relatively low. As the salt concentration increases, differences in EM between pH 7.5 and pH 9.0 became greater (Fig. 3 and 4). The same effect was observed at SAR 20 and 80 ( $\text{mmol } L^{-1}$ ) $^{0.5}$ .

As the pH is increased, the Al groups at the edge sites of the octahedral layer change from a hydrolyzed state to an anionic species. This increase in negative charge increases the EM of the colloidal particles. Measurements of the sorption behavior of Al oxide surfaces have been made by several authors using electrokinetic techniques, ion exchange, and potentiometric titrations. Schulthess and Sparks (1986) reported on a potentiometric titration of  $\gamma\text{-Al}_2\text{O}_3$  colloidal suspensions. They found that, at a fixed pH value above the  $\text{pH}_{ZPC}$ , an increase in electrolyte concentration increased the surface charge (more negative); consequently, more base was needed to attain the pH value desired.

An additional experiment was conducted in order to study the pH effect across a wider range of pH and to evaluate the role of OM in the changes of EM with

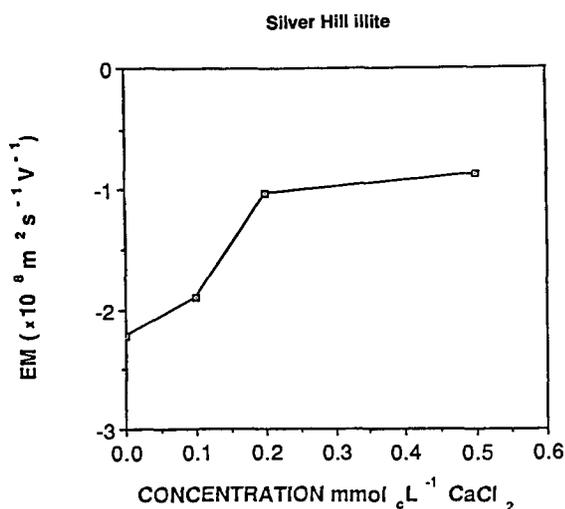


Fig. 5. Electrophoretic mobility as related to salt concentration for a Ca-saturated Silver Hill illite (sodium adsorption ratio [SAR] = 0).

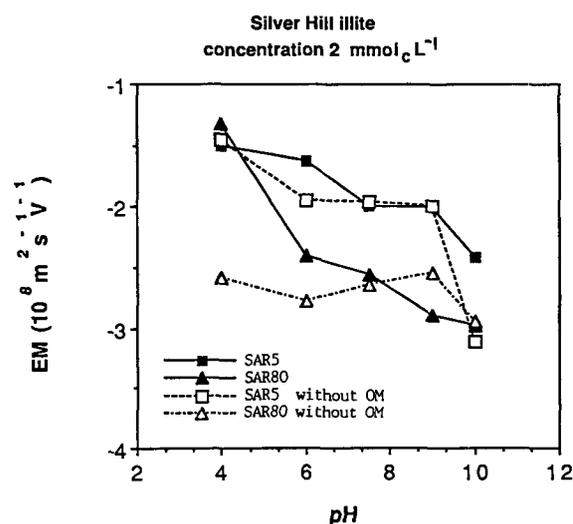


Fig. 6. Electrophoretic mobility as related to pH and sodium adsorption ratio (SAR) for Silver Hill illite. Curves are for the native fraction (solid lines) and after removal of organic matter (dashed lines).

pH. Figure 6 shows the increases in EM for Silver Hill illite at SAR 5 and 80 (concentration  $2 \text{ mmol}_c \text{ L}^{-1}$ ) with increasing pH (solid lines). Similar trends were obtained for the EM of the soil clays, as shown in Table 3. The OM content of Silver Hill illite was  $2.4 \text{ g C kg}^{-1}$ .

After treatment for removal of the OM, samples had  $<0.05 \text{ g C kg}^{-1}$ . The EM of the treated clays (dashed lines in Fig. 6) at SAR 5 ( $\text{mmol L}^{-1})^{0.5}$  and for all pH values was greater (more negative) than that for the untreated fraction (solid lines). At SAR 80 ( $\text{mmol L}^{-1})^{0.5}$ , when the pH was  $\geq 9.0$ , the EM was lower (less negative) in the samples without OM for Silver Hill illite. These results (except SAR 80, pH  $>8.0$ ) are in disagreement with the results from soils from different horizons (with different OM content). Dixit (1978 and 1982) found that colloids from surface horizons always had greater EM than colloids from subsurface horizons. However, the methodologies for removal of OM may cause changes in soil properties. Sequi and Aringhieri (1977) compared the effect of two different methods of OM removal on the electropositive, electronegative, and the external surface area, and concluded that the metals released from OM may precipitate as a hydroxide coating on the clay particles. Some sorption sites are also apparently occluded by a surface coating of OM. If true, this suggests that changes in soil properties after peroxidation cannot be solely attributed to OM. It is necessary to combine these two aspects in order to interpret the observation that removal of C leads to larger values of EM across the entire pH range.

#### Relation between Electrophoretic Mobility and Critical Coagulation Concentration

From Table 2 and Fig. 1, 2, 3, and 4 we cannot conclude that increases in the percentage of dispersed clay are associated with increased mobility of the particles for the three micaceous clay soils. Gu and Doner (1990) found that additions of increasing amounts of hydroxy-Al polycations resulted in a sharp decrease in dispersion and EM for illite and montmorillonite. A value of zero for EM is generally associated with a flocculated system. When the particle is stationary, there is no shear plane and the double layer is established. If the EM is zero,  $\zeta$  is also zero (O'Brien and White, 1978). This indicates that the repulsive forces are minimum and the attractive forces can act with

the help of Brownian movement. As was mentioned above, CCC can be deduced from  $\zeta$ .

Determining the EM of a dispersed soil in a microelectrophoresis experiment makes it possible, at least in theory, to determine the minimum electrolyte concentration that a soil needs for flocculation. In the Overbeek (1952) formula (Eq. [2] above), however, CCC is shown to be dependent on  $\zeta$  only when  $\zeta$  is  $<20 \text{ mV}$ . This value is equivalent, using the Smoluchowski equation [ $\text{EM} = \epsilon\zeta/\eta$ , where  $\epsilon$  is the permittivity of the dielectric and  $\eta$  is the viscosity of the suspending liquid (Hunter, 1981)], to  $\approx 1 \times 10^8 \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ . The lowest EM values registered in our study were at SAR 5 ( $\text{mmol L}^{-1})^{0.5}$ . According to the equation of Overbeek (1952), the CCC of our samples at SAR 5 ( $\text{mmol L}^{-1})^{0.5}$  are very close to those in which the CCC is not dependent on  $\zeta$ . The calculated CCC for higher values of  $\zeta$  become essentially independent of  $\zeta$  and the calculated solution concentration at increased  $\zeta$  is  $150 \text{ mmol L}^{-1}$  for 1:1 electrolytes.

It is also necessary to consider the methodological limitations of microelectrophoresis. One of these limitations is caused by convection currents resulting from temperature gradients. The increases in temperature depend on the conductivity of the sample and the applied voltage. This limitation occurs when particles have relatively low charge at the shear plane. Another limitation is the polarization of the electrodes at high electrolyte concentrations. We detected polarization at concentration values higher than  $\approx 10 \text{ mmol}_c \text{ L}^{-1}$ . Very low pH ( $<4$ ) and very high pH ( $>10$ ) also exhibited experimental difficulties for accurate measurement of the tracking distance of the particles. A more detailed study of EM of soil particles using concentrations in the operational range of the microelectrophoresis technique must be carried out before the CCC can be predicted using mobility measurements.

The EM behavior of illite clay as a function of changes in salt concentration, SAR and pH cannot be explained by considering a simplified double-layer theory alone. The EM results obtained may be explained by allowing for the spillover of face charge into the edges and changes in edge charge with salt concentration and pH, as well as changes in double-layer thickness with concentration and SAR. For Ca-saturated clay, at near-neutral pH, EM decreases with increasing salt concentration as expected by double-layer theory. Due to compression of the double layer,

Table 3. Electrophoretic mobility as related to pH and sodium adsorption ratio (SAR) for the micaceous clay soils Ramona and Clarence. Data for native fractions and after removal of organic matter.

	Electrophoretic mobility salt concentration = $2 \text{ mmol}_c \text{ L}^{-1}$									
	SAR = 5					SAR = 80				
	pH 4	pH 6	pH 7.5	pH 9	pH 10	pH 4	pH 6	pH 7.5	pH 9	pH 10
	$10^8 \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$									
	<u>With organic matter</u>									
Ramona	-1.84	-1.63	-1.82	-1.81	-2.17	-2.32	-2.17	-1.98	-2.10	-2.55
Clarence	-1.46	-1.72	-2.08	-1.99	-2.61	-1.97	-2.74	-2.57	-3.13	-3.18
	<u>Without organic matter</u>									
Ramona	-1.53	-1.85	-2.01	-2.32	-3.75	-2.69	-3.59	-3.18	-3.01	-3.40
Clarence	-1.80	-2.11	-2.83	-2.93	-4.03	-2.21	-4.21	-4.09	-3.77	-4.91

the spillover of surface charge onto the edges is negligible. The salt concentration at which spillover becomes less important increases with increasing exchangeable Na. This change is reflected by the EM values at SAR 5 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup>, which first increase in magnitude and then decrease with increasing salt concentration. At SAR 20 and 80 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup> the salt concentration at which this reversal occurs is apparently  $>10 \text{ mmol L}^{-1}$ . At pH 9.0, EM increased more sharply than at pH 7.5 with increasing concentration due to increasing negative charge of the edges at pH 9.0. Increasing negative edge charge with concentration also explains why we observed increased differences in EM between pH 7.5 and 9.0 with increasing concentration. At a fixed concentration, EM increased sharply to SAR 20 ( $\text{mmol L}^{-1}$ )<sup>0.5</sup>, with subsequently little change with increasing SAR. These results are consistent with current understanding of domain formation and existence of ion demixing in illite.

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